

## Ferromagnetism: magnetization curves

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# FERROMAGNETISM: MAGNETIZATION CURVES

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## § 1. INTRODUCTION

**T**HIS report, dealing mainly with work since 1934 on the variation with field of the magnetization of ferromagnetics and associated phenomena, concludes a survey of ferromagnetism of which the first section (Stoner 1948) appears in an earlier volume of these *Reports*. To quote from the previous report (which will be referred to as I): ‘The subject matter which might appropriately be considered under the title “Ferromagnetism” has been thought of as falling into three parts: the first, the general ideas and principles gained from the work up to about 1934, giving what may be called the “Background” to the more recent developments; the second, the theoretical and experimental work since that date connected with the first major theme, “Intrinsic Magnetization”; and the third, the more recent work connected with the second major theme, which can be indicated by the title “Magnetization Curves”.’ The first two parts were covered in I, in which the introduction and account of the background (I, pp. 43–65) are to be regarded as prefatory to the present account of magnetization curves as well as to the earlier account of intrinsic magnetization (I, pp. 65–108). As it is clearly impracticable in a report of this kind to deal adequately with work since 1934 on all aspects of the field covered by the title ‘Magnetization Curves’,

it is perhaps desirable first to indicate the general approach and the criteria adopted in the selection of subject matter and in deciding on the degree of detail with which it is to be reviewed.

It has long been established that a ferromagnetic below the Curie point is magnetized even in the absence of an applied field. The spontaneous magnetization is, however, not in general uniform throughout a specimen, but varies in direction from one region to another, the regions of unidirectional magnetization usually being referred to as 'domains'. At temperatures well below the Curie point (e.g. at room temperature for iron, cobalt and nickel), as the 'apparent' magnetization varies with applied field from zero to 'saturation', the intrinsic magnetization changes little, and the spontaneous magnetization in zero field is approximately equal to the saturation magnetization as ordinarily measured. Ferromagnetics are characterized essentially by the magnitude and temperature variation of the spontaneous magnetization up to the Curie point, and above the Curie point by the magnitude and temperature variation of the susceptibility. The fundamental theoretical problem of ferromagnetism is to account for the occurrence of spontaneous magnetization and for its magnitude in different elements, alloys and compounds. A reasonably full survey has already been given of both the theoretical (I, pp. 65-78) and experimental work (I, pp. 78-108) since 1934 primarily concerned with intrinsic as distinct from apparent magnetization. The occurrence of spontaneous magnetization having been satisfactorily explained in terms of relatively strong exchange interaction forces tending to align the elementary carriers of the magnetic moment (in metallic ferromagnetics, electron spins), the basic problem presented by the field variation of apparent magnetization is to account for the non-attainment of saturation in relatively weak, even vanishingly small, applied fields. It is worth noting in this connection that the field required to produce approximate saturation, even if it is as high as several thousand oersteds, is still very much less than the effective field (the molecular field) corresponding to exchange interaction, which is of the order of  $10^7$  oersteds. The whole complex of behaviour represented by the magnetization curves of ferromagnetics may thus be regarded as arising from small perturbations. The sorting out and quantitative characterization of the main perturbing effects is essential to the understanding of magnetization curves, and particular consideration will be given to experimental and theoretical work concerned with this aspect of the subject.

The greater part of experimental work on ferromagnetism, stimulated in no small degree by the technological requirement for materials with particular magnetic properties or combinations of these with other properties, is concerned with the measurement of the variation in low and moderate fields of the apparent magnetization of different materials, including innumerable commercial alloys and special laboratory samples prepared in the course of their development. There is astonishing variety in these magnetization curves, as exemplified by the fact that materials whose saturation magnetization is much the same may have coercivities ranging from a few hundredths of an oersted to several hundred oersteds, and maximum permeabilities ranging from less than a hundred to more than a million. It is not intended in this report to provide a compilation of results on the many materials which have been examined, but reference will be made to sources where such data are collected. The intention is rather to select for consideration those magnetic and associated investigations which provide

quantitative information about the elementary processes of magnetization, which exemplify general methods of attack on representative problems, or which illustrate general principles. It is kept in mind that a dominant aim in research on ferromagnetism is the determination, with such precision as may be possible, of just what is happening on a microscopic scale, sub-crystalline or atomic, when the state of bulk magnetization changes in any material, and the linking up of the magnetic properties with other properties and with what may be known or presumed about the microscopic constitution of the material.

As the various topics to be considered have close interconnections, a fair amount of cross-reference between the four main sections, as well as between the sub-sections, is unavoidable. To reduce forward reference to a minimum, the order of presentation is very roughly one of decreasing generality. The work on single crystals (§ 2) gives clear-cut information about one type of magnetization change, by the rotation of domain magnetization vectors, which is of general occurrence. A fully satisfactory quantitative interpretation has only recently been developed of the simplest types of magnetization curves, those of single crystals over effectively a purely rotational range, treating the magneto-crystalline anisotropy coefficients as parameters to be determined experimentally. This is an indication of the complexity of the problem presented by magnetization curves generally. A satisfactorily quantitative 'explanation', on an atomic theory basis, of the magnitudes of these anisotropy coefficients is still far from having been obtained. The investigations on domain structure (§ 3) theoretically, and experimentally by the powder pattern method, and through the study of the Barkhausen effect, again give information which is very wide in its bearings. The sections on single crystals and domain structure provide a basis for a more detailed consideration of the analysis of magnetization curves generally (§ 4). Accounts are given of some of the more recent work on reversible and irreversible domain boundary movement and rotational processes, on the contribution of these to change of magnetization along magnetization curves, and on their relation to such characteristics as permeability, coercivity and remanence. A short general survey of ferromagnetic materials is followed by slightly fuller accounts of work on a few representative materials, chosen in part to illustrate how various types of technological requirement are being met (§ 5). In some concluding remarks (§ 6), attention is drawn to what are believed to be the main lacunae in the report within the field which the title might be presumed to cover, and comment is made on the relation between this report and various books and general articles which have appeared during the period under review.

## § 2. SINGLE CRYSTALS

### 2(i). *Introductory*

Work on the magnetic properties of single crystals up to 1934 (I, pp. 58–61) has been very fully reviewed by McKeehan (1934 a). This work included measurement of the magnetization curves with the field along the main axial directions for iron, cobalt and nickel at room temperature, and for iron and cobalt over a wide temperature range, and measurement of torque curves (giving essentially the component of magnetization normal to the field) for single crystal discs, and a fairly complete development of the formal theory of magneto-crystalline anisotropy. Since 1934 the experimental techniques have been improved, and the modified methods have been applied to single crystals of alloys as well as of the ferromagnetic

elements; treatments of the magnetization curves applicable to the lower as well as the higher magnetization ranges have been developed; and further attacks have been made on the atomic theory of magneto-crystalline anisotropy. The work will be reviewed under three corresponding headings.

Expressions consistent with the crystal symmetry for the part of the (internal) free energy dependent on the direction of the magnetization may first be recalled (cf. I, pp. 59, 60). For a cubic crystal the expression, including only terms which are practically significant, may put be in the form

$$F_c = K_4(\alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2 + \alpha_1^2\alpha_2^2) + K_6\alpha_1^2\alpha_2^2\alpha_3^2, \quad \dots \dots \quad (2.1)$$

where the  $\alpha_i$  are direction cosines of the magnetization,  $I_0$ , referred to a coordinate system defined by the cubic axes. For a hexagonal crystal which is isotropic in the basal plane (as is hexagonal cobalt, with close approximation) a convenient form of expression is

$$F_c = K_2' \sin^2 \psi + K_4' \sin^4 \psi, \quad \dots \dots \quad (2.2)$$

where  $\psi$  is the angle between  $I_0$  and the hexagonal axis. The anisotropy coefficients, as used here, are to be regarded as defined by the above equations, which are those most commonly used. It has seemed desirable to give these equations explicitly, since by adding or subtracting constants (including functions of the angles which are constant), various alternative expressions may be obtained, in which the coefficients will have different numerical values; and it not infrequently happens in the literature that numerical values are quoted for anisotropy coefficients which are incorrect for the form of the free energy expression which may be implied or actually given. It may be noted that in a cubic crystal, unless  $K_6$  is numerically greater than  $9K_4/4$ , and of opposite sign, if  $K_4$  is positive, as for iron, the energy is a minimum for magnetization along a cube edge direction; the cube edges are directions of easy magnetization, and in the demagnetized state the domain magnetization vectors will be equally distributed along the six equivalent cube edge directions. With  $K_4$  negative, as for nickel, the easy directions are the cube diagonals. For cobalt, the easy direction is along the hexagonal axis, and  $K_2'$  is positive. Reference will be made below to the methods, largely developed before 1934, for determining the anisotropy coefficients from the experimental magnetization and torque curves.

## 2(ii). Experimental Methods and Results

The experimental measurements on single crystals are essentially of the components of magnetization parallel and normal to the field,  $I_p$  and  $I_n$ , as functions of the field for different orientations of the field relative to the crystal axes. In principle, leaving aside the low field region, full information for cubic crystals (i.e. the values of  $K_4$  and  $K_6$  in (2.1)) can be obtained from  $I_p$  curves for the field along the three directions [100], [110] and [111], for which  $I_n$  is zero. Such measurements have been made by ballistic methods, particularly by the Japanese investigators, the search coil arrangements being adapted to the small monocrystalline rods or discs of suitable crystal orientation which are available. (A typical size of 'rod' is 2 cm. long by 0.01 cm<sup>2</sup> cross section.) Ballistic methods have also been used for determining the normal component of magnetization,  $I_n$ , but this is usually obtained from measurements of the couple on a circular disc, or preferably an oblate spheroid, suspended horizontally in a horizontal field, with the equatorial plane as near as possible to a simple crystal plane. From

curves (torque curves) giving the couple against field orientation, the anisotropy coefficients can again in principle be determined most readily if results are available for a series of high field values. (As the field increases, the torque tends asymptotically to a limit, and the calculations are greatly simplified if these limiting torque curves can be estimated with precision.) Torque methods have also been used to determine  $I_p$  by suspending the disc vertically, and measuring the couple required to maintain it at a small angle to the field, but the corrections are difficult to estimate with adequate precision.

*Torque and ballistic methods.* A number of torque magnetometers have been developed since 1934 for the study both of single crystals and of rolled sheet material. A simple and sensitive form has been fully described by Williams (1937 a), a more robust balance arrangement with a rotating magnet by Tarasov and Bitter (1937) (see also Tarasov 1939), and an instrument specially suited to sheet material by Brailsford (1938). The experimental determination of torque curves is fairly straightforward, and there is no fundamental difficulty in the analysis of the results. When the ballistic method is used with rod-shaped specimens there are unavoidable uncertainties in connection with demagnetizing effects. These uncertainties have been ingeniously avoided by Williams (1937 b), who has succeeded in cutting single crystals in 'picture frame' form with the sides along tetragonal or digonal directions in a (100) plane, and along trigonal directions in a (110) plane. The picture frames are small (the sides of a rectangular tetragonal (100) specimen had mean lengths of 1.72 and 1.23 cm., and the cross-sectional area was about 0.07 cm<sup>2</sup>), but they are large enough to take adequate primary and secondary windings as in the classical anchor ring arrangement, and reliable and accurate measurements can be made in low fields (below 0.1 oersted) as well as in high.

*The pendulum magnetometer.* A new method for the study of single crystals has been introduced by McKeehan by a development of the Weiss-Foëx translational balance, previously used only for dia- and paramagnetics (McKeehan 1934 b, McKeehan, Piety and Kleis 1936). The 'pendulum magnetometer', as the instrument is called, consists of a light bar supported by a quinquefilar suspension in such a way that it is constrained to move only in the direction of its length and without rotation. The bar, on which the small ferromagnetic specimen is suitably mounted, passes through the solenoid producing the main field so that the specimen is on the axis. The solenoid may be moved along its length, and is so placed that the specimen is central. Two coaxial coils (a Helmholtz type of arrangement), separated by spacers, can slide as a unit over the solenoid. Traversed by the same current in opposite directions, these coils provide a field gradient. If  $I_p$  is the component of magnetization of the specimen along the direction, say  $x$ , of the bar, the force per unit volume is given by

$$f_x = I_p(\partial H / \partial x),$$

and  $(\partial H / \partial x)$  can be adjusted independently of the main field  $H$ . Corrections are made for lack of uniformity of the field over the small range of displacement of the specimen. The force is measured by the deflection, suitably magnified, of the pendulum from its equilibrium position in the earth's gravitational field, observation being made of the movement on a distant scale of the image of an illuminated cross wire, or, as described by Grabbe (1940), a portion of a replica grating, mounted on the pendulum bar. Overall sensitivities of the order

100 mm. dyne<sup>-1</sup> have been obtained. The specimens are prepared in the form of small oblate spheroids. (It is to be noted that for homogeneous material in a uniform field, the magnetization is also uniform for an ellipsoid, and the demagnetizing factors may be expressed, in the general case, in terms of elliptic integrals. For ellipsoids of revolution, i.e. oblate or prolate spheroids, the demagnetizing factors are expressible in terms of elementary functions. The evaluation is straightforward, but tiresome. Tables of values which would be useful in the present connection, and others, are given by Stoner (1945). It is surprising how often calculated values in the literature are in error to a physically significant extent.) In preparing the spheroid, a disc-shaped blank is mounted on the end of a vertical shaft of a variable slow speed motor, and cut by fine files while rotating. A magnified image is thrown on a screen, and the cutting operation continued until the silhouette fits accurately a carefully plotted ellipse of the required form. Typical spheroids have a thickness (polar diameter) of about 0.2 mm., and an equatorial diameter of about 4 mm. Etch reflection and x-ray methods are used for determining the crystal orientation of the initial single crystal blanks and of the final spheroids. The most convenient orientation for the equatorial plane is (110), as this includes the three main axial directions. Appropriate annealing treatments are applied to remove strains. The pendulum magnetometer has been successfully applied to the determination of the single crystal magnetization curves ( $I_p$ ,  $H$  with the field along different axes) of iron and of a large number of alloys by McKeehan and his co-workers Shih, Piety, Kleis and Grabbe, referred to below.

*Derivation of anisotropy coefficients.* In the treatment of single crystal magnetization it has usually been assumed that in the demagnetized state the domain magnetization vectors are equally distributed along the equivalent easy directions of magnetization, and that, as the applied field in a particular direction is increased, domain boundary movements take place until, still in a relatively small field, all the domain magnetization vectors are pointing along the easy direction nearest to the field. There is then a single magnetization vector to be considered, and this, as the field increases further, rotates gradually towards the field direction. The earlier formal theory was mainly concerned with this 'single-vector treatment' as it has been called (von Engel and Wills 1947), which is usually taken to include the special cases 'in which the field direction is symmetrically between two or three easy directions (e.g. the field along [110] or [111] for cubic crystals with  $K_4$  positive)', as then it is necessary to consider only one of the two or three magnetization vectors which are equal in magnitude and make equal angles with the field. The deficiencies, both recognized and unrecognized (see § 2 (iii) below), of this treatment do not appreciably affect the validity of the methods which have usually been applied to the derivation of the anisotropy coefficients.

The first and probably most widely used method is from energy density differences, obtained from the measurement of areas between the  $I$  axis and the magnetization curves for different directions. The increase in internal energy in change of magnetization from zero to saturation may be written

$$W = \int_0^{I_0} H dI. \quad \dots \dots \quad (2.3)$$

For a cubic crystal the value of  $W$  for magnetization in any given direction is obtainable from the difference between the values of  $F_c$  in (2.1) for the final and

initial values of the  $\alpha_{\nu}$ . To allow for the effect of random irregularities, assumed to affect the magnetization curves in all directions equally, differences are taken, giving

$$\left. \begin{aligned} W_{110} - W_{100} &= K_4/4, \\ W_{111} - W_{100} &= K_4/3 - K_6/27, \end{aligned} \right\} \quad \dots \dots \quad (2.4)$$

or

$$\left. \begin{aligned} K_4 &= 4(W_{110} - W_{100}), \\ K_6 &= 9\{4(W_{110} - W_{100}) - 3(W_{111} - W_{100})\}. \end{aligned} \right\} \quad \dots \dots \quad (2.5)$$

Some magnetization curves for iron, copied from those given by Piety (1936) as obtained by the pendulum magnetometer method, are shown in Figure 2.1. In so far as these curves are a 'fair' representation of the experimental results, it would seem that reliable values for the required areas could be obtained from the data in this particular work.

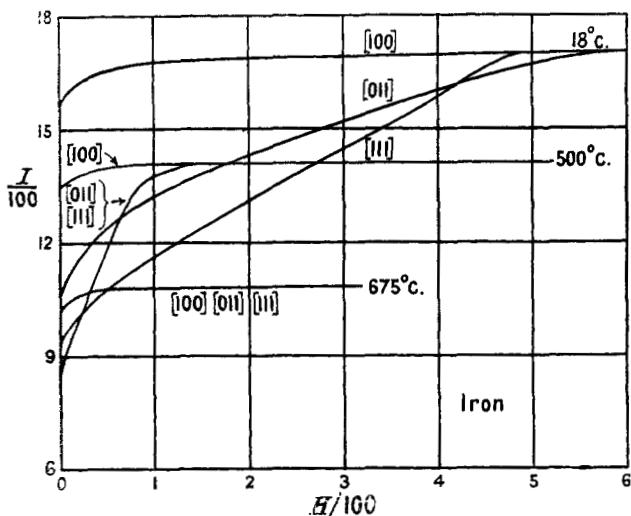


Figure 2.1. Magnetization curves for single crystals of iron at 18°, 500° and 675° c.  
After Piety (1936).

In Figure 2.2 some representative curves for nickel are shown. These have been drawn smoothly through points plotted from the numerical data of Honda, Masumoto and Shirakawa (1935), obtained by the ballistic method, using monocrystalline rods.

It is clear, to some extent from the figure itself, that the values of the anisotropy coefficients obtained from an evaluation of the areas, which has been carried out by McKeehan (1937 a, p. 139), cannot here be particularly reliable. It is very questionable whether departures from the ideal strain-free state can be allowed for satisfactorily by taking differences, as in (2.4), when different specimens must be used in determining the magnetization curves in different directions. Further, unless particular care has been taken in connection with the measurements in the higher fields, there may be large errors in the estimates of the areas up to saturation.

The form of the magnetization curve for a particular direction of the field may be calculated for the single-vector region by minimizing the total free energy (obtained by adding to  $F_c$  the external field energy,  $-HI_0 \cos \phi$ , where  $\phi$  is the angle between  $H$  and  $I_0$ ) with respect to the direction of  $I_0$ . By appropriate choice of the anisotropy coefficients good general agreement with the observed curves can usually be obtained. In view of experimental irregularities and the imperfections of the specimens, however, the criterion of 'best fit' cannot usually be satisfactorily applied for a primary determination of the coefficients, for which a more clear-cut method is desirable.

The basic theory of the torque curve method of investigating single crystals, due mainly to Akulov (1931) and Gans (1932), has been developed in considerable detail by Bozorth (1936), Schlechtweg (1936), Tarasov and Bitter (1937) and Bozorth and Williams (1941). The general theory of the torque on a spheroid

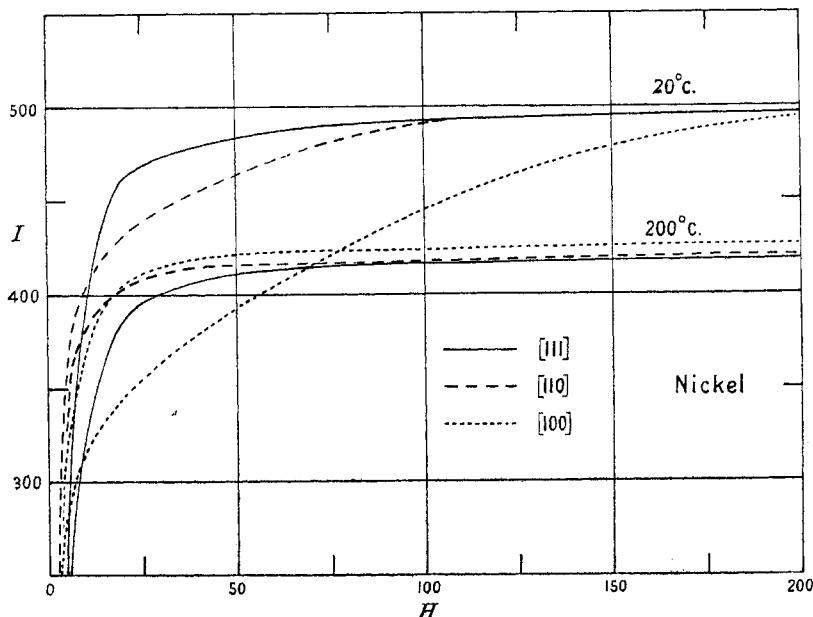


Figure 2.2. Magnetization curves for single crystals of nickel at 20° and 200° c.  
From the data of Honda, Masumoto and Shirakawa (1935).

when the equatorial plane has any crystal orientation is very complicated geometrically (or trigonometrically) even when the single vector assumption is made. If the aim is primarily the determination of the anisotropy coefficients, attention may be restricted to the equatorial orientations (100), for which the torque curves depend on  $K_4$  only, and (110), for which the curves depend on both  $K_4$  and  $K_6$ . These cases, with others, are dealt with by Bozorth (1936), and it will be sufficient to take one particular case in illustration. For a (110) spheroid,  $I_0$  is confined (except in small fields) to the equatorial plane. Denoting the angles between a chosen reference direction, say [001], and  $H$  and  $I_0$  by  $\theta$  and  $\psi$  respectively, the torque,  $T$ , is given by

$$T = -\partial F / \partial \theta, \quad \dots \dots (2.6)$$

where

$$F = F_c - HI_0 \cos(\theta - \psi), \quad \dots \dots (2.7)$$

and  $F_c$  is given by (2.1). Further, the equilibrium direction of  $I_0$  is given by

$$\partial F / \partial \psi = 0. \quad \dots \dots \quad (2.8)$$

From these equations it may be shown without difficulty that

$$T = -(K_4/8)(2 \sin 2\psi + 3 \sin 4\psi) \\ - (K_6/64)(\sin 2\psi + 4 \sin 4\psi - 3 \sin 6\psi). \quad \dots \dots \quad (2.9)$$

Now in this equation the torque is expressed in terms of the angle,  $\psi$ , not directly known, between  $I_0$  and the reference direction, rather than in terms of  $\theta$ , the known angle between  $H$  and the reference direction. From (2.8) and (2.7) a manageable expression is obtainable for  $\theta$  as a function of  $\psi$ , but not in general for  $\psi$  in terms of  $\theta$ . The complications are evaded (cf. Bozorth 1936) by the consideration that as  $H$  increases indefinitely, the direction of  $I_0$  approaches that of  $H$ , and  $\theta - \psi$  tends to zero. In (2.9), in the limit,  $\psi$  may be replaced by  $\theta$ . Good agreement can be obtained between the experimental results in high fields, and the torque curve calculated from (2.9) in this way, adjusting the coefficients to give the closest fit, as illustrated in Figure 2.3, showing the results of Williams (1937 b) for a disc (1.77 cm. in diameter, 0.222 cm. thick) of 3.85% silicon iron.

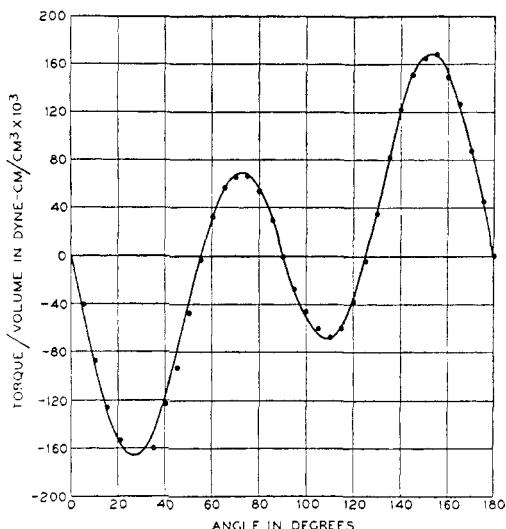


Figure 2.3. Torque curve for a single crystal disc of silicon iron in the (110) plane, taken with an applied field of 5,800 oersteds.

The line is drawn according to equation (2.9), with  $K_4 = 28.7 \times 10^4$ ,  $K_6 = 10.0 \times 10^4$  (Williams 1937 b).  
(Reproduced, by kind permission, from 'The Physical Review'.)

It has been found by Tarasov (1939) that the maximum torque in a field  $H$ , which may be denoted by  $T_H$ , can be closely represented over the higher field range by

$$T_H = T_\infty(1 - H_0/H_a), \quad \dots \dots \quad (2.10)$$

where  $H_a$  is the applied field, and  $H_0$  an empirical constant. Later work by Bozorth and Williams (1941) shows that this equation is not generally valid, but that, applied with discretion to high field results, it will usually give a good approximation to the limiting torque.

The above outline gives the essentials of the main methods which have been used for the determination of anisotropy coefficients, and it is unnecessary to consider the minor variants. Experimental investigations to test whether the different methods yield consistent results are clearly desirable. Such an investigation has been made by Williams (1937 b), who determined the coefficients for 3·85% silicon iron by three methods: from the  $(I_p, H)$  curves obtained with picture frame crystals; by measurement of areas and by curve fitting; and from torque measurements (Figure 2.3). The values obtained for  $K_4$  (in units of  $10^5$  erg cm $^{-3}$ ) were 2·72, 2·80 and 2·87; and for  $K_6$ , 1·5, 1·0 and 1·0. The agreement must be regarded as extremely satisfactory and would seem to indicate that different methods do give consistent results for a particular material when the experimental work and the analysis of the results are carried out with sufficient care. In general, however, there is a wide spread in the values given for the anisotropy coefficients as derived from the data (either by the experimentalists themselves or by others) on materials differing little in composition, and similarly heat treated. It will be clear from (2.5) that comparatively small experimental errors may result in large errors in the estimated values of  $K_6$ , and this is probably sufficient to account for the very different values given. For  $K_4$  the agreement is closer, but the range of values is still much wider than would be expected from the estimated accuracy of the experimental results. A thorough critical survey of the data, such as is desirable, cannot be undertaken here. Rather crudely estimated most probable values will be given, with some indication of the spread. General surveys of the experimental work, and lists, of varying degrees of completeness to the dates indicated, of the values derived for the anisotropy coefficients are given in papers by McKeehan (1934 a, 1937 a) and Bozorth (1937) and in the books by Stoner (1934), Bitter (1937), Becker and Döring (1939) and Bates (1950).

#### *Numerical values of anisotropy coefficients.*

*Iron.* McKeehan (1934 a, p. 27) lists the values he obtains for  $W_{110} - W_{100}$  and  $W_{111} - W_{100}$  from the data of Beck (1918), Webster (1925), Honda and Kaya (1926) and Honda, Masumoto and Kaya (1928). From these energy density differences, using (2.5),  $K_4$  and  $K_6$  may be derived. Expressing the anisotropy coefficients in units of  $10^5$  erg cm $^{-3}$ , the mean and mean deviation are for  $K_4$  (7 values)  $4\cdot16 \pm 0\cdot53$ , and for  $K_6$  (5 values),  $-1\cdot2 \pm 1\cdot9$ . It may be noted that some of the same experimental data have been analysed by Gans and Czerlinski (1932, 1933), whose values for  $K_4$  and  $K_6$  are listed by Becker and Döring (1939, p. 123). From the same sets of experimental results for which McKeehan's analysis gives, as a mean of three values, 4·69 for  $K_4$ , Gans and Czerlinski obtain 4·35; and the means of two values of  $K_6$  are, respectively, -2·7 and +2·6.

The later work on iron includes that of Piety (1936) by the pendulum magnetometer method (see Figure 2.1) and of Tarasov (1939), by the torque magnetometer method. For one specimen Piety obtained  $K_4 = 4\cdot42$ ,  $K_6 = +1\cdot4$  and for another  $K_4 = 4\cdot27$ ,  $K_6 = -1\cdot7$ . It is obvious from these results, and those above, that no significant 'probable value' can be given for  $K_6$  for iron. The  $K_4$  values agree reasonably well with each other, and with the mean of the earlier values. Tarasov's torque measurements, however, on one of the spheroids which had been used by Piety, gave a value of 5·29, considerably higher than any previously listed, and for a second specimen 4·74. In an excellent discussion of his own and relevant previous work on iron, Tarasov concludes that the earlier torque

curve data, properly treated, are not incompatible with values of  $K_4$  higher than those usually given, and comparable with his own; but he cannot account for the lower values obtained by the area method from  $I_p$  curves. The position is clearly very unsatisfactory, but until further investigations are made, the best that can be done is to take as a working probable value of  $K_4$  the mean of the just quoted values of Piety and Tarasov, since the iron used was of high purity (better than 99.9%) and each investigator was aware of such possible sources of error as have so far been recognized in the method he used. This gives  $K_4 = 4.68 \pm 0.34$ , or, nearly enough,  $K_4 = 4.7$ , with an uncertainty of at least 10%.

The most extensive investigation of the temperature variation of the ( $I_p$ ,  $H$ ) curves for different crystal directions is that of Honda, Masumoto and Kaya (1928), whose measurements covered a range from 5°C. to 770°C. Piety (1936)

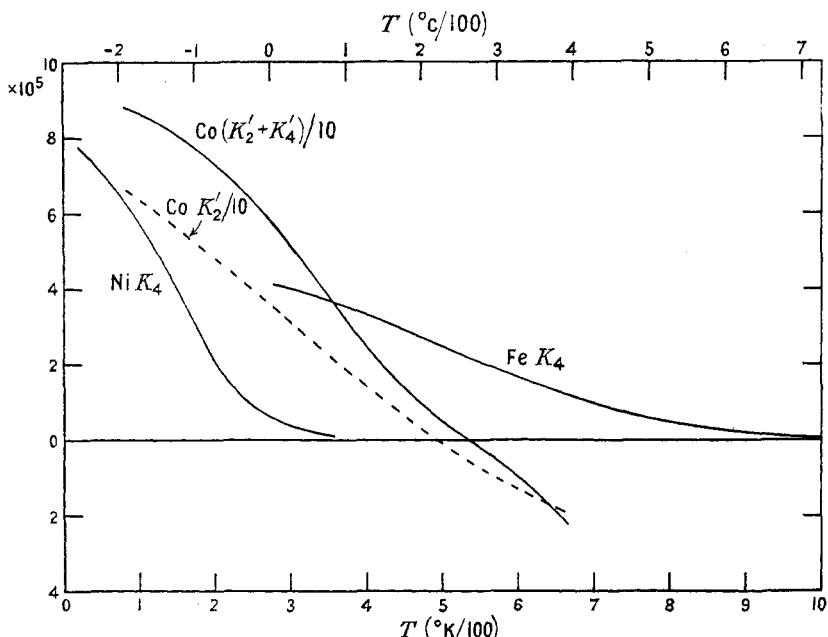


Figure 2.4. Temperature variation of the magneto-crystalline anisotropy coefficients of iron, nickel and cobalt.

Based on the experimental data of Honda, Masumoto and Kaya (1928) for iron, of Brukhatov and Kirensky (1937) and of Williams and Bozorth (1939) for nickel, and of Honda and Masumoto (1931) for cobalt. For definitions of  $K_4$ ,  $K'_2$  and  $K'_4$  see equations (2.1) and (2.2). The coefficients are expressed in erg cm<sup>-3</sup>. The methods of evaluation are described in the text.

has evaluated  $K_4$  (and also  $K_6$ ) from their results, and gives a list of values obtained by interpolation for conveniently spaced temperatures over the range. A curve drawn through points plotted from his values is shown in Figure 2.4. Piety's own results give systematically higher values for  $K_4$  at 18°, 296° and 500°C., but are consistent with a curve of the same form. At 675°C. (see Figure 2.1) and 696°C., to the accuracy of the measurements, his magnetization curves for the [100], [110] and [111] directions coincide, corresponding, formally, to a zero value of  $K_4$ ; but a tailing off, as in the curve shown, is not precluded. A curve given by Titow (1936), showing the relative values of  $K_4$  over the range 0° to 450°C., as obtained from torque measurements, is of the same general form as that in Figure 2.4.

*Nickel.* The earliest measurements on single crystals of nickel are those of Sucksmith, Potter and Broadway (1928) and of Kaya (1928). The values of the anisotropy coefficients which have been obtained from them are remarkably consistent. The areas obtained by McKeehan (1934 a) from the  $(I_p, H)$  curves correspond in both cases to  $K_4 = -0.51$  (in units of  $10^5 \text{ erg cm}^{-3}$ ). Gans and Czerlinski (1933) derive the same value from Kaya's  $(I_p, H)$  curves, by curve fitting, and their values from four sets of  $(I_n, H)$  curves of Sucksmith *et al.* correspond to  $K_4 = -0.48 \pm 0.05$ . The various results are fitted reasonably well without taking the  $K_6$  term into account, being consistent with a value of  $K_6$  numerically less than 0.1.

The later work of Honda, Masumoto and Shirakawa (1935), covering a range of temperature from  $-252^\circ$  to  $+370^\circ\text{C}$ ., has already been mentioned (see Figure 2.2). From an evaluation of areas McKeehan (1937 a) obtains the very different room temperature values  $K_4 = -0.34$ ,  $K_6 = +0.53$ . The results of Brukhatov and Kirenski (1937), obtained by the torque method, using a spherical specimen, cover the range from  $77^\circ$  to  $390^\circ\text{K}$ . At room temperature (taken here, for definiteness, as  $290^\circ\text{K}$ .) their value of  $K_4$  is  $-0.50$ . (No values are given for  $K_6$ .) They find that, apart from a slight deviation over the upper part of the range covered, the results are represented closely by

$$K_4 = (K_4)_0 \exp(-aT^2),$$

where

$$(K_4)_0 = -8.0 \times 10^5, \quad a = 3.4 \times 10^{-5}.$$

At the lower temperatures the magnetization curves of Honda *et al.* indicate enormously higher values than those given by the above equation. Torque measurements by Williams and Bozorth (1939) gave 1.2 (to an accuracy of within about 10%) as the ratio of the values of  $K_4$  at  $20^\circ\text{K}$ . and  $77^\circ\text{K}$ . This agrees with the ratio of 1.21 given by the equation, while the Honda results correspond to a ratio of about 5. At  $77^\circ\text{K}$ . and above Williams and Bozorth obtained absolute values which were very close to those of Brukhatov and Kirenski, whose results are shown graphically in Figure 2.4. The change in order of ease of magnetization along different axes indicated by the Honda curves (Figure 2.2) is very striking, but it is clearly unjustifiable to attach much weight to the numerical estimates of anisotropy coefficients which may be obtained from them.

The salient facts to be noticed are that at room temperature  $K_4$  for nickel is numerically about one tenth of  $K_4$  for iron and of opposite sign; and that the temperature variation is more pronounced, but of somewhat similar character. For neither element can a satisfactory estimate be made at present of the value of  $K_6$  for an 'ideal' crystal.

*Cobalt.* The only measurements so far available on single crystals of cobalt are those of Kaya (1928), at room temperature, and of Honda and Masumoto (1931), over a temperature range from  $-190^\circ$  to  $+390^\circ\text{C}$ . (The stable form of cobalt is hexagonal below and face-centred cubic above a temperature of about  $470^\circ\text{C}$ .) At room temperature the easy direction of magnetization is that of the hexagonal axis, [0001], for which the magnetization rises almost to the saturation value in low fields. For directions in the basal plane, (0001), the magnetization increases slowly, and the curve, which is concave towards the  $H$  axis, can be represented reasonably well by an equation derivable from (2.2) with a suitable choice of

$K_2'$  and  $K_4'$ . The curves are slightly different along the axes of closest packing of the rows of atoms, typified by  $[11\bar{2}0]$ , and the axes bisecting these,  $[10\bar{1}0]$ , the curves for the latter being slightly higher (magnetization is 'easier') than for the former; but the energy difference is very small compared with that between either and the hexagonal axis, and will not be considered here. If isotropy in the basal plane is assumed, it will be clear from (2.2) that the sum  $K_2' + K_4'$  gives directly the energy density difference for magnetization along and normal to the hexagonal axis. This may be directly derived by the area method from  $(I_p, H)$  curves for the two directions. The determination of  $K_2'$  and  $K_4'$  separately is possible only by a curve fitting method.

From Kaya's results the area evaluations of McKeehan give at room temperature  $K_2' + K_4' = 52$  (in units of  $10^5 \text{ erg cm}^{-3}$ ), while Gans and Czerlinski obtain for the separate coefficients  $K_2' = 41$ ,  $K_4' = 10$ . The values of  $K_2' + K_4'$  corresponding to the areas evaluated by McKeehan from the curves of Honda and Masumoto are plotted in Figure 2.4. The value at room temperature is about 59. For  $K_2'$  and  $K_4'$  separately the literature provides a wide choice (see, for example, Bozorth 1937, Van Vleck 1937, p. 1198). The curve for  $K_2'$  in Figure 2.4, which is plotted from values given by Bitter (1937, p. 212), who has made 'slight alterations and corrections' to values given earlier by Gans and Czerlinski, must therefore be regarded as having a lower degree of certainty than that for the sum of the two coefficients. The reliability of the sum curve must be assessed from the fact that values of 52 and 59 are obtained at room temperature from two different sets of results.

The magneto-crystalline anisotropy coefficients of the ferromagnetic elements have been considered in detail (a detail much greater than will be possible for other topics in this report) mainly because a knowledge of the values of these coefficients is a basic requirement in any quantitative treatment of magnetization curves of polycrystalline as well as monocrystalline material, and the uncertainty of the values is not generally appreciated. There is, however, no doubt about general orders of magnitude, and it may be well to summarize the broad facts, which is conveniently done by reference to the difference between the energy densities for magnetization in the easiest and most difficult directions. For cubic crystals this difference is given with sufficient accuracy by  $K_4/3$ , and for hexagonal crystals by  $K_2' + K_4'$ . The values at room temperature for nickel, iron and cobalt are about  $1.7 \times 10^4$ ,  $1.4 \times 10^5$  and  $5.9 \times 10^6$  respectively. Much of the diversity of the 'ordinary' magnetic properties of the three metals can be linked with the differences in these basic characteristics. The maximum energy density difference for nickel increases considerably below room temperature and the trend of the curves of Figure 2.4 suggests that it would be greater than that for iron, but of the same order of magnitude, at the lowest temperatures, the value for cobalt maintaining its relatively high magnitude. The values of the anisotropy coefficients at room temperature only give a quite misleading impression of the problem confronting the atomic theory of these effects.

*Alloys.* Measurements on single crystals of binary alloys of the ferromagnetic elements have been made by the pendulum magnetometer method by Shih (1934, 1936) for iron-cobalt, and nickel-cobalt, and by Kleis (1936) for iron-nickel. Eight ternary alloys in the face-centred region have been examined by McKeehan (1937 a), who summarizes the main results on both the ternary and

binary alloys in two figures, reproduced in Figure 2.5, showing the derived values of  $K_4$  at 20° c. and 200° c.

The main features of the results for  $K_4$  are brought out so clearly in McKeehan's diagrams that no verbal description is necessary, but it should be noted that the  $K_4$  values for nickel differ from those plotted in Figure 2.4, as they are derived from the earlier work of Honda, Masumoto and Shirakawa. The estimated values of

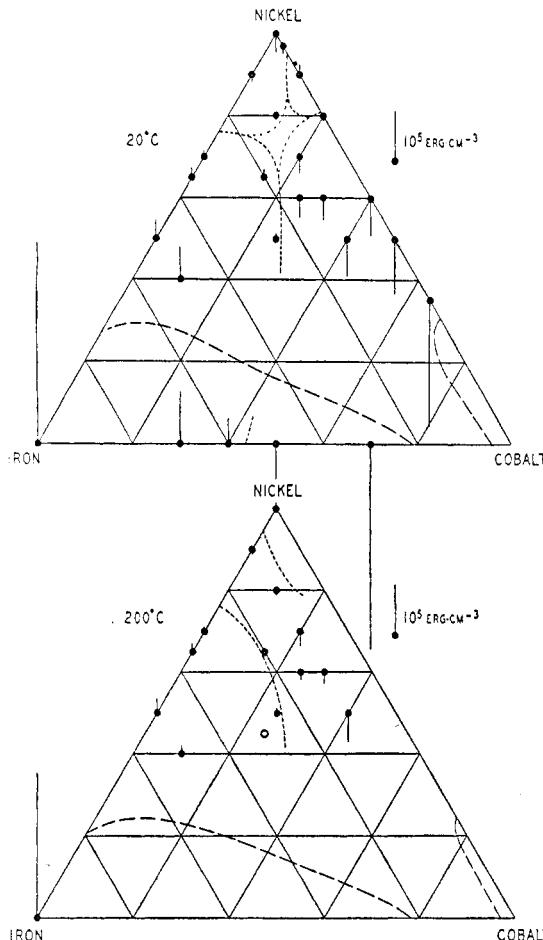


Figure 2.5. Principal anisotropy coefficient,  $K_4$ , of nickel-iron-cobalt alloys at 20° c. (upper figure) and 200° c. (lower figure), as determined from the results of Shih (Fe-Co and Ni-Co), Kleis (Ni-Fe) and McKeehan (ternary alloys).

Lines up or down from a dot indicate positive or negative  $K_4$ , according to the scale on the right. Broken lines show approximate phase boundaries (hexagonal round cobalt, body-centred cubic round iron, face-centred cubic otherwise). The dotted curves are provisional estimates of the zero  $K_4$  lines. (McKeehan 1937 a.)

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$K_6$ , which, as is stated, are very uncertain, show no obvious regularities. None the less, as has been stressed particularly by Bozorth (1936, 1937), a satisfactory formal coordination of the observed magnetization curves cannot in general be obtained unless account is taken of the  $K_6$  term; this is shown most clearly by the occurrence of orders of ease of magnetization other than [100], [110], [111] or the converse in certain composition or temperature ranges.

The results of a detailed investigation of the anisotropy of iron–nickel alloys with from 65 to 80% nickel by Grabbe (1940), using the same method, are most appropriately left for consideration in a later section (§ 5 (iii)).

Extensive measurements have been made by the torque magnetometer method on iron–silicon alloys with an atomic percentage,  $A$ , of silicon up to 13·7 by Tarasov (1939), who finds that the values he obtains for  $K_4$  (in units of  $10^5 \text{ erg cm}^{-3}$ ) are closely represented by

$$K_4 = 5.29 - 0.279 A \quad (A < 9.86),$$

$$K_4 = 4.43 - 0.192 A \quad (A > 9.86).$$

A later value for  $K_4$  obtained by Bozorth and Williams (1941) for a 3·6% specimen (atomic per cent,  $A$ , 6·9) is 3·5, about 7% higher than the value given by Tarasov's first equation. Williams's earlier values, mentioned above, for a 3·85% specimen, are about 14% lower.

It may be noted that although added silicon reduces the anisotropy coefficient of iron considerably (1% by weight gives a reduction of about 10%) the effect is not so large as to suggest that more than a small part of the spread of the 'observed' values for ordinarily pure iron can be accounted for in terms of the presence of impurities.

*Miscellaneous.* A considerable number of investigations have been made on diverse magnetic characteristics of single crystals, the results of which are peculiar to particular materials and specimens rather than being of general relevance. Bare reference must therefore suffice to work on the variation with direction of initial permeability by Williams (1937 c), which has been discussed by Bozorth (1937), Kondorski (1938), and Becker and Döring (1939, p. 133), and supplemented by further experiments of Shoenberg and Wilson (1946); on the coercivity of iron–silicon by Sixtus (1937 b) and Jaanus and Schur (1937), and on the coercivity and maximum permeability of very pure iron and iron nickel (66% Ni) by Cioffi, Williams and Bozorth (1937); and on the hysteresis losses in iron–silicon (2.1% Si) by Wilson (1946).

### 2 (iii). Theory of Magnetization Curves

It will be clear from the discussion of the derivation of anisotropy coefficients from experimental data on single crystals that a simple formal treatment covers satisfactorily first the variation with field of  $I_p$  when  $H$  is along an axis of symmetry ( $I_n$  then being zero), and secondly the variation of  $I_n$  with both direction and magnitude of the field provided that the field is large. In view of the extensive application made of them, it may be useful to give the expressions, first derived by Akulov (1929, 1931) and Gans and Czerlinski (1932), for the magnetization with the field along the axes of symmetry. Writing  $I_p/I_0=j$ , the expressions are as follows:

$$H \text{ along } [100], \quad j = 1, \quad \dots \dots \dots \quad (2.11)$$

$$H \text{ along } [110], \quad j^3 - \frac{1}{2}j = HI_0/4K_4, \quad \dots \dots \dots \quad (2.12)$$

$$H \text{ along } [111], \quad \frac{K_4}{3} \{j(7j^2 - 3) + 2^{\frac{1}{2}}(1 - j^2)^{\frac{1}{2}}(4j^2 - 1)\} + \frac{K_6}{18} \{j(23j^4 - 16j^2 + 1) \\ - 2^{\frac{1}{2}}(1 - j^2)^{\frac{1}{2}}(10j^4 - 9j^2 + 1)\} = HI_0. \quad \dots \dots \dots \quad (2.13)$$

Although it has been recognized for some considerable time that the variation of  $I_p$  and  $I_n$  in lower fields of arbitrary direction could not readily be reconciled with the theoretical scheme, it is only recently that a quantitative assessment of the apparent discordance has been made by von Engel and Wills (1947), and that a new method of approach to the problem, which removes most of the difficulties, has been developed independently by Néel (1944 a) and by Lawton and Stewart (1948). (It may be noted in passing that even the existence of papers published during the 1939–45 period could often not be known to many of those interested until much later.)

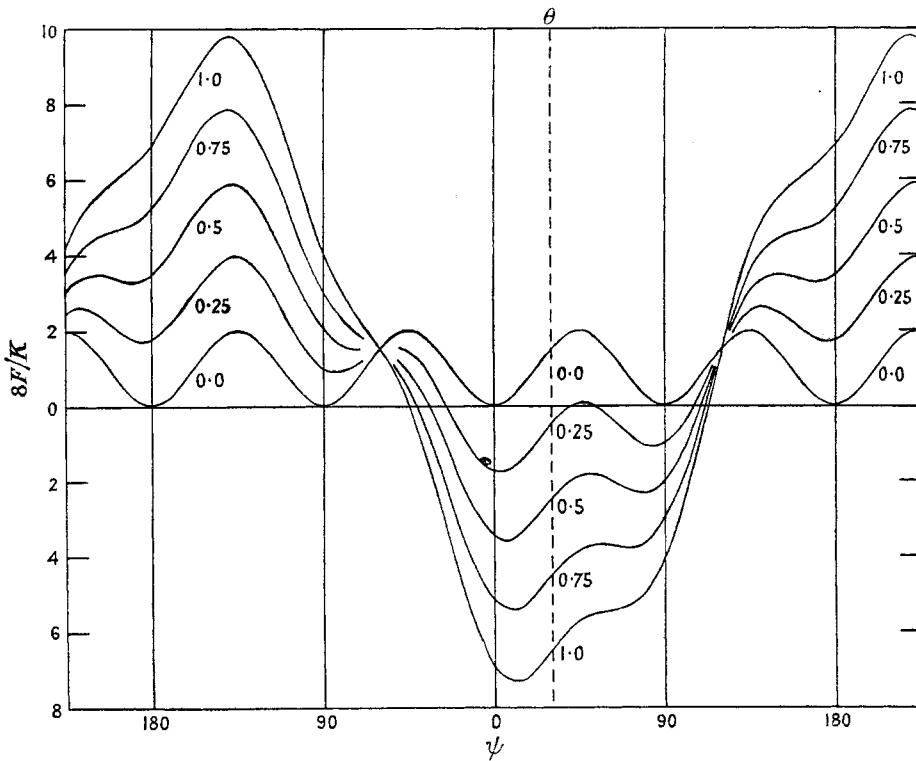


Figure 2.6. Relation between energy and direction of magnetization for a single iron-like crystal in a (100) plane.  $\psi$ , angle between [100] and  $I_0$ .  $h = HI_0/K$ . Angle,  $\theta$ , between [100] and  $H$ ,  $30^\circ$ . The numbers on the curves give the values of  $h$ .

Following the general treatment of von Engel and Wills, the essentials of the problem can be made clear by considering the dependence on direction of magnetization of the relevant part of the free energy of a uniformly magnetized iron-like crystal ( $K = K_4$  positive,  $K_6$  negligible; see (2.1)), with field and magnetization in the (100) plane. It is readily found from (2.1) that

$$F/K = \frac{1}{8}(1 - \cos 4\psi) - h \cos(\theta - \psi), \quad \dots \dots \quad (2.14)$$

where  $\psi$  and  $\theta$  are the angles between a [100] reference axis and  $I_0$  and  $H$  respectively, and  $h = HI_0/K$ . Energy contours for various values of  $h$  are shown in Figure 2.6.

Of the four equal energy minima in zero field the one nearest to the field direction becomes more and more pronounced as the field increases, and moves towards the field direction. On the assumption that the domain magnetization vectors

come into alignment along the direction corresponding to the deepest energy minimum by domain boundary movements, it would be expected that a single vector treatment would cover the behaviour (that is, the variation of  $I_p$  and of  $I_n$  with  $H$ ) except possibly in very low fields. Detailed calculations have been made by von Engel and Wills on this basis of the variation of the direction of  $I_0$  (i.e. the value of  $\psi_{\min}$ ) with  $h$  for various values of  $\theta$ , and of  $I_n/I_0$  with  $\theta$  for various values of  $h$  for the (100), (110) and (111) planes. The curves for  $I_n/I_0$  against  $\theta$  are, in general, surprisingly complicated, and reference must be made to the original paper for details. Roughly, it is only for values of  $h$  well above unity (corresponding, for iron, to values of  $H$  well above 280 oersteds) that the curves have a continuous periodic form similar to that found experimentally. The inadequacy of the theoretical treatment is shown most convincingly by a comparison of the theoretical curves for the variation of  $I_n/I_0$  with  $h$  for particular values of  $\theta$  with the curves derivable from experimental results (Webster 1925, Honda and Kaya 1926). For  $\theta = 30^\circ$ , for example, as is apparent from Figure 2.6,  $I_n/I_0$  should increase monotonically as  $h$  decreases, reaching the value  $\sin \theta$  for zero  $h$  (or, strictly, for  $h$  just greater than zero). The experimental results are in agreement for high values of  $h$  (say  $h > 10$ ), but, as  $h$  decreases, the experimental curve, diverging more and more from the theoretical curve, passes through a maximum, and approaches zero for zero field. It is to be noted that the direct experimental data are in terms of the applied field,  $H_e$  (e.g. a set of values may be available for  $I_n$  and  $I_p$  for  $H_e$  constant in magnitude and varying in direction), and the reduction of the data to a form appropriate to the use of  $H$ , the field 'corrected' for demagnetization effects, as the field variable, is, in general, both troublesome and uncertain. None the less, there is no doubt that the discrepancies between the single vector treatment and experiment are not in the main attributable to uncertainties arising in this way.

The experimental results in the lower fields are in fact inexplicable if the domain magnetization vectors are sharply restricted to the direction of a single deepest energy minimum. It was therefore proposed by von Engel and Wills that the domain directions might be distributed according to an expression of the form

$$dv_\psi = C \exp(-F/F_0) d\omega, \quad \dots \dots \quad (2.15)$$

where  $dv_\psi/d\omega$  is the volume of domains per unit solid angle with  $I_0$  at an angle  $\psi$  to the reference direction,  $F$  the corresponding energy per unit volume (given by an expression of the type (2.1)), and  $F_0$  a constant reference energy. The single vector treatment already considered would correspond to the limiting case  $F_0/K \rightarrow 0$ . The larger the value of  $F_0/K$ , the wider the angular spread of domain magnetization directions. In low fields there might be an appreciable 'occupation' of directions not only near the lowest energy minimum but also near other low minima, but in high fields, as is required, only the lowest energy minimum need be considered. The particular experimental results examined by von Engel and Wills (those of Honda and Kaya on spheroids of iron) were fairly well (but by no means perfectly) covered, after correction for demagnetization, by taking for  $F_0$  a value of about  $K/8$ . Now if the directional distribution (2.15) were of thermal origin,  $F_0$  would be of the order  $kT/v_d$  where  $v_d$  is a suitably averaged single domain volume. With  $F_0$  equal to  $K/8$ , this would give for the number of atoms per domain in iron about  $200T$ , i.e. about  $6 \times 10^4$  at room temperature, a number which is too small by a factor of at least  $10^8$ . Alternatively expressed, with

domains of the size indicated by other evidence, the 'thermal' spread of the directions of magnetization would be completely negligible in its effects. This was fully appreciated by von Engel and Wills, but they were unable to make any plausible suggestion as to the physical origin of a distribution parameter of the required order of magnitude. Unknown to them, a very general and detailed statistical treatment of the consequences of a formal assumption of the kind expressed by (2.15) had previously been developed by Takagi (1939), who also could find no physical justification of the magnitude apparently required for  $F_0$ . Since in the work now to be described very close agreement with experiment is obtained without any *ad hoc* assumptions in the theory, Takagi's extensive papers must be passed over here, though it should be stated that there is much of interest in the mathematical treatment, and that the various functions evaluated and tabulated may well have other fields of application.

The theoretical schemes of Néel (1944 a) and of Lawton and Stewart (1948) for the interpretation of the magnetization curves of single crystals are in essentials identical, and it would be out of proportion to dwell here on interesting and characteristic differences in detail in the manner of approach. The simplest assumption of the domain theory is adopted, namely that the domain magnetization vectors lie along the direction of the lowest energy minimum, as determined

Table 2.1  
Modes of Magnetization of Iron-like Single Crystals

The direction cosines of  $H$ , the resultant field,  $\beta_1, \beta_2, \beta_3$ , and of  $I_0, x_1, x_2, x_3$ , are with respect to the crystal axes.

Mode	Resultant field, $H$	Phases of magnetization		
	Magnitude	Direction cosines	No.	Direction cosines
I	$H=0$	—	6	$\langle 100 \rangle$
II	$H>0$	$\beta_1=\beta_2=\beta_3$	3	$[p, p, q], [p, q, p], [q, p, p]$
III	$H>0$	$\beta_1=\beta_2>\beta_3$	2	$[p, q, r], [q, p, r]$
IV	$H>0$	$\beta_1>\beta_2>\beta_3$	1	$[p, q, r]$

jointly by the crystal anisotropy and the effective field,  $H$ , a resultant of the applied field,  $H_e$  and the demagnetizing field. There can therefore be two (or more) groups of domains with different directions of magnetization (constituting distinct 'phases', in Néel's terminology) only if there are two (or more) equal deepest energy minima. (In Figure 2.6, there are four such minima in zero field, but only one if the resultant field is not zero. If the angle,  $\theta$ , between the  $[100]$  direction and the field were  $45^\circ$ , there would be two equal deepest minima.) Moreover, for the co-existence of two (or more) phases the resultant field direction must be symmetrical with respect to two (or more) easy axes. For an iron-like crystal (with cube edges as easy axes) there are four possible 'modes' of magnetization, corresponding to different numbers of distinct phases, as shown in Table 2.1 (cf. Néel 1944a, Lawton 1949).

The range of the external field,  $H_e$  for each mode depends on its direction, on the demagnetizing factors (i.e. the shape) of the specimen, and, of course, on the magnitude of the crystal anisotropy coefficients. In the general case the four modes would succeed each other as  $H_e$  increases, but in a number of cases of practical importance one or two of the last three modes may not occur.

In determining the state of magnetization for a given applied field the basic condition to be satisfied is that the energy of the crystal specimen as a whole is a minimum with respect to variation of the directions of magnetization (there being one direction for each phase present) and of the fractional volumes of each phase. In the work under review this condition is not applied directly (except in the single-vector, or mode IV case) but rather the consequential condition, already described, as to the direction of the resultant field when two or more phases are present. The fact that in an applied field a two- or three-phase state may have a lower energy than a one-phase state is essentially due to the demagnetizing field energy, equal to  $+\frac{1}{2}NI^2$ , where  $I$  is the resultant magnetization, always being smaller in the former state than in the latter, for which its value is  $+\frac{1}{2}NI_0^2$ . The smaller the relevant demagnetizing coefficients,  $N$ , the wider the range of applicability of

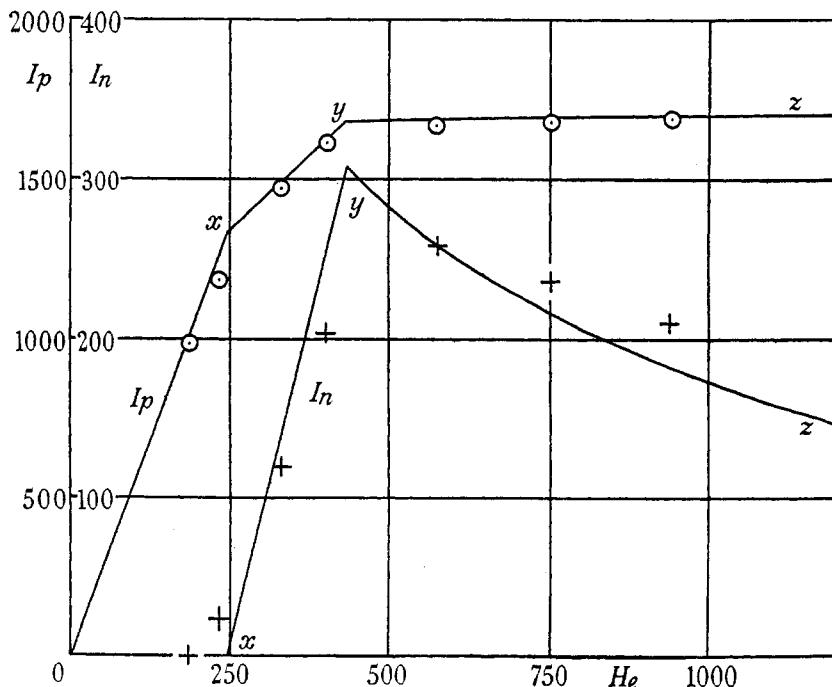


Figure 2.7. Calculated magnetization curves for an oblate spheroid of iron, equatorial plane (100).

Applied field,  $H_e$ , at  $20^\circ$  to [100]. Demagnetizing coefficient,  $N$ , 0.184. Experimental points from Honda and Kaya (1926). Assumed values:  $K_4 = 4.2 \times 10^6$  erg cm $^{-3}$ ,  $I_0 = 1720$  gauss. (Lawton and Stewart 1948.)

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the single vector treatment. Within a given mode, as the applied field is increased, the adjustment to the minimum energy state occurs physically by change of the directions of magnetization and change in the relative volumes of the phases. The reduction to zero of the fractional volume of any phase marks the transition to another mode.

In all but the very simplest cases (essentially those considered in § 2(ii)) the calculation of the magnetization curves (i.e. of  $I_p$  and  $I_n$  as functions of  $H_e$  and  $\theta$ ) is troublesome and lengthy, and reference must be made to the original papers for details. In Figure 2.7, due to Lawton and Stewart, illustrative theoretical curves and experimental points are shown for a fairly simple case, that of a (100) spheroid,

with the angle,  $\theta$ , between the applied field and the [100] direction equal to  $20^\circ$ . The parts  $Ox$  of the curves correspond to the mode I region (see Table 2.1) for which the resultant field,  $H$ , is zero. From this,

$$H_e - NI_p = 0, \quad NI_n = 0,$$

giving

$$I_p = H_e/N, \quad I_n = 0. \quad \dots \quad (2.16)$$

The details of the changes in the relative volumes of the phases present during this stage are not required and are, in fact, indeterminate with the conditions assumed. The limit of the range occurs when there are two groups of domains (two phases) with magnetization directions along the two easy axis directions, [100], [010], nearest to the field, the resultant field still being zero. It may easily be shown that for the state corresponding to the 'knee' at  $x$ ,

$$H_e = \frac{NI_0}{\cos \theta + \sin \theta}, \quad I_p = \frac{I_0}{\cos \theta + \sin \theta}, \quad I_n = 0, \quad \dots \quad (2.17)$$

and that the volumes of the [100] and [010] phases are proportional to  $\cos \theta$  and  $\sin \theta$ .

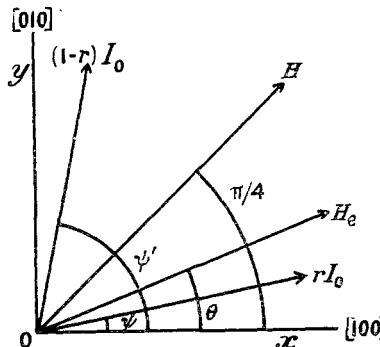


Figure 2.8. Magnetization of a (100) spheroid with the applied field in the (100) plane for the two-phase range (mode III).

$H_e$ , applied field.  $H$ , resultant of applied and demagnetizing fields.  $r$ , fractional volume of phase with domains with  $I_0$  at an angle  $\psi$  to the [100] axis.

At  $x$  the mode of magnetization changes from I (or a modified form of I, since there are effectively four rather than six phases) to III, with two phases. The directions of field and magnetization in this two-vector range ( $xy$  in Figure 2.7) are illustrated in Figure 2.8.

The resultant field,  $H$ , is symmetrical with respect to the easy axes (i.e.  $H$  is along [110]), and the angles between the magnetization vectors and the nearest easy axis are equal (i.e.  $\psi + \psi' = \pi/2$ ). The variation of  $I_p$  and  $I_n$  with  $H_e$ , for a given  $\theta$ , can be determined numerically from equations expressing the basic condition (that the energy is a minimum) or the consequential conditions, various short cuts being possible (e.g. by making use of the already known relation (2.12)). Physically, as  $H_e$  increases, the change occurs partly by rotation of the domain magnetization vectors, and partly by boundary movement processes resulting in a change in the relative volumes of the two phases. Referring to Figure 2.8,  $\psi$  increases and  $\psi'$  decreases, the sum remaining constant, and  $r$  increases from the value  $\cos \theta$  (for  $\psi=0$ ) to unity. With the disappearance of the second phase ( $1-r=0$ ), at the points  $y$  in Figure 2.7, mode III is succeeded by mode IV, and

the variation of  $I_p$  and  $I_n$  with  $H$  ( $yz$  in Figure 2.7) can be calculated by the single vector treatment. The good agreement between theory and experiment is clearly apparent in Figure 2.7.

Treatments of the magnetization of iron crystals in the form of (100) spheroids and of 'long rods' of particular crystal orientations are given both by Néel and by Lawton and Stewart, comparison being made with the experimental results of Webster (1925), Honda and Kaya (1926), Sizoo (1929) and Kaya (1933). In later work Lawton (1949) has considered in detail the case of the oblate spheroid with a (110) equatorial plane, and Stewart (1949) has extended the general treatment to cover the effects of tension. In most cases there is no significant difference between theory and experiment. That the experimental curves are usually more rounded than the theoretical ones is probably attributable to an effect of internal strains. The wider discrepancies occasionally found seem more likely to be due to experimental uncertainties (e.g. as to the composition, degree of homogeneity and freedom from internal strain, and precise crystal orientation of the specimen) than to any inherent defect in the theoretical treatment. Hysteresis effects and effects associated with domain boundary energies are deliberately left out of consideration. Tidier methods of developing the treatment may be evolved, and further applications and extensions of it will no doubt be made. It may be said, however, that in principle, as a result of the work outlined, the formal theory of the magnetic properties of ferromagnetic single crystals is now complete, in that the observable properties within its scope can be completely coordinated. The explanation of the magnitude and the temperature variation of the formal coefficients, the magneto-crystalline anisotropy coefficients, is a problem for atomic, as distinct from macroscopic, theory.

#### 2(iv). Atomic Theory

The atomic and statistical theory of the magneto-crystalline anisotropy of metallic ferromagnetics is extremely complex, and no quantitatively satisfactory treatment has yet been developed. The papers which have appeared on this subject since 1934, though few in number, are concentrated in content and do not lend themselves to brief summary. All that can be done here is to indicate the methods of approach adopted and the general character of the conclusions reached.

*Magnetic interaction.* It is convenient to refer first to the work McKeehan (1933, 1937 b). After the slow and reluctant abandonment of the venerable hypothesis that the basic characteristics of ferromagnetics might be due to magnetic interactions between elementary carriers of the magnetic moment, appropriately shaped and disposed, it was still reasonable to suppose that these interactions might account for some of the secondary effects. McKeehan's work is essentially a detailed quantitative investigation of this possibility. Assuming that the elementary carriers are multipoles of moment  $\mathbf{P}$ , and that the multipole structure has axial and polar symmetry, the expression for half the mutual potential energy of a pair of multipoles with the moments parallel may be written

$$U = -(P^2 F_2)(ar)^{-3} P_2 \{ \cos(\mathbf{P}_1, \mathbf{r}_1) - (P^2 F^4 a^2)(ar)^{-5} P_4 \{ \cos(\mathbf{P}_1, \mathbf{r}_1) \} \\ - (P^2 F_6 a^4)(ar)^{-7} P_6 \{ \cos(\mathbf{P}_1, \mathbf{r}_1) \} \}, \dots \quad (2.18)$$

where  $\mathbf{P}_1$  and  $\mathbf{r}_1$  are unit vectors in the directions of  $\mathbf{P}$  and  $\mathbf{r}$ , whose numerical magnitudes are  $P$  and  $ar$ ,  $a$  an appropriately chosen unit of length related to the

lattice constant, the  $F$ , magnetic form factors, and the  $P$ , zonal surface harmonics. The successive terms correspond to dipole, quadrupole, sextupole . . . energy. The form factors may be calculated without undue difficulty for particular multipole structures, corresponding to specific distributions of magnetic moment. Distributions of sufficient generality are obtained by supposing the moment to be spread along two symmetrical parallels of latitude on a sphere of radius  $\rho a$ , and directed parallel to the polar axis; the limiting cases correspond to an equatorial and polar distribution of magnetic moment. To find the dependence of the energy per unit volume on the direction of magnetization relative to the crystal axes, it is necessary to determine the sum of expressions of the form (2.18) over all pairs of magnets with one magnet in common. Extensive tables giving the results of the laborious evaluations of most of the required lattice sums are presented in McKeehan's earlier papers (1933). In the later paper (1937 b) further sums are evaluated, the form factor is introduced, and explicit calculations are made of the anisotropy coefficients for assemblies of multipoles of moment and lattice distribution in accordance with the experimental data for various ferromagnetic metals and alloys. (Only bare reference can be made here to McKeehan's subsequent extensions of his general methods of calculation to the treatment of homogeneously strained crystals of the ferromagnetic elements (1938 a), and of crystals of pyrrhotite and magnetite (1938 b).) The results depend, of course, on the structure assumed for the multipole; this is taken to correspond either to the equatorial or to the polar distribution of magnetic moment, as mentioned above, on a sphere of radius equal to that estimated for the mean radius of the 3d shell (Slater 1930). For cubic crystals there is no contribution to the anisotropy from the dipole interaction. For iron, assuming an equatorial distribution, the calculated value of  $K_4$  (in  $10^5 \text{ erg cm}^{-3}$ ) is +255 and of  $K_6$  -1671. It may be recalled that the 'observed' value of  $K_4$  at room temperature is about 4.7, and that the value at absolute zero is probably not much greater (see Figure 2.4). For nickel, assuming a polar distribution, the values obtained for  $K_4$  and  $K_6$  are -36 and +287, again much higher than the observed values. It may be noted that for both iron and nickel the sextupole part of  $K_4$  is considerably greater than the quadrupole part. The difference in sign of  $K_4$  for iron and nickel is a consequence of the assumed difference in the distribution of moment in the multipoles, an assumption which is to be regarded as a tentative suggestion to account for the observations. For hexagonal cobalt, the dipole contribution to the anisotropy term  $K_2'$  is appreciable, and of the right sign, but by itself far too small. Inclusion of the quadrupole and sextupole contributions, with either extreme form of moment distribution, gives a total roughly of the order of magnitude required, but of the wrong sign. Values for the anisotropy coefficients calculated in the way outlined are given by McKeehan for many alloys as well as for the elements. It is to be noted that, throughout, the linear dimensions of the multipole structure are assigned in a non-arbitrary manner, and that the distribution of moment is assumed to be either of the extreme polar or equatorial form. With intermediate forms, and with arbitrarily adjusted dimensions, it would undoubtedly be possible to obtain agreement with the observed value of the leading anisotropy coefficient at a particular temperature, but this in itself would mean very little. McKeehan himself makes surprisingly little comment on the significance of the agreement (or disagreement) with experiment of the results of these extensive calculations. The general conclusion to be drawn, it may be suggested, is that the formal

characteristics of magneto-crystalline anisotropy are consistent with basic interactions formally similar to those between magnetic multipoles (implying, essentially, elementary carriers with a distribution of magnetic moment over a space of atomic dimensions); but that, quite apart from the fact that temperature effects are entirely unaccounted for, the type of structure required to give agreement with experiment even as to order of magnitude is incompatible with what is now known about the effective magnetic 'elements' in ferromagnetic metals. McKeehan's papers, in short, do not give a satisfactory atomic theory of magneto-crystalline anisotropy; but they contribute indirectly towards such a theory, and the precise and extensive numerical results for the energies and internal fields associated with the purely magnetic interactions in arrays of multipoles have a permanent value in this and other connections.

*Spin-orbit and orbit-orbit interaction.* The problem of magneto-crystalline anisotropy may be approached in a physically more satisfying manner by considering first what is known, from other evidence, about the elementary carriers of the magnetic moment. For the ferromagnetic metals experiments on the gyromagnetic effect give a  $g$  value equal to, or only a few per cent less than, 2, the value corresponding to electron spins as carriers. The orbital contribution to the magnetization, though not necessarily zero, can hardly in metals be as much as one tenth of the whole. Now in cubic crystals the purely magnetic dipole interaction of the spins gives no anisotropy, and quite generally the magnetic interaction is far too small to account for the observed effects. The very much larger exchange interaction which is responsible for the 'molecular field' in ferromagnetics may be expressed as formally equivalent to a coupling between spins, but this, depending on the angle between two spins but not on the direction of the line joining them, does not give rise to anisotropy. It is now usually accepted that the anisotropy arises in some way from spin-orbit coupling, a view apparently first suggested by Bloch and Gentile (1931), and developed in detail by Van Vleck (1937). Van Vleck gives a long discussion of the whole problem, with full references to earlier work. The almost complete quenching of an orbital moment effect in the magnetization of metals may be attributed to a strong orbit-orbit coupling between different atoms of anti-ferromagnetic sign. Alternatively expressed, the energy distribution of orbital states (conditioned by, and itself conditioning, the crystal symmetry and lattice dimensions) is such that the occupational distribution is little modified by changes in direction of the resultant local magnetization arising from the spins. There is, however, some degree of spin-orbit coupling, with the result that the orbital distribution will vary to some extent with the direction of the magnetization relative to the crystal axes, and, in consequence, the orbit-orbit coupling between different atoms will change. This orbit-orbit coupling is not thought of as being primarily magnetic in character, but rather of the 'orbital valence' type. An exact treatment of the perturbation problem which arises is virtually impossible. Van Vleck shows, however, that the Hamiltonian function containing the formally correct terms corresponding to the spin-orbit and the orbital valence effects may be replaced, with good approximation, by a Hamiltonian containing terms of the dipole and quadrupole type with appropriate coupling coefficients. Even with this simplified Hamiltonian, the problem remains very complex, and in the second part of his paper Van Vleck develops the elaborate mathematical machinery required to deal with it. In view of the uncertainties in the detailed formulation of the problem, and its inherent difficulty, it is not

surprising that no precise numerical results emerge. Little more can be said than that the experimental anisotropy coefficients are consistent as to order of magnitude (to within a factor of 10, say) with such rough estimates as can be made of the various coupling coefficients. This also applies to the contemporary work of van Pepye (1938), who treats a limited aspect of the problem more rigorously than Van Vleck, and to the later work of Brooks (1940), who bases his mathematical treatment on the 'itinerant' or collective electron approximation (I, pp. 69-75) rather than on the Heitler-London approximation (I, pp. 53-58, 66-68).

The theoretical results for the temperature variation of  $K_4$  as given by Van Vleck (1937, pp. 1194, 1196) show rough qualitative agreement with experiment for iron, for which a quadrupole 'model' is used. With the dipole model used for nickel (which would give the wrong sign of  $K_4$  for iron), the calculated temperature variation is widely different from that observed in that there is no indication of the large increase in the magnitude of  $K_4$  below room temperature (see Figure 2.4). An expression derived by Akulov (1936) indicating a variation of  $K_4$  with temperature approximately as  $I_{0T}^{10}$ , where  $I_{0T}$  is the saturation magnetization at temperature  $T$ , has often been quoted as giving good agreement for iron over a fairly wide temperature range. The premises of Akulov's theoretical treatment are, however, so artificial that any such agreement can only be regarded as fortuitous; moreover, even if the premises were valid, the power relation would be a good approximation only for values of  $(I_{00} - I_{0T})/I_{00}$  much less than unity. The temperature dependence of the anisotropy of cobalt has been treated theoretically by Vonsovski (1940), who follows the general method of Bloch and Gentile. An expression is obtained of the form

$$K'_2 = (K'_2)_0 (1 + 2e^{-a/T} - 3e^{-b/T}), \quad \dots \dots \quad (2.19)$$

which fits the observations reasonably well, including the change of sign of  $K'_2$  (see Figure 2.4), with values for  $a$  and  $b$  which are of the same order of magnitude as the very rough theoretical estimates.

In view of the central importance of magneto-crystalline anisotropy in connection with the general behaviour of ferromagnetics in low and moderate fields it is unfortunate that the atomic theory of the effect, as developed up to the present, is quantitatively so imperfect. In dealing with the problem, however, the starting point is necessarily some theoretical scheme for the basic electronic structure of the metal, and a (preferably consistent) theoretical scheme for the effects of exchange interaction; and when the quantitative deficiencies of all such schemes are borne in mind it is somewhat remarkable that any theoretical treatment of further complicating effects can lead to results in even the roughest quantitative agreement with observation. It may be hoped that different methods of approach to the various problems may lead to simpler theoretical coordinating schemes by which the essential significance of the diversity in magnitude, sign and temperature variation of the anisotropy coefficients of different materials may be more clearly understood. This, however, is perhaps over-optimistic, and it may be well to conclude this section with a quotation from the published version (1947) of some lectures given in Paris in 1939 by Van Vleck, who has made the most determined and elaborate attack on this problem of magneto-crystalline anisotropy: 'Le problème est tellement compliqué que des résultats quantitatifs satisfaisants ne pourront être obtenus, si jamais on les obtient, que dans un avenir très éloigné.'

## § 3. DOMAIN STRUCTURE

## 3(i). Theoretical and General

In this section consideration is given to experimental and theoretical work which bears directly on the question of the size, shape and distribution of domains in ferromagnetics. With the acceptance of a basic explanation of ferromagnetism in terms of exchange interaction giving rise to molecular field effects (I, pp. 65–78), the behaviour of ferromagnetics in low and moderate fields provides indirect but irrefutable evidence of a domain ‘structure’ of some kind. It does not, however, enable the character of that structure to be specified in any detail. The hope that the study of Bitter patterns (§ 3(ii)), of the Barkhausen and related effects (§ 3(iii)), and of small particles and thin films (§ 3(iv)) might yield more precise and unambiguous information was long deferred (cf. I, p. 65), and is only now being fulfilled. Attention must here be devoted mainly to a few of the more recent papers, and it is not possible to trace the course of development in detail. It should be understood, however, that the very rapid advance which has recently been made is due not so much to the introduction of essentially novel theoretical ideas or experimental methods as to the effective following up of earlier investigations along different lines which have converged on the domain structure problem. For general reviews of the subject matter of this section, reference may be made to the books of Bitter (1937) and of Becker and Döring (1939), to papers by Brown (1940 a, 1945), and by Kittel (1949).

The term ‘domain’ has been used in more than one sense (cf. Stoner 1938). It will be used here not of a fixed region of the specimen, free from heterogeneities of composition or of strain, but in the more usual sense of a bounded region throughout which the magnetization is uniform, except, possibly, for slight fluctuations in the direction or the intensity. The shape and size (and consequently the number) of domains in a specimen changes with change in magnetization of the specimen as a whole. The domain structure is not therefore static, nor is it, in general, uniquely dependent on the macroscopic state of magnetization of the specimen. When the specimen is saturated or, more generally, in a one-phase state (see § 2(iii)), the whole specimen constitutes a single domain. The direction of magnetization of a domain depends on the magneto-crystalline and strain anisotropy, and on the effective field. When strain effects are negligible, and the effective field is small, a domain is magnetized along one or other of the equivalent easy axis directions; in iron along a cube edge, in nickel a cube diagonal, and in cobalt along the hexagonal axis. Within a single crystal region of an iron-like specimen, the directions of magnetization in contiguous domains, under the conditions mentioned, may therefore be at angles of  $90^\circ$  or  $180^\circ$ , and the transition zones between them are referred to as  $90^\circ$  or  $180^\circ$  boundaries, or walls. (In nickel-like crystals, under the same conditions, the possible angles are  $70.53^\circ$ ,  $109.47^\circ$ , and  $180^\circ$ ; in cobalt-like crystals, only  $180^\circ$  walls could occur.) As such extensive reference is made to  $90^\circ$  and  $180^\circ$  walls, and they are usually considered in numerical calculations, the erroneous impression is liable to be gained that (at least in iron-like crystals) boundaries are invariably of one of these two types. Brief consideration of the course of magnetization of single crystals, as already described (§ 2(iii)) shows, however, that  $180^\circ$  boundaries are present only in the first mode of magnetization of cubic crystals (when more than three phases are present). Further, in the three- and two-phase modes, the angle between domain

magnetization directions, initially  $90^\circ$ , gradually decreases as the resultant magnetization increases (cf. Figure 2.8). Néel (1944 b, c) gives some numerical results showing how the boundary energy decreases to zero as the domain magnetization vectors approach parallelism. The obvious problem raised by grain boundaries in polycrystalline materials has not yet been considered in any detail in the present connection.

*Boundary energy.* Domain boundaries are sometimes referred to as Bloch walls, the first rough estimates of the energy associated with them and of their effective thickness having been made by Bloch in 1932. Bloch's general treatment has since been refined and extended, notably by Landau and Lifshitz (1935) and by Néel (1944 c). In the following account, based mainly on their papers, the results of some supplementary calculations have been included.

A characteristic of domain boundaries, a full recognition of the importance of which underlies much of Néel's work (1944 a, b, c), is that, in general, the normal component of the magnetization has the same value not only on both sides of the boundary, but also in the transition region. This is because the development of internal free poles (corresponding to a non-zero value of  $\text{div } \mathbf{I}$ ) would usually involve an increase of energy very much greater than in some other possible arrangement in which free pole formation does not occur. Thus if the magnetization vector,  $\mathbf{I}_0$ , makes an angle  $\theta$  with the normal to the boundary, and its projection on the boundary surface an angle  $\phi$  with some selected zero direction, the change of direction of  $\mathbf{I}_0$  in passing through the boundary occurs by a gradual rotation of  $\mathbf{I}_0$  about the normal,  $\theta$  remaining constant, and  $\phi$  changing from, say,  $\phi_1$  to  $\phi_2$ . For a  $180^\circ$  boundary, for example,  $\theta$  is necessarily  $90^\circ$ , and  $\phi$  changes from  $\phi_1$  to  $\phi_1 \pm 180^\circ$ .

Taking the  $180^\circ$  boundary in illustration, suppose that the boundary is parallel to the  $yz$  plane, the normal being along  $x$ , and that an easy direction of magnetization of the crystal (e.g. a cube edge for unstrained iron) lies along the  $z$  axis; further, that in passing through the boundary the direction of magnetization changes from  $+z$  to  $-z$ . The boundary energy arises from both exchange interaction and magneto-crystalline or strain anisotropy. The exchange energy is proportional to  $1 - \cos \delta\phi$ , where  $\delta\phi$  is the angle between the spin directions in neighbouring layers. The contribution per unit volume may therefore be expressed in the form

$$F_e = \alpha a^2 (d\phi/dx)^2, \quad \dots \dots \quad (3.1)$$

where  $a$  is a lattice constant, and  $\alpha$  is proportional to the exchange energy per unit volume (in terms of the Weiss molecular field treatment to  $\frac{1}{2}N_w I_0^2$ ), with a numerical factor, usually of the order  $10^{-1}$ , depending on the lattice type and the number of effective spins per atom. The anisotropy energy per unit volume may be written

$$F_a = \beta f(\theta, \phi), \quad \dots \dots \quad (3.2)$$

where  $\beta$  is a non-particularized anisotropy coefficient. The energy and effective thickness of the boundary are determined from the condition that the sum of the energies  $F_e$  and  $F_a$ , integrated over the  $x$  range in which  $\phi$  changes from  $0^\circ$  to  $180^\circ$ , shall be a minimum.

There is usually no difficulty in determining the form of  $f(\theta, \phi)$  for the type of boundary under consideration. The general method may be illustrated by putting

$$F_a = \beta \sin^2 \phi. \quad \dots \dots \quad (3.3)$$

This relation holds, at least approximately, if the  $z$  direction is the easy direction in an unstrained cobalt-like crystal (when  $\beta = K_2'$ ), or if it is the direction of application of tension (compression) in a material of positive (negative) isotropic magnetostriction (when  $\beta = 3\lambda z/2$ , where  $\lambda$  is the saturation magnetostriction coefficient and  $\sigma$  the tension), provided it can be assumed that the natural magneto-crystalline effect is relatively small. The energy per unit area of the domain boundary, usually denoted by  $\gamma$ , is then given by

$$\gamma = \int \{\alpha a^2 (d\phi/dx)^2 + \beta \sin^2 \phi\} dx, \quad \dots \dots (3.4)$$

where the integral extends over the  $x$  range in which  $\phi$  changes from  $\phi_1$  to  $\phi_1 + \pi$ . A straightforward variational treatment then gives, as a condition that the integral shall have a stationary value,

$$\alpha a^2 \frac{d}{dx} \left( \frac{d\phi}{dx} \right)^2 = \beta \frac{d}{dx} (\sin^2 \phi). \quad \dots \dots (3.5)$$

Integrating this equation,

$$\alpha a^2 \left( \frac{d\phi}{dx} \right)^2 = \beta \sin^2 \phi + c. \quad \dots \dots (3.6)$$

For  $|x| \rightarrow \infty$ ,  $\phi \rightarrow 0$  or  $\pi$ , and  $d\phi/dx \rightarrow 0$ , and the integration constant is therefore zero. The two terms in the integrand of (3.4) are therefore equal, i.e. the exchange and anisotropy contributions to the energy are equal. It is convenient to introduce

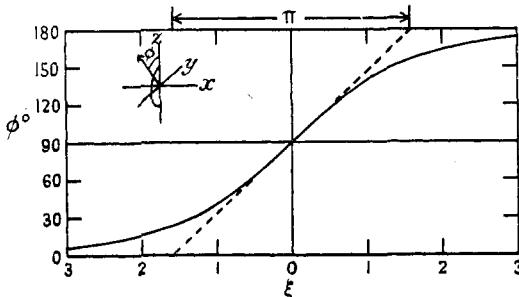


Figure 3.1. Variation of direction of magnetization in a  $180^\circ$  domain boundary in a specimen with a single easy axis of magnetization.

$x$ , distance along normal to boundary.  $\phi$ , angle between  $I_0$  and easy axis in the  $yz$  plane.  $\xi = x/b_0$ .  $b_0 = (\alpha a^2/\beta)^{1/2}$ .  $\alpha, \beta$ , exchange and anisotropy energy density coefficients.  $a$ , lattice constant.

a unit of length,  $b_0$ , normal to the boundary, and a unit,  $\gamma_0$ , for the energy per unit area of the boundary, given by

$$b_0 = (\alpha a^2/\beta)^{1/2}, \quad \gamma_0 = (\alpha a^2 \beta)^{1/2} = \beta b_0 = \alpha a^2/b_0, \quad \dots \dots (3.7)$$

and to use a non-dimensional parameter,  $\xi$ , for length measured normal to the boundary (i.e. along  $x$ ), given by

$$\xi = (x/b_0). \quad \dots \dots (3.8)$$

Putting  $\phi = \pi/2$  at  $\xi = 0$ , integration of (3.6) yields the relation between  $\phi$  and  $\xi$  in the forms

$$\begin{aligned} \cos \phi &= -\tanh \xi, & \sin \phi &= \operatorname{sech} \xi, \\ \phi &= 2 \tan^{-1} e^\xi, & \text{or } \xi &= \ln \tan(\phi/2). \end{aligned} \quad \left. \right\} \quad \dots \dots (3.9)$$

The character of the transition from  $\phi = 0^\circ$  to  $\phi = 180^\circ$  is shown in Figure 3.1.

It will be clear that the boundary, if it satisfies the minimum energy condition, has no sharply defined width, but as shown in the figure, the effective width in this case may be conveniently taken as  $\pi b_0$  (approximately 0.74 of the total change in  $\phi$  takes place over this distance). The energy per unit area of the boundary is readily found by integration as

$$\gamma = 4\gamma_0. \quad \dots \dots \quad (3.10)$$

The last expression for  $\gamma_0$  in (3.7) shows at once how the energy arising from departure from parallelism of the spins is reduced by the gradualness of the transition, for, with an abrupt change of direction of  $I_0$ ,  $\gamma_0$  would be of the order  $\alpha a$ . It may be noted (see further below) that  $b_0$  is usually of the order  $10^{-6}$  cm., and  $\gamma_0$  of the order  $1 \text{ erg cm}^{-2}$ .

The method of treatment of domain boundary energy and thickness outlined above for the 'uniaxial' case is generally applicable, but the problem is naturally more troublesome when there is more than one easy axis and the required anisotropy energy expression (3.2) has to be derived from a basic expression of the type (2.1). Néel (1944 c) has considered in detail the energy of boundaries in an iron crystal, and some of his results are shown in Table 3.1. In all cases the change is from one easy direction (cube edge) to another, the normal component of the magnetization remaining constant.

Table 3.1

Relative Energies of Domain Boundaries in Iron (as calculated by Néel 1944 c)

The values tabulated are of  $\gamma/\gamma_0$ , where  $\gamma$  is the energy per unit area, and the estimated value of  $\gamma_0$  is  $0.7 \text{ erg cm}^{-2}$ .

Type of boundary	Direction of normal to boundary		
	[100]	[110]	[111]
90°	1.0	1.727	1.185
180°	2.0	2.760	—

The character of the transition in the 90° boundaries is similar to that shown in Figure 3.1. For the 180° boundaries, however, a difficulty arises. A 180° boundary parallel to a (100) plane might be regarded as two successive 90° boundaries; but the minimum energy condition would require an infinite separation between them. Néel shows that this difficulty is overcome when magnetostrictive anisotropy energy is also taken into account. This gives rise, in the general case, to an effective attraction between neighbouring 90° boundaries, and in an ideal crystal of iron, in which boundaries can move freely, the only stable 90° boundaries would be those normal to a binary axis. Although magnetostrictive energy is an important factor in determining the effective width and stability of boundaries, its effect on the overall boundary energy is negligible. Graphs plotted from Néel's formulae for the variation of direction of  $I_0$  in 90° and 180° boundaries normal to a [100] direction are shown in Figure 3.2.

It will be clear from the above account that by the methods now available reliable theoretical estimates may be made of the relative energies of boundaries of different types in any particular material whose magnetic, magneto-crystalline and (more particularly if material under stress is to be considered) magnetostrictive characteristics are known. Estimates of the absolute values of the energy per unit area, and of the relative energies of boundaries in different materials, are much

more uncertain, mainly owing to the many uncertainties in the detailed treatment of exchange interaction effects (cf. I, pp. 65–78). It is usually assumed in the calculations that have been made that the interaction is effectively between nearest neighbours, and proportional to the cosine of the angle between the spins, and that the difference in energy per unit volume between the states of random and parallel spin orientation is  $\frac{1}{2}N_W I_0^2$ ,  $N_W$  being the Weiss molecular field coefficient. It is then not difficult to show (cf. Landau and Lifshitz 1935) that for a simple cubic lattice, with lattice constant  $a$ , the exchange energy per unit volume for a transition region in which the magnetization vectors are normal to a cube axis, say the  $x$  axis, and vary in direction only with  $x$  (cf. (3.1)) is given by

$$F_e = \frac{1}{6}(\frac{1}{2}N_W I_0^2)a^2(d\phi/dx)^2. \quad \dots \dots \dots (3.11)$$

A generalization of this expression is given by Stoner and Wohlfarth (1948, p. 634). By using, rather than the lattice constant  $a$ , a parameter  $a_1$ , where  $a_1^3$  is the volume per atom, the same numerical factor, to within a few per cent, is obtained for both face-centred and body-centred cubic lattices. The coefficient  $N_W$  is

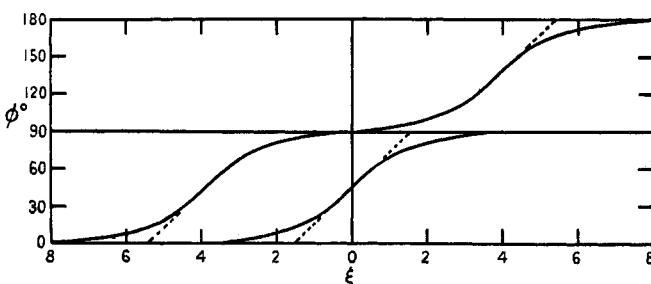


Figure 3.2. Variation of direction of magnetization in  $90^\circ$  and  $180^\circ$  boundaries normal to a [100] direction in iron. (From formulae given by Néel 1944 c.)

$\xi = x/b_0$ .  $x$ , distance normal to boundary. Estimated value of  $b_0$  (Néel),  $165 \times 10^{-8}$  cm.

expressed in terms of experimentally determinable quantities, including the Curie temperature,  $\theta$ , using the modified molecular field treatment (I, pp. 55–58), for this purpose a reasonable approximation. Further, explicit allowance is made for the number,  $q$ , of effective spins per atom (2.22 for iron, 0.60<sub>5</sub> for nickel, see I, Table 4.1, p. 86) in what appears to be the most plausible way consistent with present knowledge. When the intensity of magnetization,  $I_{0T}$ , is approximately equal to that at absolute zero,  $I_{00}$ , the final expression (derived from equation (6.6), *i.e.*, which, together with (6.5), should be corrected by the insertion of a multiplying factor  $q$ ) takes the very simple form

$$F_e = \frac{1}{10}q^{1/3} \frac{k\theta}{a_1} \left( \frac{d\phi}{dx} \right)^2 = \alpha_1 a_1^2 \left( \frac{d\phi}{dx} \right)^2. \quad \dots \dots \dots (3.12)$$

By substituting  $\alpha_1 a_1^2$  for  $\alpha a^2$  in (3.7), and using for  $\beta$  the values of  $K_4$  for iron and nickel, and of  $K'_2$  for cobalt, approximate estimates of the unit lengths,  $b_0$ , and unit energies,  $\gamma_0$ , may readily be obtained. These are given in Table 3.2.

No rigour would be claimed for any of the expressions which have been used for  $F_e$ . In the light of the collective electron treatment of ferromagnetism it is believed that (3.12) almost certainly gives an underestimate, possibly by a factor of 2, but that it can be used with reasonable confidence for comparative purposes. It may be noted that the values of  $\gamma_0$  and  $b_0$  for iron in Table 3.2 agree closely with

those given by Néel (0.7 and 165 respectively), but this agreement is partly fortuitous as there are significant differences in the methods of derivation. In a method given by Lifshitz (1944) a quantity corresponding to  $\alpha_1 a_1^2$  in Table 3.2 is evaluated from the coefficient of  $T^{3/2}$  in Bloch's law of approach to saturation at absolute zero (I, p. 66). Bloch's spin-wave treatment is on a Heitler-London-Heisenberg basis, and the  $T^{3/2}$  law is a rigorous solution of the formal problem which is considered, or, at least, a first approximation, valid in fact over only a very narrow temperature range, to such a solution. It has been shown by Wohlfarth (1949), however, that the conditions presupposed do not, in general, have a sufficiently close correspondence to those in actual ferromagnetic metals for the treatment to be applicable to them. The values of  $\gamma_0$  to which the results of Lifshitz lead would be some 50% higher than those in Table 3.2, values which, as already stated, are almost certainly underestimates. Even if experimental values for boundary energies are eventually found to be in agreement with estimates made by Lifshitz, the theoretical method would require much fuller justification than it has so far received.

The most interesting point in Table 3.2 is the wide difference in the values for the different elements. For the 180° boundaries in cobalt (see (3.10) and Figure 3.1) and iron (see Table 3.1 and Figure 3.2), the estimated values of  $\gamma_0$  are 8.2 and 1.2 erg cm<sup>-2</sup>, and of the effective widths (in 10<sup>-8</sup> cm.) about 160 and 1,400

Table 3.2. Estimated Energy and Width Units for Domain Boundaries

	$\alpha_1 a_1^2$ 10 <sup>-7</sup> erg cm <sup>-1</sup>	$\beta$ 10 <sup>5</sup> erg cm <sup>-3</sup>	$\gamma_0$ erg cm <sup>-2</sup>	$b_0$ 10 <sup>-8</sup> cm.
Fe	8.3	4.7	0.62	130
Ni	3.4	0.51	0.14	260
Co	10.3	41	2.05	50

respectively. The indication is that for nickel the energy would be about a quarter, and the effective width twice as great as that for iron. These comparisons have a bearing on the domain sizes in the different elements, and on the character of powder pattern lines.

*Domain shapes and sizes.* The first soundly based attempt to estimate domain shapes and sizes quantitatively is that of Landau and Lifshitz (1935), who considered the particular case of a crystal with a single easy axis of magnetization. The principles implicit in their treatment have been concisely and very clearly discussed by Elmore (1938 a). The method has been developed further by Lifshitz (1944), and applied to iron as well as cobalt. The most detailed discussion of the whole problem of the magnetization curves, and the subdivision into domains of single crystals, more particularly of iron, is that of Néel. The first part of this work (1944 a), on the different modes of magnetization of a single crystal has already been considered (§ 2(iii)). The second and third parts (1944 b) deal with the shape and orientation of the domains, and with the secondary superficial domain structure and the thickness of domain layers.

The general principles can be brought out by consideration of a cobalt-like crystal in a demagnetized state in zero applied field. The domain structure proposed by Landau and Lifshitz is shown diagrammatically in Figure 3.3. The condition determining the dimensions of the domain pattern is that the free

energy of the crystal as a whole (or more conveniently, the average energy density) shall be a minimum. The direction of magnetization may differ in different domains, but the intensity is effectively constant, and equal, sufficiently closely, to the saturation magnetization,  $I_0$ . The main contributions to the energy, additional to that associated directly with the intrinsic magnetization in the domains (i.e. the exchange energy, which can be represented by  $-\frac{1}{2}N_w I_0^2$ , where  $N_w$  is the Weiss molecular field coefficient), arise from (a) the field energy,  $F_H$ , (b) the domain boundary energy,  $F_\gamma$ , and (c) the anisotropy energy,  $F_a$ . Symbolically, the condition is that  $F$  shall be a minimum, where

$$F = F_H + F_\gamma + F_a. \quad \dots \dots \quad (3.13)$$

The field energy, in general, arises from both the external and the internal fields,  $H_e$  and  $H_i$  respectively, and, on the understanding that energies are to be integrated over the volume of the crystal and averaged, may be written

$$F_H = F(H_i) + F(H_e) = -\frac{1}{2}\mathbf{H}_i \cdot \mathbf{I}_0 - \mathbf{H}_e \cdot \mathbf{I}_0. \quad \dots \dots \quad (3.14)$$

For the demagnetized state (or when the applied field is zero) the contribution from the last term is zero. The internal magnetic field,  $H_i$ , is derivable from a potential given by Poisson's equation,

$$\Omega = \int \frac{\mathbf{I} \cdot \mathbf{n}}{r} dS - \int \frac{\operatorname{div} \mathbf{I}}{r} dv. \quad \dots \dots \quad (3.15)$$

The internal field energy (which is always positive or zero) arises from the presence of 'free poles', either superficial ( $\mathbf{I} \cdot \mathbf{n}_i \neq 0$ ) or internal ( $\operatorname{div} \mathbf{I} \neq 0$ ). The energy

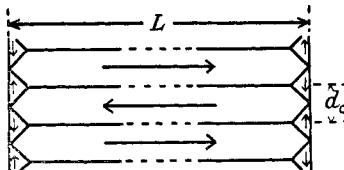


Figure 3.3. Domain structure in a magnetically uniaxial crystal in the demagnetized state.  
(After Landau and Lifshitz 1935.)

The easy axis is horizontal in the plane of the diagram. The domain boundaries are perpendicular to this plane. The arrows show the directions of magnetization.

associated with the presence of free poles is usually relatively large, and, except for the free pole distribution necessarily associated with the macroscopic state of magnetization of the specimen, any arrangement satisfying the minimum energy condition will be one in which, to a close approximation, free poles do not occur. The bearing of this on the character of the transition in domain boundaries has already been discussed. An important corollary, pointed out by Néel, is that domain boundaries must be plane or nearly plane. In particular, corrugated boundaries, represented in cross section by wavy lines, are precluded. In the case illustrated in Figure 3.3, it is clear that a high energy would result from superficial free poles if the primary domains extended right up to the surface. This energy may be reduced by the formation of superficial 'closure domains' of the type shown, triangular prisms normal to the plane of the diagram. With this arrangement  $F(H_i)$  in (3.14) is zero, and consequently also  $F_H$  in (3.13). The energy to be minimized is thus the sum of the domain boundary

energy, and the anisotropy energy due to the deviation of the magnetization in the prisms from an easy direction. Taking the form (3.3) for the anisotropy energy, and using  $\gamma$  as above for the energy per unit area of the primary boundaries (the contribution from the prism boundaries may be neglected), it is easily found that the energy per unit volume is given by

$$F = \frac{\gamma}{d} + \frac{1}{2} \frac{d}{L} \beta, \quad \dots \dots \quad (3.16)$$

where  $d$  is the thickness of the domain layers and  $L$  the length of the crystal in the easy axis direction (see Figure 3.3). The energy is a minimum for

$$d = d_0 = (2L\gamma/\beta)^{\frac{1}{2}}, \quad \dots \dots \quad (3.17)$$

when

$$F_{\min} = (2\beta\gamma/L)^{\frac{1}{2}}. \quad \dots \dots \quad (3.18)$$

A comparison of 'theoretical' and experimental values of  $d_0$ , as obtained from patterns, is made below (§ 3(ii)), but it may be mentioned here that, using the values of  $\gamma_0$  and  $\beta$  in Table 3.2, the value estimated from (3.17), with  $L = 1$  cm., for  $d_0$  in cobalt ( $\gamma = 4\gamma_0$ ) is about  $2 \times 10^{-3}$  cm., which is at least of the order of

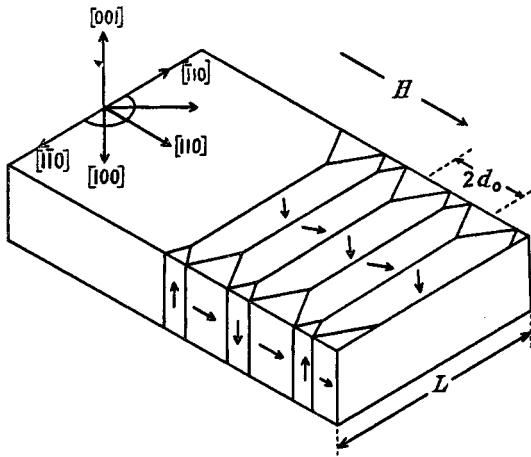


Figure 3.4. Domain structure in a monocrystalline iron strip, with field and magnetization along a [110] direction.  
(After Néel 1944 b.)

magnitude observed. It is noteworthy that, with the proposed model, the thickness of the domain layers depends explicitly on the length of the crystal parallel to the easy axis.

The domain structure problem is more complicated for cubic crystals with three equivalent easy axes, but Néel shows that in the two- and three-phase modes of magnetization in iron the primary domains are again of the layer type, the domains being piled on top of each other like the leaves (*feuilles*) of a book. He considers in detail the case of a monocrystalline strip or slab with the field and resultant magnetization in a [110] direction. The proposed domain structure is shown diagrammatically in Figure 3.4.

The diagram applies to the two-phase range of magnetization between remanence and saturation. At remanence the magnetization vectors on the (100) surface are alternately along [100] and [010] directions, but as the magnetization

increases they turn towards the [110] direction. At the same time there is a change in the relative sizes of the two types of prismatic closure domain on the (110) and ( $\bar{1}\bar{1}0$ ) surfaces, corresponding to a preferential growth of those magnetized parallel to the field. It is shown that the magnetization in these prismatic domains is either along the field direction or very nearly perpendicular to it. The domain width,  $d_0$ , is calculated by a method similar to that used in deriving (3.17), but more complicated, for both the anisotropy energy and the boundary energy depend on the resultant magnetization. Néel's final result is that  $d_0$ , proportional to  $L^{1/2}$  as before, decreases from a high value near the remanence point, for which  $I/I_0 = 0.707$ , to a value, for  $L = 1$  cm., between  $65$  and  $70 \times 10^{-4}$  cm. for  $I/I_0 = 0.85$  (corresponding to an effective field of about 190 oersted). A diagram is given showing that the estimated theoretical curve passes reasonably well through the somewhat scattered values obtained from observations on powder patterns by Kaya (1934 a, b).

It is, of course, not possible to enter here into the details of the theoretical derivation of even the relatively simple structure illustrated in Figure 3.4, or to consider more complex cases which have been discussed to some extent by both Néel and Lifshitz. Essentially, once the general character of the domain pattern has been established, the scale of the pattern is determined by a balance between the boundary energy of the primary domains and the anisotropy energy (including a sometimes not negligible magneto-elastic contribution) of the closure domains. The relation (3.17) sufficiently indicates the general orders of magnitude. It must be remembered that as regards absolute dimensions, little more than order of magnitude estimates can at present be made. This is due partly to the possible complexity of the superficial closure domain structure, partly to the uncertain values of the anisotropy and related coefficients (cf. § 2(ii)), but mainly to the uncertainties in estimating the energies associated with exchange interaction in domain boundaries.

There are a number of special matters which have been examined theoretically which are conveniently deferred for consideration in connection with experimental results. These include the simple and multiple branching of domain layers, under certain conditions, as a surface is approached (Lifshitz 1944), the formation of special domain structures round holes or non-ferromagnetic inclusions to reduce free pole energy (Néel 1944 d), the behaviour of large domains in stressed material (Döring 1938, Haake 1939), and formation or non-formation of domain boundaries in thin films and small particles (Kittel 1946, and others).

It may be useful, in closing this theoretical section, to draw attention briefly to a few general points in the treatment of the domain structure problem. Running through the inter-related series of investigations, as presented here, is a search for states of minimum energy. These states can, in principle at least, be described with increasing precision and detail as effects corresponding to successively decreasing energy changes are taken into account. In the first approximation, considering only exchange interaction, the largest energy effect, a single crystal would be magnetized to the saturation value appropriate to the temperature. Next, the effects of an applied field and crystalline or strain anisotropy are considered, and also, in the Néel-Lawton-Stewart work (§ 2(iii)) the effect of the demagnetizing field. The at first sight remarkable result of their investigations is that the number of 'phases', each associated with a particular direction of magnetization, which can co-exist in a single crystal is very limited, not more than

six for cubic crystals, and, in general, over most of the magnetization range, only two or three. For given conditions, the magnetic characteristics (i.e. the directions of magnetization) and the relative volumes of these phases can be calculated (and hence the change of bulk magnetization with change of field), not perhaps easily, but, in most of the physically more important cases, without undue difficulty. This greatly facilitates the consideration of domain structure, for the starting point of the treatment can be taken as the already known number of domain types (as specified by their directions of magnetization) under the given conditions, and, to very close approximation, the proportions of the volume which they occupy. At this stage, to determine the actual spatial distribution of domains, other energy effects, in general smaller, must be taken into account, as already described. The complex problem of the enhanced exchange energy associated with the deviation from parallelism of the spins can be isolated in the boundary energy problem, and the calculated boundary energies can then be utilized, without further direct reference to exchange interaction, in determining the domain boundary pattern consistent with minimum energy. It should perhaps be stated explicitly that the pattern cannot be determined unambiguously merely by the application of a minimum energy criterion. This criterion fixes the scale of any given pattern, and enables a choice to be made between such patterns as may be devised. In devising patterns the most important working rule is perhaps that, for a first approximation, the arrangement should be such as not to give rise to internal or superficial free poles other than those necessarily associated with the bulk state of magnetization.

Finally, brief comment is perhaps desirable on a possible objection to domain theory which has been made by Brown (1945) in an interesting paper on the virtues and weaknesses of the domain concept, to the effect that although the theory may explain a great deal once domains are assumed, it does not explain their formation. He considers a single crystal specimen in the form of an ellipsoid with a direction of easy magnetization along a principal axis, initially saturated in this direction by a large applied field. He then shows that any small deviation of  $I_0$  from the easy direction will increase the energy, and that as the field decreases no change will occur until the field becomes negative, and at least of the order of magnitude  $K/I_0$ , where  $K$  is an anisotropy coefficient. The magnetization would then reverse completely at this relatively high value of the field, and no subdivision into small domains (such as that shown in Figure 3.3) would occur at any stage. A tentative answer to this implicit objection to domain theory is that under the conditions assumed the course of the change with changing field would be as described. For an ideal ellipsoidal single crystal, perfectly uniform, no domain boundaries would be formed, in spite of the fact that in low fields, in zero applied field in particular, the saturated state is metastable, with a higher energy than for a state of low resultant magnetization, with domains magnetized in opposite directions. Any actual crystal, however, is imperfect, and as the field is reduced, domain boundary growth can take place, starting at holes, cracks or inclusions. The energy required to start the boundary formation is provided, so to speak, by the free pole energy. The extension of boundaries, once started, does not present so formidable a problem; it will be possible so long as it is accompanied by a continuous decrease in energy. There is no suggestion in domain theory that a ferromagnetic always necessarily takes up a domain configuration corresponding to the lowest possible energy, but the

possibility that a perfect crystal, in which domain boundary movement would be least restricted, might not form domains at all is at first sight somewhat startling. It may be suggested, however, that even the perfect ellipsoidal crystal might be persuaded to behave somewhat more normally by a few scratches with a pin.

### 3 (ii). Powder Patterns

*General.* Cracks and flaws in large ferromagnetic samples may be detected by dusting relatively coarse ferromagnetic powder over the surface. An analogous method, equally depending on the attraction of ferromagnetic particles from weaker to stronger fields, was introduced independently by Bitter and by von Hamos and Thiessen in 1931 for the examination of fine scale magnetic structure. Since then many investigations of powder patterns have been made, and the technique has been greatly refined. Powders have been used dry with some success (e.g. carbonyl iron powder), but for most purposes colloidal suspensions are more convenient. With a size greater than about  $1\mu$ , the particles tend to settle out; with a size less than about  $0.1\mu$ , Brownian movement becomes prominent, and the particles, though they still concentrate satisfactorily in the stronger field regions if they are not too small, remain mobile, and the changing of a pattern with changing field can be readily observed (McKeehan and Elmore 1934 a, b). In recent years the most widely used 'powder' has been a colloidal suspension of magnetite  $\text{Fe}_3\text{O}_4$ , protected by soap (Elmore 1938 b). Clear patterns with recognizable regularities have been observed with unstrained material only on surfaces nearly coincident with simple crystallographic planes. The production of single crystal specimens, or at least of large-grained samples, is therefore an essential preliminary if significant results are to be obtained; the careful grinding of surfaces in required crystallographic planes, and the optical or x-ray determination of orientations are incidental techniques. Finally the surfaces must be suitably prepared, a mirror-like smoothness being desirable. With surfaces prepared by metallurgical polishing, McKeehan and Elmore (1934 a, b, 1936) obtained many intriguing maze-like patterns, some of which have often been reproduced. These patterns usually show, individually, a remarkable regularity of spacing, and this, together with their behaviour in changing vertical and horizontal fields suggested the presence of a stable block structure, possibly superficial, in the crystal. Later work, particularly by Elmore (1937), showed conclusively that any such structure must originate in the polishing operation; the maze patterns do not occur on smooth unpolished crystalline strips, but they are readily obtained in the region of broad shallow scratches made on them. To produce mirror-like surfaces free from strains, Elmore finally adapted and developed the method of electrolytic polishing (1939, 1940 a), a method which he applied successfully to cobalt (1938 a) and iron (1942), and which has been found satisfactory by other workers. This has greatly extended the range of powder pattern investigations, for suitable surfaces can be obtained without depending on the occurrence of smooth natural crystal surfaces of the desired orientation.

Attention here will be devoted mainly to the work of Elmore (1938 a) on cobalt, and of Williams, Bozorth and Shockley (1949) on iron, as the earlier work has often been reviewed, notably by Elmore in Bitter's *Introduction to Ferromagnetism* (1937, pp. 55–66). It is evident that, at the time of Elmore's writing, no satisfying interpretation had been given of any of the observed powder patterns in terms of a

magnetic domain structure proper, although the patterns were generally accepted as giving some kind of qualitative evidence for such a structure. Quantitatively relevant material was, however, available in the powder pattern photographs obtained by Kaya (1934 a, b) for iron, and by Kaya and Sekiya (1935) for nickel, as well as in earlier photographs by Bitter and others, though its significance was not appreciated till later. The occurrence on iron of three or four distinct types of pattern, as found by Kaya, was confirmed by Sixtus (1937 a), but only bare reference to this work can be made here, as also to the magnetic powder experiments of Snoek (1936) and Snoek and Louwerse (1937) on rolled nickel-iron. The first reasonably satisfactory quantitative interpretation of a powder pattern photograph was that by Elmore (1938 a), on the basis of the theoretical work of Landau and Lifshitz (1935), which, together with the comprehensive treatment of Néel (1944 b), provides the starting point for the detailed quantitative interpretation of particular observed patterns by Williams, Bozorth and Shockley (1949).

*Formation of patterns.* Although consideration has been given to certain special problems of the distribution and movement of colloid particles (e.g. by Elmore 1940 b), the elementary principles underlying the relation between a powder pattern and the magnetic structure at and near the surface seem usually to be regarded as so obvious as not to require discussion. Since powder patterns are easily misunderstood, however, brief comment may not be out of place. The force on the particles is proportional approximately (i.e. neglecting the effect of any permanent particle moment) to the gradient of  $H^2$ , and they therefore tend to move to regions in which  $H^2$  has a local maximum. Since the particles are very small and very near the surface their motion is primarily controlled by the surface distribution of poles. The surface density of magnetic charge is equal to the magnetic intensity normal to the surface. Over regions in which the magnetization is tangential to the surface the force is zero; over regions in which there is a uniform normal component, there is a normal force attracting the particles to the surface, but no tangential force such as is required for pattern formation. Regions with different uniform surface pole densities may be differentiated to some extent by differences in the general density of the powder 'deposit'. The formation of a pattern line requires either a line of pole density differing in strength or sign from the surroundings on either side (e.g. the domain boundaries in the surfaces in Figures 3.3 and 3.4), or a boundary between two regions of differing surface pole density. The intensity of pattern lines, for a given colloid concentration, must depend on the saturation intensity of magnetization of the material (giving a measure of the attainable normal intensities) and on the effective widths of the transition regions (giving an inverse measure of the attainable local fields). From the comparative figures for domain boundary widths,  $b_0$ , in Table 3.2, clear patterns should be more readily obtainable on cobalt than on iron, for the second reason, and on either of these than on nickel, for both reasons. Materials with low anisotropy, and hence large domain boundary widths, would be expected to give poor patterns; in this connection it is noteworthy that on an unstressed crystal of permalloy (76 Ni, balance Fe) Williams, Bozorth and Shockley (1949, p. 171) could obtain no distinct patterns at all.

*Patterns on cobalt.* In his study of cobalt, Elmore (1938 a) used specimens containing a number of large crystal grains (of linear dimensions up to about 0.3 cm.). On these, surfaces were prepared approximating to prism planes and basal planes, parallel and perpendicular respectively to the hexagonal axis, the

easy axis. The specimen was mounted with the surface under observation horizontal on the pole of a vertical electromagnet, so that a field normal to the surface, outward or inward, could be applied. Some powder patterns obtained are shown in Figures 3.5 and 3.6 (Plate I). These patterns, which correspond to portions of those in the figures in Elmore's paper, are reproduced from original photographs kindly supplied by the author.

The three patterns (*a*), (*b*), (*c*) in Figure 3.5 correspond to the same region of the surface (approximately  $0.8 \times 0.3$  mm.) with the applied field outward, zero and inward; and similarly the three patterns in Figure 3.6. Considering first the prism plane pattern in zero field, it is apparent that it is consistent with the theoretical scheme of layer magnetization illustrated in Figure 3.3, alternate layers being magnetized in opposite directions along the easy axis. The surface is slightly inclined to the easy axis, and there is a corresponding normal component of magnetization alternately outward and inward. An applied normal field has two effects: first, owing to the component along the easy axis, it gives rise to boundary displacement, with an increase in the volume (in cross section, of the width) of domains magnetized with a component in the field direction; secondly, the slight rotation of the magnetization vectors increases the surface pole density in these same domains, and decreases that on alternate domains. Thus, with an outward field, the width of domains in one of the two alternate sets increases, and the colloid density on them is relatively increased. With an inward field, the other set of domains is similarly affected. The colloid density remains greatest along the boundaries, but, starting from the zero field state, the colloid spreads in one direction or the opposite from any particular boundary according to whether the applied field is outward or inward. As is well shown in the photographs, in an applied field the colloid is practically cleared from alternate domains, and with reversal of the field, the clear and dark spaces interchange.

The beautiful patterns in the basal plane in Figure 3.6, in which the same interchange of light and dark regions is apparent, show that the domain structure in detail is much more complex than is suggested by the simple scheme of Figure 3.3. The transition from a prism plane to a basal plane pattern could to some extent be followed. On approaching a corner connecting these two planes, V-shaped line deposits appeared which multiplied the number of lines at the edge of the prism pattern; and on planes more inclined to the hexagonal axis than that of Figure 3.5, patterns were observed resembling those of Figure 3.6, but elongated in one direction. Elmore suggested that for a crystal magnetized to saturation along an easy direction, with a surface basal plane, reduction of magnetization might proceed by the starting of reverse regions from many centres on this basal plane, and their thread-like growth inwards, the threads fusing with threads from an opposite surface, and also laterally, eventually forming the layer-like structure over the greater part of the crystal. The theoretical work of Lifshitz (1944) shows that a decrease in energy may in fact be obtained by a branching of the layers near a basal plane much in the way that Elmore suggested, though quantitative calculations, particularly for multiple branching, would present formidable difficulties.

It was observed that the smaller grains gave the closer spacing in the prism plane patterns, in qualitative accordance with the theory. The spacing of the lines in Figure 3.5 is about  $60 \mu$ , a rough value of the relevant crystal length being  $0.3$  cm. This spacing is some three or four times greater than that calculated

from the simple formula (3.17), but the domain structure on the basal planes is so different from that assumed that this discrepancy, which is in the right direction, is not serious. Unfortunately, owing to the ill-defined crystal lengths, and the complexities of the closure domain structure, it is not possible, proceeding in the reverse way, to derive any really precise information about domain boundary energies from measurements of the patterns. None the less, through this work on cobalt, the relation between domain theory and observable powder patterns could at last justifiably be regarded as irrefutably established.

*Patterns on iron.* It is impossible to do justice in a short summary to the comprehensive work of Williams, Bozorth and Shockley (1949) and of Williams and Shockley (1949) on domain patterns on single crystals of iron. Fortunately, no more than an indication of some of the salient points is necessary, as these two papers should be read in their entirety by all who are interested in ferromagnetism, and also by others who are not yet. The material used consisted of carefully prepared single crystals of iron containing 3·8 weight per cent of silicon. Specimens were cut with surfaces approximately parallel to (100), (110) and (111) planes, and electrolytic polishing was carried out in a chromic acid-phosphoric acid bath. Patterns were obtained with a soap-protected colloidal suspension of magnetite. The patterns shown in subsequent figures are a small selection from a much larger number which, with the exception of Figure 3.12, have appeared in the papers just mentioned, or in an earlier preliminary paper by Williams (1947). They are, however, reproduced directly from original photographs kindly supplied for this purpose by the authors.

A number of methods were developed for determining the direction and sense of the surface magnetization in the areas between the powder pattern lines. A light scratch made on the surface results in the formation of poles if the magnetization is not parallel to the scratch. Figure 3.7(a) shows part of a typical 'tree pattern' on a surface slightly inclined to a (100) plane. In (b), light parallel scratches have been made, with a ruling engine, in an EW direction; these are shown up by deposition of colloid only where the magnetization is NS. In (c), both NS and EW scratches have been made by a glass fibre brush. The interpretation of the pattern is given in (d). Even without scratches the directions of magnetization can be assessed from the form of colloid striations, which are always elongated in a direction at right angles to the field. This effect, shown in several of the figures, is particularly clear in Figure 3.11, where a more concentrated colloid has been used, and is probably due to a very slight unevenness in the electrolytically polished surface. (Over-etching gives the surface a microscopic appearance 'not unlike that of an orange peel'.) Confirmatory evidence is provided by subjecting the specimen to tension. Iron has a positive magnetostriction, and regions magnetized along the tension direction increase at the expense of those magnetized transversely, as shown in Figure 3.8. The sense of the magnetization could be determined by placing a long thin permanently magnetized probe on the surface under examination. The additional field due to the probe induces the formation of small additional reverse domains in a domain magnetized in the opposite direction, but has no effect on a domain magnetized in the same direction. The sense of the magnetization can ordinarily be found by observing the relative changes of area of different parts of the pattern in an applied field. Useful information can sometimes be obtained by the use of vertical as well as horizontal fields.

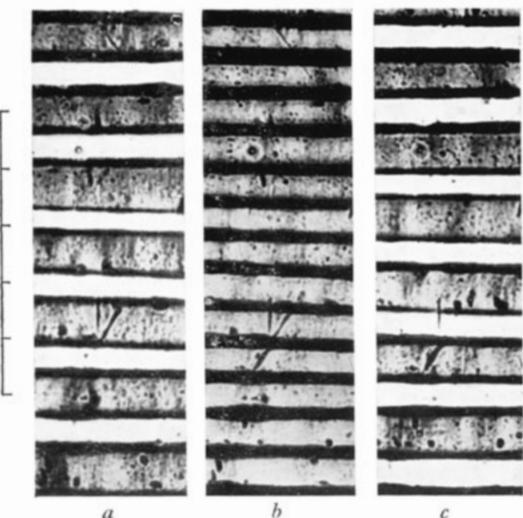


Figure 3.5. Patterns of magnetic colloid on cobalt surfaces approximately perpendicular to the basal plane.

a, b, c, applied normal field outward, zero, inward. (Elmore 1938)

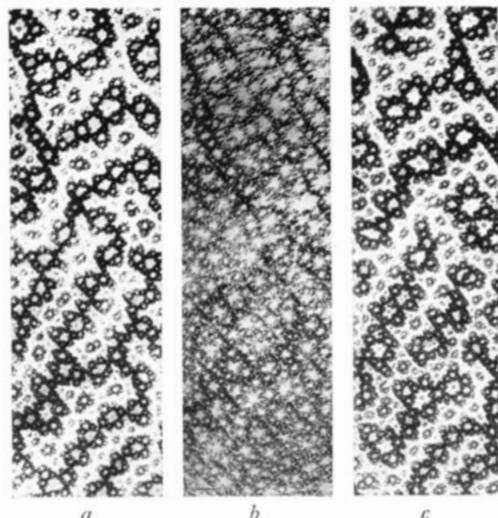


Figure 3.6. Patterns of magnetic colloid on cobalt surfaces approximately in the basal plane.

a, b, c, applied normal field outward, zero, inward. (Elmore 1938)

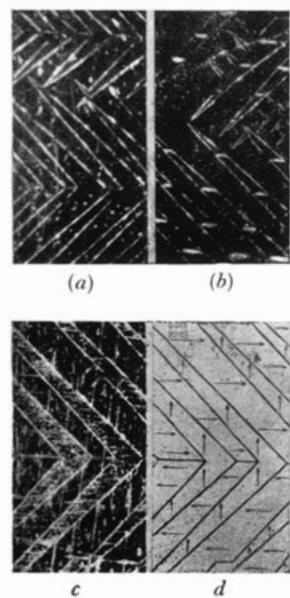


Figure 3.7. Patterns on (100) surface of iron.

Axes NS, EW. In b, parallel EW scratches have been made, in c, EW and NS scratches. The directions of magnetization corresponding to c are shown in d. (Williams 1947)

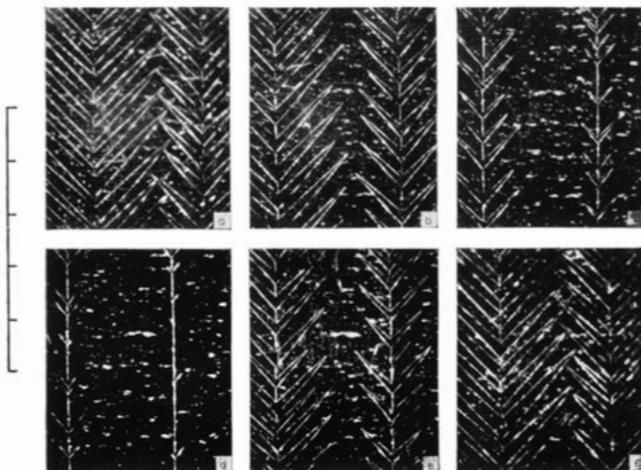


Figure 3.8. Effect of tension on patterns on (100) surface of iron.

Axes NS, EW. Tension, NS, increasing a to d, decreasing d to f, zero a and f. (Williams, Bozorth and Shockley 1949)

The scale divisions for all figures correspond to 0.1 mm.  
With acknowledgments to the authors and to the *Physical Review*.

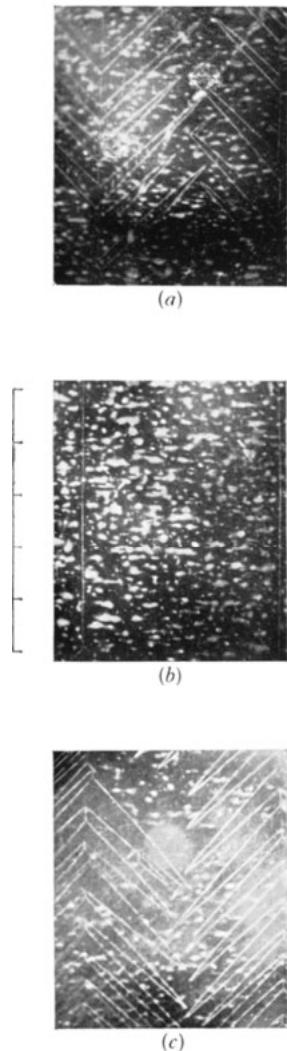


Figure 3.10. Patterns at successive positions, (a) to (f), on a curved surface.

Crystal axes NS, EW. (Williams, Bozorth and Shockley 1949)

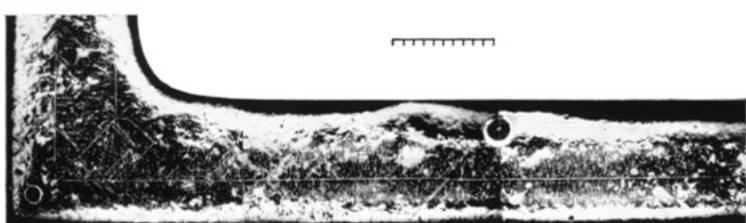


Figure 3.14. Composite of patterns on three adjacent areas of hollow rectangular single crystal. (Williams and Shockley 1949)

The scale divisions for all figures correspond to 0.1 mm.  
With acknowledgments to the authors and to the *Physical Review*.

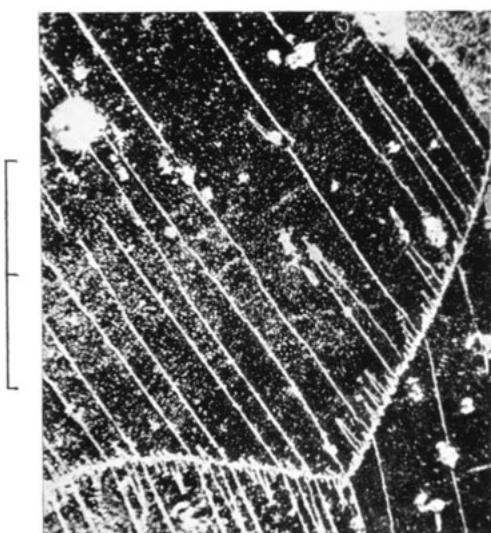


Figure 3.13. Domain pattern on cold-rolled polycrystalline iron-silicon sheet. (Williams)

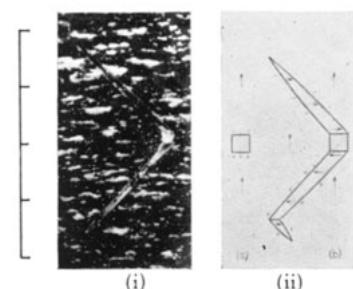


Figure 3.12. Domain structure round a hole in a crystal, (i) as observed, and (ii) interpreted. (Williams 1947)

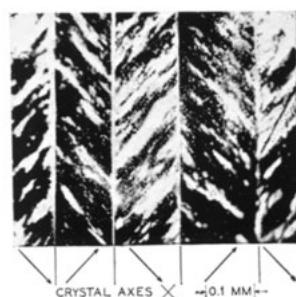


Figure 3.11. Pattern obtained with concentrated colloid on a (100) surface, magnetized in a [110] direction. (Williams, Bozorth and Shockley 1949)

The patterns of Figure 3.8, reminiscent of spiky pinnate leaves, but usually referred to as 'tree patterns', are characteristic of (100) surfaces. The central line corresponds to a  $180^\circ$  boundary. Careful experiment showed that the branches occur only when the surface is slightly inclined to the (100) plane, and that they correspond to shallow superficial domains as represented in Figure 3.9, a slightly simplified version of a diagram given by Bozorth (1949). The twin branches (or leaflets) are partial closure domains (in the sense of § 3(i)), which reduce the magnetostatic energy associated with the surface poles by carrying flux through the crystal in a direction transverse to that of the magnetization of the main domains. This involves an increase in boundary energy (but not, in this case, in anisotropy energy). The minimum energy problem is extremely difficult, but an approximate treatment gives results in good agreement with the observations, such as those shown in the series of patterns in Figure 3.10, obtained at successive positions on a curved surface cut on a single crystal. In (a) the branches point upwards. This corresponds to Figure 3.9; the theory shows that the branches should point 'downhill' with reference to the (100) planes. In (b) the (100) plane

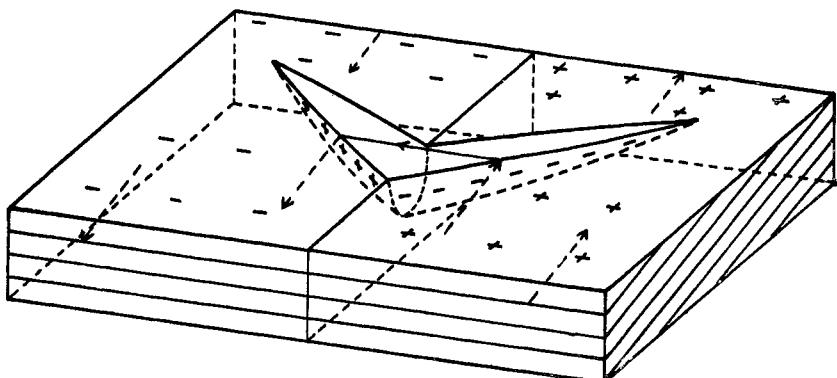


Figure 3.9. Interpretation of tree patterns. The lines on the side surface are traces of (100) planes.

is tangential to the surface, and only the centre lines appear, these corresponding to the  $180^\circ$  boundaries, with the magnetization on either side parallel to them. In (c) the branches point downwards, and as the slope increases the transversely magnetized region expands until in (f) only a relatively narrow jagged strip remains magnetized in the original direction. It is to be noted that in (e) and (f) the branched strip is what is left by the expansion of the original branches; it is a residual region on which there is surface magnetic charge, and the centre line does not, as in (a) and (c), correspond to a  $180^\circ$  boundary. A good indication of the directions of magnetization is given by the colloid striations.

A pattern obtained with concentrated colloid on a (100) surface magnetized in a [110] direction ( $B = 15,900$ ) is shown in Figure 3.11. This corresponds to the top surface in Figure 3.4, and is clearly in agreement with Néel's theoretical treatment. On a (011) surface (the front surface of Figure 3.4) two types of domain surface were observed, whose relative areas changed with increasing field in the way predicted. The detailed character of the colloid deposition on (011) surfaces, and also on the edges of (100) surfaces shows, however, that the structure of the closure domains is much more complex than that suggested by Figure 3.4.

Many interesting patterns other than those illustrated here were obtained; studies were made of the effect of compression as well as tension; and the change

in spacing and in the form of the patterns with change of field were examined. Such matters as the course of spin orientation change in domain walls of the type illustrated in Figure 3.9 are fully discussed. In an appendix a theoretical interpretation is developed, in considerable detail, of the patterns. The observed forms are accounted for, and there is usually agreement between calculated and observed linear dimensions to a factor of about two.

There is, of course, scope for much further quantitative work, to which a first contribution has been made by Bates and Neale (1949), who have obtained excellent parallel line patterns on a (100) surface of a thin single crystal strip of silicon iron about 2 cm. wide and 4 cm. long, with the field as in Figure 3.4. The applied field was measured directly with a magnetic potentiometer (cf. Bates 1945). The spacing of the lines varied with the field at first rapidly and then more slowly, from about  $300\mu$  for  $H=4$  to a fairly constant value of rather more than  $100\mu$  for  $H$  ranging from 200 to 400. The agreement with Néel's theoretical curve is reasonably good, but further investigation is required before a precise comparison can be made. A fuller account of this work is in course of publication (Bates and Neale 1950).

The patterns so far considered have been those characteristic of the perfect crystal. Mention should also be made of the domain patterns round cavities and inclusions, of which an example is shown in Figure 3.12. It was first clearly shown by Néel (1944 d) that the magnetostatic energy associated with free poles on the surface of a cavity could be greatly reduced by the formation of suitable secondary domains round it. The pattern of Figure 3.12(i) conforms to the general type predicted by Néel. The directions of magnetization, shown in Figure 3.12(ii), which is self-explanatory, have been arrived at by careful study of the colloid striations. The formation of these secondary domain structures, here rendered visible, is of great importance in its bearing on the effect of inhomogeneities of structure or composition on ordinary magnetic properties.

Lest it should be thought that the effects of crystal grain boundaries are being entirely overlooked, a pattern obtained on an annealed cold-rolled polycrystalline iron-silicon sheet is shown in Figure 3.13. This photograph, hitherto unpublished, is due to Williams. The complex secondary domain structure suggests that the effect of grain boundaries on magnetic properties may be much more important than is sometimes supposed.

*The picture frame crystal.* This account of powder patterns may well be concluded by reference to the beautiful experiments of Williams and Shockley (1949) on a single crystal in the form of a hollow rectangle of the type already mentioned (§ 2 (ii)). This crystal, of 3.8% silicon-iron, with sides parallel to [100] type directions, had overall dimensions of  $1.9 \times 1.3$  cm., a thickness of 0.074 cm., and a leg width of 0.102 cm. The surfaces were carefully ground parallel to (100) planes (to avoid the formation of superficial tree pattern domains) and polished for powder pattern observations. A pattern obtained after application of a field is shown in Figure 3.14. The salient features of this pattern are the diagonal line running across the corner, and the straight, slightly off-centre lines running down the limbs. The domain structure of this picture frame crystal is shown diagrammatically in Figure 3.15. After cooling from  $1000^\circ\text{C}$ , the crystal is fully magnetized and consists, apart from small superficial regions, essentially of four domains, one along each side, and separated by the  $90^\circ$  boundaries which show in the powder patterns as the diagonal lines at the corners. When a

suitably directed field is applied the  $180^\circ$  boundaries appear. Photographs taken while tracing a hysteresis loop showed that the position of one of these walls varied linearly with the resultant induction. In Figure 3.14 there is an inner wall due to excess material on the inside corner of the frame.

Although the motion of a  $180^\circ$  wall in a slowly changing field was relatively steady, the Barkhausen effect could be heard simultaneously with an amplifier and loudspeaker system. The movement is, in fact, slightly jerky. Superficial domain structures round small holes or other imperfections appear to unite with the wall and form irregularities in it. These secondary walls are extended as

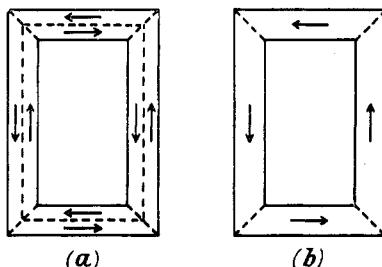


Figure 3.15. Domain structure in picture frame single crystal, with (100) surface plane, and sides parallel to [100] directions.

(a) After applying a field. (b) After cooling from  $1,000^\circ$  C.  
(After Williams and Shockley 1949.)

the main wall progresses, until they suddenly break. A new structure is formed round the imperfection, and the main wall straightens out. Photographs are given in the original paper illustrating this process.

A method is incidentally proposed by which it is hoped to make an almost direct determination of the domain boundary energy, in effect by measuring the curvature of the domain boundary in suitably disposed magnetic fields. Apart from this, these experiments have shown, in an ideally simple case, that there is a direct correlation of the domain structure with the magnetization, and they have provided immediate visual information about primary and secondary processes taking place when a ferromagnetic is magnetized.

### 3 (iii). Discontinuities in Magnetization: the Barkhausen Effect

*General survey.* When the field applied to a ferromagnetic is changed continuously, in general the change in magnetization is, at least in part, discontinuous. It is convenient to distinguish the small scale discontinuities in ordinary materials, first observed by Barkhausen (1919) by the frequently repeated method involving the use of a search coil, amplifier and loudspeaker, from the large scale discontinuities which occur in materials under stress (§ 3 (iv)), and which appear to have been first investigated systematically by Forrer (1926).

During the ten to fifteen years following its discovery, numerous investigations were made on the Barkhausen effect, culminating in the work of Dillinger and Bozorth (1929–32) (I, pp. 61–2). This work was far more thorough than any that had preceded it, but greater finality has been attributed to the tentative conclusions as to domain sizes and the aggregate extent of the discontinuous changes than was, perhaps, justified, with the result that, until this type of investigation was taken up again by Bush and Tebble (1948) little further systematic experimental work was carried out on the central problem. Brief mention should, however, be made-

of a few of the investigations in the intervening period. Following earlier work by McKeehan, a method for determining the directions of the discontinuous changes of magnetization was developed by Clash and Beck (1935). A rotating field was applied to a single crystal (100) disc of silicon-iron, and the voltage impulses due to the discontinuities were picked up by two coils at right angles, amplified, and fed to an oscillograph in such a way that traces were obtained corresponding in direction to the original discontinuous changes in magnetization. It was found that, in medium applied fields, practically all the large changes could be attributed to simple reversals along one of the axes of easy magnetization. The distribution in detail, however, is complicated and not readily explained. Extensive oscillographic studies of the Barkhausen effect have been made by Murakawa (1936, 1937), who noted the occurrence, as the field changed gradually, of concentrated groups of peaks, which, it was suggested, might arise from a series of changes occurring in rapid succession along a 'filament' in the wire specimen. Takagi (1937) examined the effect at different temperatures for nickel and a ferronickel. He found that the magnitude of the discontinuous changes diminished with increasing temperature, and that at the same time prominent groups of peaks, which could be 'recognized', were displaced to smaller fields. Heaps (1941) concluded, from an investigation of the sound waves due to the magnetostrictive changes for jumps through angles other than  $180^\circ$ , that in nickel the  $180^\circ$  changes were predominant for small values of  $I/I_0$ , but that changes through other angles occurred over most of the range. In an investigation of the low field region for iron, nickel and a ferronickel, Montalenti (1948) found that the Rayleigh law ceases to hold at approximately the value of the field for which the Barkhausen effect first becomes noticeable.

*The Bozorth-Dillinger work.* Although a description of the work of Bozorth and Dillinger is hardly necessary here, as it has been so often summarized, certain aspects of it call for brief comment. In view of the obvious difficulties of more direct measurements of the sizes of discontinuities sufficiently extended in range and number to be representative, the indirect method used had the great advantage that, in principle at least, it enabled the mean size of the discontinuities, and their contribution to the change of magnetization, to be determined for any part of the magnetization curve. Apart from the admitted approximations involved, however, the significance of 'mean size' or the associated 'mean volume',  $\bar{v}$ , is somewhat problematical. The mean size must depend on the smallest discontinuity which can be detected, and the negative statement that discontinuities corresponding to volumes, in iron, of  $10^{-18} \text{ cm}^3$  or less would not appreciably affect the measuring system does not clarify the position, for the effect of such discontinuities would almost certainly be far below the inevitable noise level of the amplifier. It is thus by no means clear just what information is conveyed by the well known curves (e.g. I, Figure 2.7, p. 62) giving the variation of  $\bar{v}$  over the magnetization curve, and showing a maximum in the region of the coercive field. From the results generally it was concluded that 'the changes in magnetization which take place suddenly in large groups of atoms account quantitatively for the whole change in magnetization which corresponds to the steeper part of the hysteresis loop'. This is, indeed, rendered plausible by the curves shown for some materials (e.g. hard drawn permalloy) but for others the actual observed values for the aggregate discontinuous change (i.e. without extrapolating to zero rate of field change) differ from the observed total change by a factor of ten or more.

Although information about the character of the Barkhausen effect was so greatly extended by the work of Bozorth and Dillinger, it is clear that wide scope remained for further investigations.

*The counting method.* The work of Bush and Tebble (1948) may be regarded as an extension and refinement of that of Bozorth and Dillinger, made possible by the methods of counting electrical pulses developed in the intervening period. The basic idea was, using a similar field changing device, to pass the amplified pulses from the search coil through a discriminator and scaling unit to a recorder, so that the size-number distribution of the discontinuities could be obtained. Apparatus for this purpose was set up, and some preliminary results obtained with it are given in the paper mentioned. In the light of the experience gained, the apparatus was rebuilt with many improvements in detail, as described by Tebble, Skidmore and Corner (1950), who give results for hard drawn iron, a specially treated iron containing large crystals, and annealed nickel.

*Pulse shapes and design of apparatus.* A necessary part of the investigation was a theoretical and experimental study of the pulse shapes due to the discontinuities. The full analysis is complicated, but in broad outline the pulse shape from the amplifier (provided certain conditions as to its frequency range are satisfied) due to a single Barkhausen discontinuity depends on the characteristic times associated with the discontinuous process itself,  $\tau_B$ , with the decay of eddy currents in the specimen,  $\tau_E$ , and with the search coil and amplifier input circuit,  $\tau_C$ . The first,  $\tau_B$ , the time taken for the initial spontaneous boundary movement, may be estimated as usually being of the order  $0.1\mu\text{sec}$ . The second,  $\tau_E$ , is proportional to  $\mu\sigma a^2$ , where  $\mu$  is the reversible permeability,  $\sigma$  the specific conductivity and  $a$  the radius of the specimen. The detailed form of the pulse, and its amplitude, considering only the  $\tau_B$  and  $\tau_E$  effects, depend on  $b/a$ , where  $b$  is the distance of the discontinuity from the axis. The third,  $\tau_C$ , is in principle calculable from the L, C, R characteristics of the coil circuit. The final form of the pulse is mainly controlled by the longest of these three characteristic times, and in general  $\tau_E$  and  $\tau_C$  are both much greater than  $\tau_B$ . For obtaining oscillograph traces which correspond to pulse shapes in the specimen, the necessary condition is  $\tau_C \ll \tau_E$ . This was readily fulfilled by suitable coil design (with a particular coil used, the value of  $\tau_C$  was about  $6\mu\text{sec}$ .), and by using specimens of slightly larger radius than for the counting experiments (e.g. with a hard drawn iron wire, for which a radius  $0.08\text{ cm}$ . was suitable,  $\tau_E$  was about  $177\mu\text{sec}$ .); the distribution of pulse widths was found to be in good accord with the detailed theory, bearing in mind the uncertainty as to the effective value of the reversible permeability, which, under the conditions of rapid change, must be appreciably smaller than the measured values at low frequencies. In the counting experiments, in which use is made of a voltage amplitude discriminator, it is obviously necessary that the pulse amplitude should be proportional to total flux change (i.e. to the change in magnetic moment) associated with the Barkhausen jump; this can be ensured only if the opposite condition,  $\tau_C \gg \tau_E$ , is satisfied. Specimens of smaller radius were used (the specimens, about  $7.5\text{ cm}$ . long, usually had a radius of about  $0.02\text{ cm}$ . and the  $\tau_E$  values for the three materials, Fe1, Fe2 and Ni, were about  $10$ ,  $46$  and  $17\mu\text{sec}$ . and a larger search coil, some  $10\text{ cm}$ . long and with  $50,000$  turns, giving a  $\tau_C$  value of about  $200\mu\text{sec}$ .

In the general design of the complete system, careful attention was given to such matters as signal to noise ratio, and the use of a sufficiently slow rate of change

of field (usually in the range 1 to  $20 \times 10^{-4}$  oe.sec $^{-1}$ ) to minimize coincidences; the original paper must be consulted for details of the various component parts of the apparatus. It must be sufficient to state that the amplifier, with an adjustable frequency range, had a maximum gain of about  $2 \times 10^5$ ; that the pulses selected by the discriminator were converted to a uniform size and passed via a 1,024 scaling unit (i.e. 10 successive scale-of-two stages) to a telephone recorder; and that, after calibration with an artificial pulse unit, counts were made of pulses corresponding to changes of magnetic moment,  $\Delta M$ , ranging from about 0.3 to  $40 \times 10^{-6}$ , the lowest discriminator setting being well above the noise level of the apparatus. The complete examination of a single specimen, it may be mentioned, requires a considerable time, for, with the necessarily slow rate of change of field, a single run over a half cycle of a magnetization curve for one discriminator setting may occupy up to twenty-four hours.

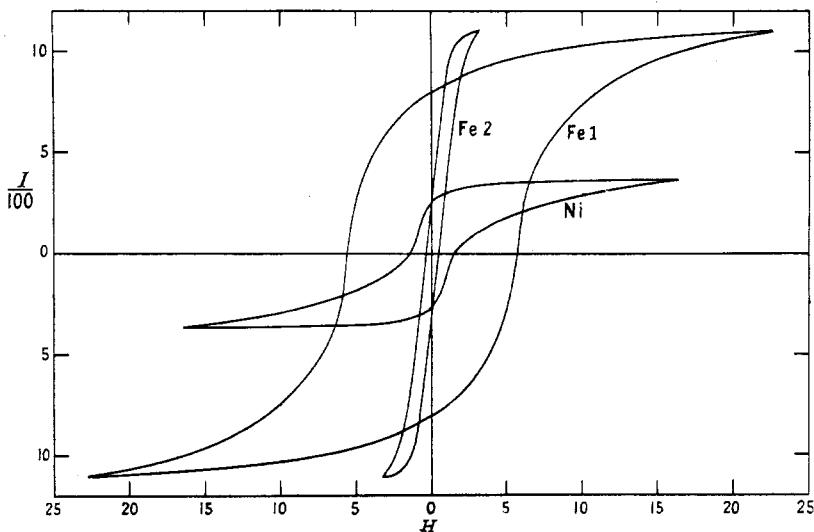


Figure 3.16. Representative hysteresis curves of materials used in Barkhausen effect investigations.  
 $H$ , applied field. Fe1, hard drawn iron; Fe2, annealed iron, large grained; Ni, annealed nickel.

(After Tebble, Skidmore and Corner 1950.)

*Experimental results.* The primary experimental results may be expressed in the form of a curve, the (number, level) curve, giving the number of discontinuities,  $N$ , per unit volume, for which the change in resolved magnetic moment is greater than  $\Delta M$ , obtainable from the discriminator setting, over a range of the magnetization curve corresponding to the total change of field. From this curve the contribution of the discontinuous changes, over any  $\Delta M$  range included, to the total change in magnetization is at once obtainable by integration. Differentiation of the curve yields a distribution curve, giving  $dN/d(\Delta M)$  against  $\Delta M$ . Finally, multiplying the ordinates of this curve by  $\Delta M$ , a contribution curve is obtained,  $\Delta M\{dN/d(\Delta M)\}$  against  $\Delta M$ , giving the contribution, per unit range of  $\Delta M$ , of the discontinuous to the total change in the magnetization. Hysteresis and contribution curves for the three materials investigated in most detail are shown in Figures 3.16 and 3.17. The iron content of the hard drawn iron (Fe1) was better than 99.9%, the main impurities being C (0.03) and Mn (0.05); the annealed iron (Fe2) was prepared from it by decarburization followed by the

standard stretching and annealing process to produce large crystals; the nickel, chosen because related magneto-thermal investigations had been carried out on similar material, had a purity of about 99.6%. For convenience in graphical representation, the abscissa for the contribution curves is taken as  $(\Delta M/2I_0)$ , so the horizontal scale gives directly the minimum volumes associated with the discontinuities. The lower limit of the curves is fixed by the minimum value of  $\Delta M$  for which reliable counts can be made ( $\Delta M \approx 0.3 \times 10^{-6}$ ), corresponding to a minimum volume of slightly less than  $10^{-10} \text{ cm}^3$  for iron, and a value about three times as great for nickel.

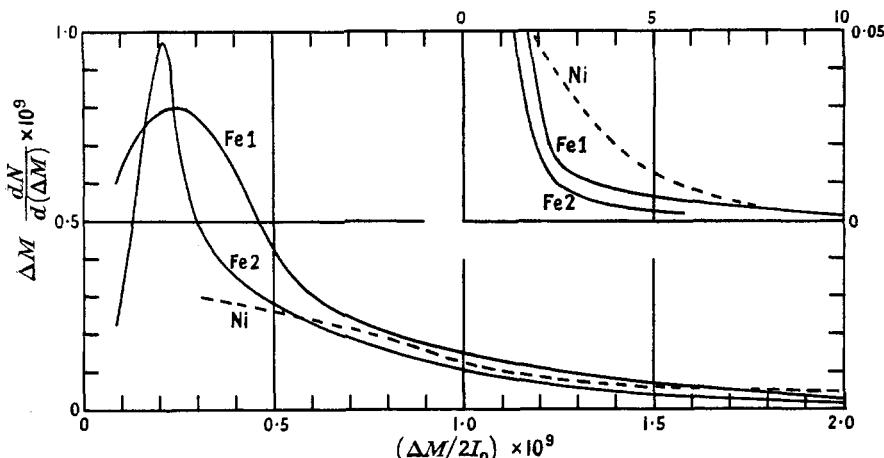


Figure 3.17. Contribution curves for iron and nickel, showing the contribution to the total change of magnetization from discontinuous changes of moment,  $\Delta M$ .

(After Tebble, Skidmore and Corner 1950.)

$(\Delta M/2I_0)$  gives the minimum volume associated with the change in resolved moment,  $\Delta M$ . Values adopted for  $2I_0$ : Fe, 3,440; Ni, 970.

Table 3.3. Contribution of Barkhausen Discontinuities to Change in Magnetization. (Tebble, Skidmore and Corner 1950.) (See text for symbols and details of materials.)

Material	Range of field	$\Delta I_T$	Range of $\Delta M \times 10^6$	$\Delta I_B$	$\Delta I_{rev}$	$\Delta I_B/\Delta I_T$
Fe1	$\pm 18.6$	2150	0.3-35	1844	180	0.86
Fe2	$\pm 3.0$	2180	0.3-20	1250	110	0.57
Ni	$\pm 14.9$	700	0.3-12	326	115	0.47

The contribution from the Barkhausen discontinuities,  $\Delta I_B$ , actually counted over the range investigated to the total change in magnetization,  $\Delta I_T$ , is shown in Table 3.3, and also the reversible contribution,  $\Delta I_{rev}$ , as estimated from measurements of the reversible susceptibility (Tebble and Corner 1950). Some representative curves showing the measured discontinuous and continuous contributions to the change of magnetization with field for nickel are shown in Figure 3.18. For hard drawn iron, from the numbers in Table 3.3, the reversible contribution accounts for 0.08 of the change in magnetization, and the measured discontinuities for 0.86. Slight extrapolation (see Figure 3.17) to cover the smaller discontinuities, gives a further 0.04. Although the closeness of the overall agreement in this case must be regarded as to some extent fortuitous, it none

the less gives convincing evidence that considerable reliance can be placed on the substantial accuracy of the size-number determinations. For nickel, extrapolation would be more uncertain, but an overall discrepancy of perhaps 20% is indicated. For annealed iron (Fe2) the discrepancy is greater, about 35%, after extrapolation. There is a possibility that the reversible contribution is underestimated, but it is unlikely that the error is large. The most probable source of the discrepancy is in the overlapping of the pulses due to temporally close discontinuities, an effect likely to be more persistent, even with the slowest practicable rates of change of field, the higher the permeability of the material. It was observed, moreover, particularly in annealed iron, that close groups or bursts of pulses occurred, and that although the intervals between the groups increased with decrease in the rate of change of field, the apparent interval between the distinguishable pulses in these groups was not appreciably affected. This

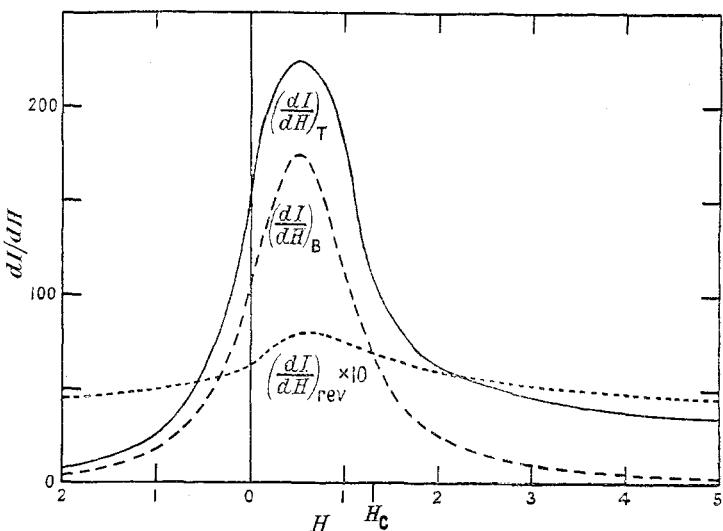


Figure 3.18. Change of magnetization with field,  $(dI/dH)_T$ , for nickel, and measured contributions from Barkhausen and reversible processes,  $(dI/dH)_B$  and  $(dI/dH)_{rev}$ .  
(After Tebble, Skidmore and Corner 1950.)

apparent effect of one discontinuous process on others, combined with incompleteness of resolution of close pulses, is probably sufficient to account for the somewhat lower counts for specimens of higher eddy current time constants,  $\tau_E$ . The check on the experimental work made by bringing together curves such as those of Figure 3.18 is very severe, and stress should be placed primarily on the general agreement rather than on discrepancies in detail.

From the results on which Figure 3.17 and Table 3.3 are based, it is clear that the bulk of the discontinuous change of magnetization occurs, in iron, by changes of moment,  $\Delta M$ , ranging for  $0.3$  to  $30 \times 10^{-6}$ , corresponding to minimum volumes from about  $10^{-10}$  to  $10^{-8} \text{ cm}^3$ , and numbers of atoms from about  $10^{13}$  to  $10^{15}$ , and that in nickel (from Figure 3.17) the volumes are much the same, and the changes in moment some three times smaller. The size distribution of the discontinuities was examined, not only for the range covered as a whole, but also for successive parts of the range. No definite indication of any significant variation in the distribution was found. Thus, although the contribution from the discontinuities

rises to a maximum roughly in the region where  $(dI/dH)_T$  is a maximum (Figure 3.18 is representative in this respect) the ‘average volume’ of the discontinuities does not, in sharp contradiction to the findings by the indirect method (I, Figure 2.7, p. 62). It should be re-emphasized that the concept of ‘average volume’ applied to Barkhausen discontinuities requires very careful definition if it is to be useful. If the contribution curves are of the type shown for Fe1 and Fe2 in Figure 3.17, the volume corresponding to the peak contribution (about 2.5 and  $2 \times 10^{-10} \text{ cm}^3$  in these two cases) might be taken as characteristic; alternatively, a volume,  $v_{\frac{1}{2}}$ , such that half the total discontinuous charge came from smaller, and half from larger volumes, might be given as an appropriate characterizing magnitude. Characteristic volumes so defined appear to be some ten times smaller than the maximum average volumes obtained by the indirect method; average volumes in the usual sense would, of course, be very much smaller still.

*Significance of sizes of discontinuities.* The experimental results for the size distribution of Barkhausen discontinuities having been considered at some length, it must now be admitted that the precise significance of these sizes (or, more specifically, of the volumes of the groups of atoms in which the changes occur) is at present very uncertain. It was originally thought that the Barkhausen volumes could be identified with domains, but this is certainly not generally true if the term ‘domain’ is used in the sense here adopted. More non-committally, and indeed almost incontrovertibly, a Barkhausen volume has for some time been considered as a volume traversed by a domain boundary (or part of a domain boundary) in moving spontaneously from one equilibrium position, which becomes unstable at a critical value of the effective field, to a new stable equilibrium position (as represented diagrammatically in Figure 4.1 below). The range of these movements must, it would seem, be limited by static irregularities in the crystal structure, giving conditions for localized boundary movement essentially distinct from those determinative of the general relatively large-scale movement of the primary domain boundaries. It is a tempting speculation that Barkhausen volumes may be closely related to the slightly disorientated mosaic blocks in metallic crystals, the volumes of which appear to be of much the same order of magnitude (e.g. Barrett 1943, pp. 219–23; Lacombe and Berghezan 1949). An extension of the work of Williams and Shockley (see § 3(ii)), in which the changing powder pattern and the Barkhausen effect are observed simultaneously, offers great promise, though it should be mentioned that the reorganization of the secondary domain structure round an imperfection shown in one of their photographs appears to involve a volume very much greater than those for typical Barkhausen discontinuities. The whole problem is a fascinating one calling for much further investigation, the bearings of which may be by no means limited to ferromagnetic materials. In recent years a much clearer understanding of the Barkhausen effect has been gained, and it seems likely that more complete and satisfying answers to some of the outstanding questions will not be long delayed.

### 3(iv). Related Investigations

*Large discontinuities.* Among other types of investigation in the general field of domain structure there are two of particular interest and importance, to which some reference must be made. The first of these is the study of large discontinuities in magnetization, such as may be obtained in wires of materials with positive magnetostriction under tension. With increasing tension, the wire axis

approximates more and more closely to an easy axis, the free energy associated with the strain anisotropy being given by

$$F_s = \frac{3}{2} \lambda Z \sin^2 \phi, \quad \dots \dots \quad (3.19)$$

where  $\lambda$  is the saturation magnetostriction coefficient,  $Z$  the tension, and  $\phi$  the angle between  $I_0$  and the axis. The relation holds more closely the greater the ratio  $\lambda Z/K$ , where  $K$  is the magneto-crystalline anisotropy coefficient. The hysteresis loops become approximately rectangular, and reversal of magnetization may occur in a single 'Barkhausen' discontinuity, the change of magnetization being  $2I_0$ . The work of Sixtus and Tonks (1931-33), Preisach (1932) and others (already briefly reviewed in I, pp. 62-4) shows that the initiation of a reversed region in a wire initially saturated in one direction requires a starting field,  $H_s$ , usually greater than the critical field,  $H_0$ , required to maintain the propagation of the reversed magnetization along the wire. Measurements were made of  $H_s$  and  $H_0$  for different stresses, and of the propagation velocity under various conditions, the materials examined usually being ferronickels in the composition range 5 to 80% nickel. The effect of combined tension and torsion was examined by Reinhart (1934 a, b). It was later found by Sixtus (1935) that the extent of growth of a reversed region could be controlled by limiting the time of application of  $H_s$ , even though the steady field was maintained at a value somewhat greater than  $H_0$ . Thus, 'frozen-in' reverse domains may be obtained, their dimensions at least approximately determined, and the conditions for their growth examined. The measurements justify their being treated theoretically, with good approximation, as ellipsoids of rotation. The manner of growth of a reversed domain, laterally and longitudinally, as dependent on the applied field, can be estimated by considering the change in the external field energy, the boundary energy and the demagnetizing field energy. The extensive experimental measurements show satisfactory agreement with the detailed theoretical calculations (Döring 1938, Döring and Haake 1938, Haake 1939). This work is very fully reviewed in Becker and Döring's book (1939, pp. 182-7, 192-203). The results of these studies of the growth process for large domains are not only of interest in themselves, but they also have some bearing on the more general question of boundary movements in ordinary materials. The difference in the large and the small discontinuities is, however, not merely one of scale. The conditions of high and uniform stress under which the large discontinuities occur are very specialized, and the shapes of the large reverse domains are very different from those of domains in ordinary materials. The study of large discontinuities does not therefore solve the problem of small discontinuities, though it does bring into clear focus some of the factors which must be taken into consideration. It is perhaps relevant to mention that in an investigation of the approximately rectangular hysteresis loops of nickel under compression, it was found by Heaps (1936) that as the magnetization changed over the nearly vertical steep part of the curve, the ordinary Barkhausen effect was apparently much the same as with unstressed material.

*Small particles.* The second group of investigations is on the behaviour of ferromagnetic bodies (or assemblies of such bodies) at least one of whose dimensions is very small, that is, with thin films, 'needles', or small particles. For bodies of ordinary size, the magnetostatic energy associated with a state of uniform magnetization is usually reduced by the formation of domains; but below a

certain size the increase of energy due to boundary formation, depending on surface, will exceed the reduction of magnetostatic energy, depending on volume, and no boundaries will be formed. By determining the minimum energies associated with various physically plausible domain boundary arrangements (using arguments similar to those outlined in § 3 (i)) and comparing these with the energy when the body is uniformly magnetized, Kittel (1946) has made estimates of the critical sizes below which the single domain state is energetically favoured. Using, for simplicity, a standard value of  $3 \text{ erg cm}^{-2}$  for the boundary energy, and the magnetization and anisotropy values for iron, he obtains the following critical dimensions: for film thickness,  $3 \times 10^{-5} \text{ cm.}$ ; for the edge of a cubical particle,  $1.5 \times 10^{-6} \text{ cm.}$ ; and for a needle, values of the diameter varying with the ratio,  $m$ , of length to diameter, from  $2.8 \times 10^{-6} \text{ cm.}$  for  $m = 5$  to  $2.4 \times 10^{-5} \text{ cm.}$  for  $m = 20$ . Somewhat similar calculations have been made by Stoner and Wohlfarth (1948) for particles in the form of ellipsoids of rotation. Using the values of  $\alpha_1 a_1^2$  in Table 3.2, it is found that spherical particles are almost certainly single domain for diameters (in  $10^{-6} \text{ cm.}$ ) below 2.4, 5.2 and 3.2 for iron, nickel and cobalt respectively; for prolate spheroids the corresponding lengths of the minor axis increase with the dimensional ratio inversely as the square root of the demagnetization coefficient.

Perhaps the most direct experimental evidence for the single domain character of small particles is provided by the magnetization curves for colloidal iron oxides (Elmore 1938 c). The curves are of the Langevin type, showing an approach to saturation in fields of a few hundred oersted, and for the magnetite sol are consistent with particles of mean diameter  $3.4 \times 10^{-6} \text{ cm.}$ , and with a 'permanent moment' corresponding to about 44% of the bulk magnetization of magnetite. In the older work on thin films and small particles, summarized by Kittel, much higher values for the coercivity and lower values for the initial permeability are recorded than for the bulk material. From much of the earlier work, however, for various reasons, it is difficult to draw any very definite quantitative conclusions. More recently Drigo and Pizzo (1948) have given a preliminary account of measurements on thin films of the ferromagnetic elements electrolytically deposited on wires or discs of copper. They find that the coercivity increases with decreasing thickness, and that Barkhausen discontinuities disappear for thicknesses (in  $10^{-6} \text{ cm.}$ ) below 13, 8 and 12 for iron, nickel and cobalt respectively. An important application of the general ideas on single domain particles is to the interpretation of the properties of the high coercivity alloys and powder materials used for permanent magnets, to which further reference is made later (§ 4(iv), § 5(iv)).

Finally, mention may be made of some interesting work by König (1948) on thin films, though it is only indirectly relevant to the theme of the present section. Films of iron, some  $25 \times 10^{-8} \text{ cm.}$  in thickness, were deposited on collodion at a low temperature. The degree of ferromagnetism of the film could be estimated from the Faraday effect in a high magnetic field, and crystal sizes from the line widths in electron diffraction patterns. Crystal formation occurs on warming the film from a low temperature. Magneto-rotation could first be detected when the estimated linear dimensions of the crystals were about  $11 \times 10^{-8} \text{ cm.}$ , corresponding to about four lattice spacings. This indicates that the minimum crystal size necessary for the development of ferromagnetic characteristics corresponds to

some 64 unit cells, or a volume of about  $1.5 \times 10^{-21} \text{ cm}^3$ , containing some 128 atoms (cf. Becker 1948). From the evidence considered in this section ferromagnetic domains are ordinarily very much larger than this, and, as has been tacitly assumed throughout, there is no reason to suppose that there is any appreciable variation of the degree of spontaneous magnetization over the relevant range of domain size.

#### § 4. THE ANALYSIS OF MAGNETIZATION CURVES

##### 4 (i). *Introductory*

The two preceding long sections on single crystals and domain structure have been concerned with the fundamental processes of change of magnetization which underlie the forms of magnetization curves generally. In view of the fact that reasonably reliable values are available for magneto-crystalline anisotropy coefficients (§ 2(ii)), and that there is remarkably close agreement between theoretically calculated and observed magnetization curves for single crystals (§ 2(iii)), it might seem that an analysis (or synthesis) of the rotational contribution to the change of magnetization in polycrystalline material would be fairly straightforward. Even if the grains were individually ideal crystals, however, it is very difficult to make proper allowance, in an averaging process, for their mutual magnetic interaction, and, indeed, until very recently this problem has been almost entirely ignored. Conversely, given the applied field and the bulk magnetization of the specimen, only the roughest estimate could be made of the effective field for particular grains, the shapes of which must in general give rise to a distribution of magnetization physically as complex as it is mathematically unmanageable. Apart from uncertainties arising in this way, which should be borne in mind, though they may not always be serious, the grains, in general, are by no means ideal crystals. They have the same kind of imperfections in the form of localized heterogeneities, depending on composition, and thermal and mechanical treatment of the material, as have single crystals, but in addition are subject to a much greater degree of strain or deformation, so that the effective anisotropy of a grain may differ enormously from that of the ideal crystal. Much the same considerations apply in connection with boundary movement processes.

It follows at once that a knowledge of the effects of stress on magnetization, or conversely of the magnetostrictive changes accompanying magnetization, are of great importance in connection with the general interpretation of magnetization curves. Many of the basic ideas in this field, and much of the related experimental work, date from the early thirties (cf. I, pp. 61–65), and need not be considered in detail in this Report (see, however, § 3(iv)). Such consideration is the less necessary, in that the subject has been dealt with, in varying degrees of detail, in many review articles and books, and particularly in Becker and Döring's *Ferromagnetismus* (1939). (This book will be referred to in this section as BD.) In fact, since about 1931 until very recently, the outlook on magnetization curves has been dominated by the 'strain theory'. The general formal theory of the joint effect of stress and field is very complicated (BD, pp. 132–146), but partly owing to this complication, and partly owing to the inadequacy of experimental data on the various elastic and magneto-elastic crystal coefficients, use is made in applications almost exclusively of a few simple approximate relations (BD, p. 145). The most important of these is the relation for the variable part of the

magneto-elastic free energy,  $F_s$ , of a ferromagnetic with isotropic saturation magnetostriction,  $\lambda$ , subjected to a tension,  $Z$ , namely

$$F_s = \frac{3}{2}\lambda Z \sin^2 \psi, \quad \dots \dots (4.1)$$

where  $\psi$  is the angle between the magnetization vector,  $I_0$ , and the direction of tension. The success of the application of (4.1) and similar relations in the coordination of the behaviour of ferromagnetics under applied stress is unimpeachable; the apparent success in the coordination of the low field properties of diverse types of ferromagnetics in terms of hypothetical distributions of internal stress is even more remarkable, but in the light of recent criticisms (see below) it must be regarded as at least in part illusory. There is always a danger, as pointed out by Brown (1938 b), 'of misinterpreting an agreement between theory and experiment as evidence for the particular forces or mechanism assumed in the theory'. In a series of papers on reversible susceptibility and related effects, Brown (1937-39) has developed with considerable success a statistical theory from which useful relations are obtained which are independent of the precise mechanism by which the equilibrium state of magnetization is established. It must be remembered, however, that some of the most characteristic features of the behaviour of ferromagnetics in low and moderate fields are due to the fact that the normal states are in general not equilibrium states of lowest free energy for the system as a whole. The problem is one of microscopic metastability, to which the methods of statistical mechanics are hardly applicable.

It is peculiarly difficult at the present time to give a coherent account of work on what may be called the 'analysis' of the ordinary magnetization curve, using that term in a broad sense to imply the determination of the character of the elementary changes occurring over any part of the various types of magnetization curves (e.g. initial, normal or 'commutation' cyclic curves) for a particular material, coupled with an explanation of the very diverse magnitudes of characteristic quantities or coefficients (e.g. remanence, coercivity, initial and maximum susceptibility or permeability) for different materials. The difficulty is largely due to the new knowledge recently gained, particularly on domain structure. This has shown that most of the earlier treatments of the magnetization curve problem are defective, as being based, at least in part, on physical assumptions now known to be untenable. Little useful purpose would be served by describing in detail theoretical treatments which the authors themselves would not now regard as satisfactory. This does not mean that the earlier treatments are valueless, for large parts of them will be incorporated in new treatments. For the most part, however, these new treatments have yet to be developed. The presentation of earlier work in this section will, therefore, be relatively brief and selective; the main aim will be to indicate how certain aspects of the problem of analysis of curves have been, or may be, approached in the light of the new knowledge.

From a theoretical standpoint, a distinguishing feature of the newer outlook is the recognition of the importance of purely magnetic interactions, previously largely overlooked. This is apparent in the treatment both of single crystal magnetization curves (§ 2(iii)), where an important factor is the demagnetizing field of the crystal as a whole, and of domain structure (§ 3(i)), where the small scale patterns are largely conditioned by a minimization of the energy due to internal free poles. It will be apparent again in the supplementary topics discussed below in connection with boundary movements (§ 4(ii)) and rotations (§ 4(iii), (iv)).

In § 4(v), recent work on magneto-thermal effects is briefly reviewed as it is believed that experimental and theoretical studies of the changes of temperature accompanying magnetization provide a most valuable means of obtaining information about the character of the magnetic changes occurring additional to that obtainable from the magnetization curves themselves. In this section little reference to experimental methods is made, as the methods are for the most part standard and well known; nor is it considered necessary to give a formal description of the various types of magnetization curve.

#### 4(ii). Boundary Movements

*Reversible and irreversible boundary movements.* Most of the factors which have been suggested as determinative of the extent and character of boundary movements can conveniently be indicated with reference to Figure 4.1. This particular figure is taken from a paper by Stoner and Rhodes (1949), but similar diagrams have often been given.

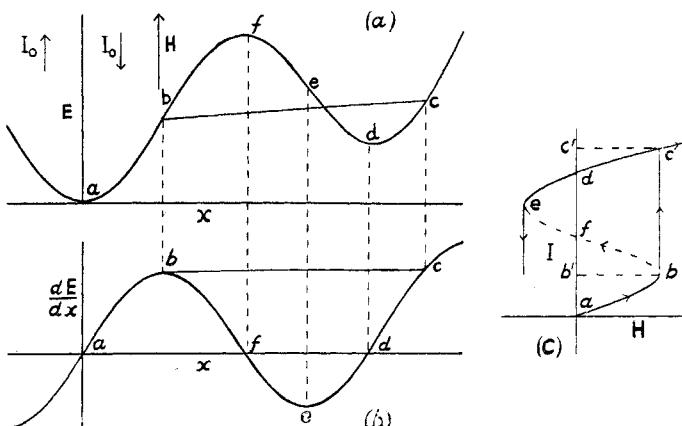


Figure 4.1. Diagrams illustrating reversible and irreversible boundary movements.

The boundary is parallel to the  $yz$  plane, with its central plane passing through the energy minimum at  $a$  in zero field. As the field increases the boundary moves in the direction of increasing  $x$ . Corresponding points in (a), (b) and (c) are marked by the same letters.

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For simplicity a  $180^\circ$  boundary is considered. The curve in Figure 4.1(a) represents a possible form for the dependence of the internal free energy of the material on the position of this one boundary. Using the symbol  $E$  for the energy per unit area of the boundary (but without necessarily implying that the energy is localized in the boundary itself), and assuming that in zero field the boundary is in equilibrium at  $x=0$ , the condition for equilibrium in a field  $H$  is

$$\frac{d}{dx}(E - 2HI_0x) = 0, \quad \dots \dots (4.2)$$

or

$$2HI_0 = dE/dx. \quad \dots \dots (4.3)$$

As the field increases the boundary moves reversibly to the right until  $dE/dx$  reaches a maximum at  $b$  when the equilibrium becomes unstable. Once the corresponding value of the field, namely

$$H_0 = \frac{1}{2I_0} \left( \frac{dE}{dx} \right)_{\max}, \quad \dots \dots (4.4)$$

is passed, the boundary moves spontaneously (i.e. without further increase of field) to a new position of equilibrium at  $c$ , the change from  $b$  to  $c$  corresponding to a Barkhausen discontinuity. With further increase of field reversible movement is resumed. The course of the changes when the field is decreased will be clear from the figure. The diagram (c) shows how the boundary movement contributes to the reversible and irreversible susceptibility (ranges  $ab$  and  $bc$  respectively) in increasing field, and to the reversible susceptibility again (range  $cde$ ) in decreasing field. The manner in which remanence, coercivity and hysteresis can arise from boundary movement are all illustrated. The assumption of a not unduly specialized type of dependence of energy on boundary position thus leads to a formal coordination of a wide variety of effects associated with a single elementary process, and it is not unreasonable to suppose that the bulk characteristics of ferromagnetics might arise from the superposition of a large number of similar processes. A variation of internal energy with boundary position must arise, in the last resort, from deviations from uniformity of the material, corresponding to a variation in internal stress or composition, and the theoretical problem is that of linking the two together. There have been three distinct lines of approach (within the same formal scheme which has been outlined), not necessarily mutually incompatible, and the treatments, as developed, may be referred to, for brevity, as the 'strain', 'inclusion' and 'disperse field' theories.

*The strain theory.* The basic idea of the strain theory, as first put forward in a systematic way in the present connection by Kondorski (1937) is that the variation of energy with boundary position is mainly due to the direct effect of the spatial variation of local stresses on the energy of the boundary itself. Thus, if the boundary energy, in the absence of stress, is given by

$$\gamma = \gamma_K = gK^{\frac{1}{2}}, \quad \dots \dots \quad (4.5)$$

where  $K$  is a magneto-crystalline anisotropy coefficient, and  $g$  a coefficient involving the exchange energy (see § 3 (i) for details), with internal stress  $Z$  (having the character of a tension or compression) the energy becomes

$$\gamma = \gamma_Z = g(K + 3b\lambda Z/2)^{\frac{1}{2}}, \quad \dots \dots \quad (4.6)$$

where  $\lambda$  is the saturation magnetostriction, assumed isotropic (cf. (4.1)), and  $b$  is a numerical factor depending on the orientation of  $Z$  relative to the boundary. In equations (4.2) to (4.4),  $E$  is replaced by  $\gamma$ . The critical field,  $H_0$ , is proportional to the maximum stress gradient, and, as may readily be shown from the relations given in § 3 (i), to the effective width,  $\delta$ , of the boundary. In Kondorski's treatment it is assumed implicitly that the variation of  $Z$  over the width of the boundary is small. This limitation is removed in a development of the treatment by Kersten (1938 a, b), who considers a stress inhomogeneity extending over a length  $l$  (perpendicular to the plane of the boundary), in which the stress rises from zero (or from the mean value over the whole of the relevant region) to a maximum  $\Delta Z$ . It may then be shown (cf. Kersten, 1938 a, b, or BD, p. 207) that the critical field is given by

$$H_0 = p_0(\lambda\Delta Z/I_0), \quad \dots \dots \quad (4.7)$$

where  $p_0$  is a numerical factor proportional to  $l/\delta$  for  $l/\delta \ll 1$  and to  $\delta/l$  for  $l/\delta \gg 1$ , and having a maximum value, of order unity, for  $l \approx \delta$ . For a stress distribution corresponding to a quasi-sinusoidal fluctuation of amplitude  $\Delta Z$ , the critical field has a maximum of order  $\lambda\Delta Z/I_0$  when the wavelength is of the order of the

effective boundary thickness. Arguments have been given which suggest that, for ordinary material, whereas the initial susceptibility is mainly dependent on  $90^\circ$  boundary movements, the coercivity corresponds to an appropriate average of the critical fields for  $180^\circ$  boundary movements.

In this necessarily brief indication of the character of the various theories, it is convenient to consider, for illustrative purposes, the quantitative expressions, such as (4.7), obtained for the critical field,  $H_0$ , associated with  $180^\circ$  boundary movements. The attraction of the strain theory, however, lay in the fact that it appeared to offer the possibility of interpreting not one, but all the ordinary low field characteristics of ferromagnetics, in a reasonably simple and inherently plausible way, in terms of the internal stress distributions in the material. The comprehensive survey of the theory by Becker and Döring (BD, pp. 147–167, 176–218) gives the impression that, although many matters of detail called for further investigation, the essential basis for a satisfactory physical explanation of the major characteristics had been established. Even if the general scheme were not open to more serious criticism, however, there are two features which detract from its value. The first is that the internal stress parameters (such as  $\Delta Z$  in (4.7)) which enter into the ‘theoretical’ expressions for different magnetic characteristics, and which are usually denoted by  $\sigma_i$ , may have a different physical significance in the different expressions, and the relation between them is generally somewhat uncertain. (For a recent discussion of certain aspects of this problem, see Köster (1948).) The coordination of different characteristics is therefore less complete than it at first appears to be, for, in general, the various characteristics neither lead to, nor can they be derived from, a unique and clearly specifiable internal stress distribution. The second point is that little progress has been made in obtaining precise quantitative estimates of the internal stress distributions in ferromagnetic (or other) materials by more direct methods, so that only the roughest independent check can be made of the magnetic estimates. Even rough independent estimates of the probable magnitudes of internal stresses, however, provide some indication of limitations to the range of applicability of the strain theory. For example, insertion of the approximate values for iron of  $I_0$  ( $1.72 \times 10^3$ ) and  $|\lambda|$  ( $2 \times 10^{-5}$ ) in (4.7), shows that the minimum value of  $\Delta Z$  (i.e. for  $p_0 = 1$ ) expressed in kg. mm $^{-2}$  is within 20% of  $H_0$ , expressed in oersteds. Now it is hardly reasonable to suppose that variations of internal stress over distances of the order of  $10^{-6}$  cm. (see Table 3.2) from zero to above the normal breaking stress can occur; and it seems clear on this ground alone that some other physical explanation than that given by the strain theory must be sought for coercivities of several hundred oersteds such as are obtained in permanent-magnet alloys. An entirely different mechanism which may here be involved is considered below (§ 5 (iv)). In many alloys of a more common type, containing, as additions to the ferromagnetic metal, non-ferromagnetic or less ferromagnetic constituents, the coercivity is often markedly increased when the limit of solid solubility is exceeded. It can hardly be denied that this might be due to stresses set up by the inclusions. In many cases, however, the stresses which would be required in annealed materials seem unduly high, and a more direct mechanism suggested by Kersten (1943), which does not involve stress effects at all, seems at first sight much more plausible.

*The inclusion theory.* The basic idea of Kersten’s *Fremdkörpertheorie* is very simple. In a ferromagnetic containing non-ferromagnetic inclusions, a boundary

between domains of the matrix may pass through or include within itself 'impurity' particles which do not contribute to the boundary energy. For a given gross area of boundary the energy will depend on the area occupied by the particles, being a maximum when no particles are included. By idealizing the impurity particles as spherical and uniformly distributed on a cubic lattice, estimates may be made of the increase of boundary energy in the movement of the boundary from a zero field equilibrium position (in which the central plane of the boundary passes through a maximum number of particles), and expressions obtained both for the contribution to the initial susceptibility and for the critical field, in terms of the volume concentration,  $v_i$ , of the undissolved non-ferromagnetic impurity, and the ratio of the mean particle diameter,  $d$ , to the effective thickness,  $\delta$ , of the boundary wall. As an approximate expression for the coercivity (obtained from an expression for  $H_0$  by multiplication by a numerical 'averaging' factor), Kersten gives

$$H_c = 2.5p(K/I_0)v_i^{2/3}, \quad \dots \quad (4.8)$$

where, for iron and nickel,  $K = K_4/3$  (cf. (2.4)), and

$$p = \frac{2(\delta/d)}{1 + 2(\delta/d)^2}, \quad \dots \quad (4.9)$$

the factor  $p$  arising in a similar way to  $p_0$  in (4.7). It is assumed that any local stress anisotropy is negligible in comparison with the crystal anisotropy. The illustrative relation (4.8) is only one of many that are derived, for cubical and rod-shaped as well as spherical particles. In later work (1948) refinements are made in some of the earlier rough calculations (though without any considerable change in the numerical coefficients in the derived relations), and the behaviour of  $90^\circ$  boundaries is examined. In a fuller presentation of the inclusion theory and its applications, published as a book (1943), in which is included an excellent survey of the strain theory, extensive data are collected on coercivities, more particularly of the technically important range of annealed iron alloys containing amounts of other elements which are usually relatively small but above the solubility limit (e.g. C, N, S, Cu), and the data are discussed from the new point of view. The relation (4.8) of the inclusion theory is more nearly amenable to experimental test than (4.7) of the strain theory, for the value of  $v_i$  (in contrast to that of  $\Delta Z$ ) is usually known (or determinable) with accuracy. The observed values of  $H_c$  can then be compared with the value of  $(H_c)_{\max}$  which, for spherical inclusions from (4.8) and (4.9), is given by

$$(H_c)_{\max} \approx 1.8(K/I_0)v_i^{2/3}, \quad \dots \quad (4.10)$$

and it may fairly be said that the very large number of results examined are at least compatible with the theory. Moreover, although the direct determination of the sizes (and shapes) of inclusions, such as is required for the independent estimate of the factor  $p$  in (4.8), would be very difficult, in favourable cases it is much more within the bounds of possibility than a determination of the extent of stress inhomogeneities. In view of such considerations, and of the elegant simplicity and wide field of application of the inclusion theory, it is not surprising that it should have been put forward by its author with so much enthusiasm. Indeed, a much more detailed account of this work of Kersten would be appropriate here, were it not that certain fundamental defects of both the strain and

inclusion theories have been brought to light by critical investigations of Néel (1946 a, b, 1947 a). Although, in the light of these criticisms, a more satisfactory reformulation of the strain and inclusion theories will no doubt be possible, it seems likely that they will then form rather contributions to, or special aspects of, a more general theory, of which a first sketch has been given by Néel.

*The disperse field theory.* The first criticism made of Kersten's inclusion theory by Néel (1944 d) is that in it the magnetostatic energy associated with inclusions is completely neglected. For a spherical non-ferromagnetic inclusion (effectively a hole) of diameter  $d$  and volume  $v$ , the difference between the minimum boundary energy (when the central plane of the boundary passes centrally through the inclusion) and the normal energy (when the boundary does not pass through the inclusion) according to Kersten's treatment (for  $\delta < d$ ) is, with sufficient approximation,  $\frac{1}{4}\pi d^2\gamma$ . The difference in the magnetostatic energy associated with the hole for these two positions of the boundary, calculated exactly by Néel, is, with close approximation,  $\frac{1}{2}(\frac{2}{3}\pi I_0^2)v$ , or about  $0.06\pi^2 I_0^2 d^3$ . For inclusions in iron the ratio of the magnetostatic to the boundary energy difference is of the order  $10^6 d$ , which exceeds 100 for some of the larger particle sizes estimated as giving the best agreement with the Kersten relations. Since the Kersten relations, such as (4.8), have been obtained by neglecting an energy effect which may be very much larger than the effect taken into account, it is clear that the whole theoretical treatment of inclusions requires reconsideration. In this same paper Néel shows that the magnetostatic energy may be reduced by the formation of appropriate secondary domain structures, as has already been mentioned (§ 3(ii)), and the general character of the powder patterns round microscopically visible inclusions (Figure 3.12) is in agreement with his predictions. Taking this effect into account, Néel outlines a modified treatment of the coercivity arising from inclusions, but this particular treatment, as he subsequently states (1947 a), is shown to be erroneous by his later work.

In his most comprehensive paper on this subject, dealing with the principles of a new general theory of the coercive field, Néel (1947 a) first puts forward a criticism of the quantitative treatment adopted in developing both the strain and inclusion theories. This criticism, as quantitatively formulated, makes it probable that, except perhaps in some very special cases, the formulae derived are invalid, or at least inapplicable, and that the mechanisms proposed could account for coercivity values only a small fraction of those observed. The method usually, if not invariably, adopted in treating the effect of stress variations on the variation of boundary energy with position is to assume, for simplicity, that the stress varies in the direction of movement of the boundary (e.g. in the  $x$  direction in Figure 4.1) but that it is constant over the plane of the boundary (e.g. in the  $yz$  plane). Any subsequent averaging process does not affect the initial assumption of a one- rather than a three-dimensional stress variation over volumes comparable in size with those traversed by a moving boundary. Similarly, in the inclusion theory, the inclusions are assumed to be uniformly distributed on the points of a lattice, the planes of which are parallel to the boundary planes considered. Once it has been pointed out, it is obvious that a purely random distribution of local stresses or inclusions can give rise only to a very much smaller positional variation of boundary energy. From a quantitative treatment of the problem Néel concludes that the maximum possible variations of boundary energy could account for coercivities of the order of only a tenth of an oersted if the boundary

is regarded as strictly plane, and of a few oersteds if allowance is made for the possibility of deformation of the boundary. It is quite impossible to account for observed coercivities of tens and even hundreds of oersteds.

Although internal stresses and inclusions may have a negligible direct effect on boundary energy variation, there is no doubt that they are responsible, in some way, for the diversity in the low field properties of different materials, or, more specifically, that they give rise indirectly to a variation of energy with boundary position. Néel suggests that the randomly distributed localized irregularities result in fluctuations in the direction and the magnitude of the intrinsic magnetization, as indeed they must do. The magnetization is therefore not strictly uniform, even within a single domain, and the fluctuations give rise to non-zero values of the divergence of  $I$ ; free poles are developed and corresponding magnetic field distributions. The energy associated with these disperse fields (*champs magnétiques de dispersion*) varies with the position of domain boundaries. The variable energy may be regarded as arising from the mutual potential energy of the free pole regions, islands of positive or negative magnetic charge. The sign of the charge depends on the general direction of magnetization; thus an island which is positive when the magnetization is in one direction (e.g.  $I_0$  upwards in Figure 4.1) would become negative when, through boundary movement, the general magnetization direction is reversed (e.g.  $I_0$  downwards); and an island 'bisected' by a boundary will be oppositely charged on the two sides. Thus the volume energy, arising from the mutual potential energy of the magnetically charged islands in any region varies with the position of boundaries in that region. Indirectly, internal stresses and inclusions can therefore give rise to a variation of energy with boundary position similar to that shown in Figure 4.1. Moreover since the magnetostatic energy associated with fluctuations in the intensity of magnetization may greatly exceed the directly produced boundary energy change (as has been noticed in connection with the first criticism of the inclusion theory), it is reasonable to expect that the disperse field effect, even with a completely random distribution of stresses or inclusions, may give rise to energy variations of the order of magnitude required to account for observed values of coercivity and other low field characteristics.

The quantitative mathematical development of the ideas which have been outlined obviously presents great difficulty, and Néel's derivation of even approximate expressions for the coercivity is a remarkable feat. Denoting by  $C$  the deformation energy affecting a fractional volume  $v_s$  of the material, for which the magneto-crystalline anisotropy coefficient is  $K$ , Néel obtains, for  $C/K \leq 1$ ,

$$H_c = \frac{4}{15\pi} \frac{v_s C^2}{KI_0} \left\{ 1.386 + \frac{1}{2} \ln \left( \frac{2\pi I_0^2}{K} \right) \right\}, \quad \dots \quad (4.11)$$

$$\text{and for } K/C \ll 1, \quad H_c = 0.69 \frac{v_s C}{I_0} \left\{ 1.386 + \frac{1}{2} \ln \left( \frac{6.8 I_0^2}{C} \right) \right\}. \quad \dots \quad (4.12)$$

For non-magnetic inclusions of fractional volume  $v_i$ , the relation derived is

$$H_c = \frac{2Kv_i}{\pi I_m} \left\{ 0.386 + \frac{1}{2} \ln \left( \frac{2\pi I_m^2}{K} \right) \right\}, \quad \dots \quad (4.13)$$

where  $I_m$  is the mean value of the spontaneous magnetization. The relation between these expressions and (4.7) and (4.8) may be noted. The numerical significance of the relations becomes clearer on taking particular examples

given by Néel. Assuming that the internal stresses are tensions,  $Z_i$ , orientated at random, and of magnitude  $30 \text{ kg. mm}^{-2}$ , affecting a fractional volume  $v_s$ , then, putting  $C = 3\lambda Z_i/2$ , and using the appropriate values for  $I_0$  and  $K$ , the formula obtained for iron is

$$H_c = 2.1v_s + 360v_i, \quad \dots \dots (4.14)$$

and for nickel,

$$H_c = 330v_s + 97v_i. \quad \dots \dots (4.15)$$

These two relations indicate that in iron the effect of inclusions is predominant, in nickel that of internal stresses. For comparison with experiment, Néel uses the data collected by Kersten for iron alloys. On a logarithmic plot of  $H_c$  against  $v_i$  the points are very scattered, but the line given by (4.14) drives centrally through them in a most convincing manner.

It is not possible to give here a satisfactory account of the detailed argument by which the relations (4.11) to (4.13) are derived. For this, reference may be made to the original paper, and to a later short outline given by Néel (1949). The mathematical treatment of so complex a physical problem is itself unavoidably complicated (e.g. in the manipulation of the Fourier representations of randomly distributed stress variations), but, apart from this, it is not unfair to say that obscurities in the presentation do not seem to arise wholly from the inherent complexities of the problem. It is important to bear in mind that the validity of a mathematical (or physico-mathematical) argument in itself cannot be confirmed merely by an agreement with experiment of approximate relations which may have been derived; and that the value of a theory as interpretative of observable phenomena cannot be properly assessed until the essential details in the argument from the premises to the conclusions have been clearly presented. The position may be expressed, loosely and incautiously, as follows. The 'conclusions' of the strain, inclusion and disperse field theories all agree (more or less) with experiment. With the first two, the deductive arguments are clear and satisfying; but the premises are wrong, or at least inadequate, as a representation of the physical situation. With the disperse field theory, the premises may be tentatively accepted as correct, or at least more nearly adequate; but before the theory can be regarded as 'established', a clearer development of the deductive arguments is required, together with a wider and more searching comparison of the theoretical conclusions with experiment.

Little useful purpose would be served by dealing here with other aspects of boundary movement in relation to magnetic characteristics, as most of these (e.g. the reversible movement in relation particularly to initial susceptibility) have so far been treated only from the standpoint of the older theories. Some of the relations obtained (e.g. that between maximum initial susceptibility and magnetostriction, cf. I, p. 65, equation (2.22)) may still be found to be applicable, though perhaps over a more limited range, while others will undoubtedly require considerable modification in interpretation, if not in quantitative expression. The particular need is for a clearer and more extended development of the disperse field theory. The more general need is for a linking together of what may be called the large scale characteristics of domain boundaries, such as the formation of regular equilibrium structures dependent on field, as indicated by theory (§ 2 (iii), § 3 (i)) and manifested in the powder pattern experiments (§ 3 (ii)), with the small scale characteristics which underlie the Barkhausen effect (§ 3 (iii)), and with which this subsection (4 (ii)), in so far as irreversible movements have been

considered, has been mainly concerned. It may well happen that substantial advances will have been made in both these directions by the time this Report is in print.

#### 4 (iii). Reversible Rotational Processes

Rotational processes in single crystals have already been fully discussed (§ 2). The main question to be considered here is the relation between the variation with field of the magnetization of a polycrystalline aggregate, over a rotational range, and that of single crystals. When the field is increased from zero, with the specimen initially in a demagnetized state, the changes in magnetization in the lower fields are mainly due to boundary movements. In higher fields rotational changes predominate, and the range to which most attention has been devoted in attempting to correlate the behaviour of single crystals and polycrystalline materials is that of approach to saturation. In a field decreasing from a high value, the predominance of rotational changes persists over a more extended range. In general, there is no good reason to suppose that the change in magnetization over the range from saturation to remanence is wholly rotational (or even wholly reversible); it is none the less of interest to compare observed values of the remanence with values which can, in some cases, be derived theoretically on the assumption that only rotational processes are involved. There is little doubt that in most materials the rotational processes which take place are entirely reversible, and only such reversible processes are here under consideration; the probability of the occurrence of irreversible rotational processes in certain types of high coercivity materials is discussed below (§ 4(iv)).

*Approach to saturation.* Empirically, in the range in which  $I/I_0$  approaches unity, the variation of magnetization with field may be represented by

$$I = I_0 \left( 1 - \frac{a}{H} - \frac{b}{H^2} \right) + cH \quad \dots \dots \quad (4.16)$$

(cf. I, p. 61, BD, p. 167.) The term in  $H$ , which may be attributed to the increase in the intrinsic magnetization above the spontaneous magnetization value at the temperature, is very small at temperatures well below the Curie point, and need not be considered here, though it is important in connection with magneto-thermal effects (§ 4(v)). The term in  $H^{-1}$  is usually dominant in fields above a few thousand oersteds, as shown particularly by the work of Weiss and his collaborators, and  $a$  is referred to as the coefficient of magnetic hardness (*dureté*). None of the earlier suggestions as to the origin of this term is satisfactory (cf. BD, pp. 175–6); an explanation recently proposed by Néel (1948 a) is outlined below. The term in  $H^{-2}$  may be connected with rotation of the magnetization vectors towards the applied field direction against the local anisotropy fields. This process gives rise to a variation of magnetization with field which may be quite generally represented by

$$1 - (I/I_0) = \sum_{n=2} b_n H^{-n}. \quad \dots \dots \quad (4.17)$$

The leading coefficients in this series have been calculated by Akulov (1931), and more completely by Gans (1932), for an aggregate of quasi-independent single crystals orientated at random. For iron and nickel the theoretical value of the first coefficient so obtained is given by

$$b' = b_2 = \frac{8}{105} (K_4/I_0)^2. \quad \dots \dots \quad (4.18)$$

Measurements on both iron and nickel in the form of polycrystalline wires by Czerlinski (1932), and more recently on nickel, over a wide temperature range, by Polley (1939), yielded values for  $b$  which, putting  $b = b'$ , gave values of  $K_4$  in excellent agreement with those obtained from measurements on single crystals (cf. BD, pp. 171-5).

This agreement is very remarkable for, as seems first to have been pointed out by Holstein and Primakoff (1941), in the derivation of (4.18) the mutual magnetic interaction of the crystalline grains is neglected. The field acting on any particular grain owing to the difference in the directions of magnetization of surrounding grains is likely to be comparable with the applied field, when this is in the usual range of a few hundred to a few thousand oersteds; the value of  $b$  given by (4.18) should be approached only for  $(H/4\pi I_0) \gg 1$ . The detailed calculation of  $b$  (or more generally of  $I/I_0$ ) as a function of  $H/4\pi I_0$ , the relevant parameter, is complicated, and it is very satisfactory that Néel (1948 b), in a later but completely independent treatment of the problem, obtains the same result as Holstein and Primakoff. Retaining  $b'$  for the theoretical value of the coefficient of  $H^{-2}$  given by (4.18), using  $b''$  for the new value, and writing

$$\alpha = H/4\pi I_0, \quad \dots \dots \dots (4.19)$$

the result may be expressed by

$$b''/b' = f(\alpha) = \frac{1}{2} \left[ 1 + \frac{\alpha}{2(1+\alpha)} + \frac{\alpha^2}{4(1+\alpha)^{3/2}} \ln \frac{(1+\alpha)^{1/2} + 1}{(1+\alpha)^{1/2} - 1} \right]. \quad \dots \dots \dots (4.20)$$

For  $\alpha \ll 1$  (i.e.  $H \ll 4\pi I_0$ ),  $f(\alpha) \rightarrow \frac{1}{2}$ ;

for  $\alpha \gg 1$  (i.e.  $H \gg 4\pi I_0$ ),  $f(\alpha) \rightarrow 1$ .

It may be noticed that for small values of  $\alpha$ ,  $f(\alpha)$  varies slowly. For  $\alpha = 1$  (corresponding to values of  $H$  of about 6,000 and 22,000 for nickel and iron),  $f(\alpha) = 0.7$ , still well below the value unity corresponding to the theoretical value when magnetic interactions are neglected. To test the new relations measurements were made by Néel on a thin wire of pure nickel subjected to a thorough annealing treatment in carefully purified hydrogen. An almost exactly linear variation of  $I$  with  $1/H^2$  was found over a field range from about 150 to 750 oersteds. The value found for  $b$  was little more than half that given by Polley's results (290 as compared with 550); over the range covered the mean value of  $f(\alpha)$  is about 0.515, so that, with the new formulae, there is entirely satisfactory agreement between the value of  $K_4$  derived from measurements on polycrystalline material and that obtained directly. The higher values of  $b$  found earlier (which, with an erroneous theoretical formula, fortuitously gave satisfactory values of  $K_4$ ) are tentatively attributed by Néel to residual strains or other imperfections in the specimens used.

In a related paper dealing with the  $a/H$  term, and also describing work virtually completed in 1945, Néel (1948 a) points out that no mechanism involving perturbing forces can give rise to a rigorous law of this type, which implies an indefinitely large work of magnetization. This rules out most of the suggestions that have been made, including those of Brown (1940 b, 1941), whose study of the effect of point, line and plane concentrations of force, or, less formally, of dislocations, is none the less of great interest. The observed temperature variation of  $a$ ,

moreover, seems to be incompatible with an at first sight promising type of explanation in terms of the statistical equilibrium of small domains, treated as molecules of large permanent moment (Stoner 1936). Néel examines both theoretically, and, with Lorin, experimentally, another possibility: that the effect may arise from the presence of cavities or non-ferromagnetic inclusions. The average state of magnetization is determined by the applied field and the internal fields due to the cavities. As in his development of a general theory of coercivity (§ 4(ii)), and the treatment of the effect of the magnetic interaction between crystalline grains on the approach to saturation, Néel makes ingenious use of the Fourier representation of an irregular distribution of spontaneous magnetization. Writing  $v$  for the volume concentration of cavities (or non-ferromagnetic inclusions)  $I_m$  for saturation magnetization of the ‘porous’ aggregate (so that  $I_m = (1-v)I_0$ , where  $I_0$  is the saturation magnetization of the ferromagnetic itself), and putting

$$\alpha = H/4\pi I_m, \quad \dots \dots \quad (4.21)$$

Néel’s final expression for the approach to saturation may be put in the form

$$1 - (I/I_m) = \frac{v}{2(1-v)} \left[ \frac{2+3\alpha}{4(1+\alpha)^{1/2}} \ln \left\{ \frac{(1+\alpha)^{1/2} + 1}{(1+\alpha)^{1/2} - 1} \right\} - \frac{3}{2} \right]. \quad \dots \dots \quad (4.22)$$

For large values of  $\alpha$ , the limiting form of the expression in square brackets is  $(2/15)\alpha^{-2}$ , so that eventually the approach to saturation is linear in  $1/H^2$ . For iron, however, this would hold only in very high fields, and over a range from a few thousand to fifty thousand oersteds the variation is nearly linear in  $1/H$ . Measurements were made on specimens of porous iron, prepared from iron powder, and of densities ranging from about 7.2 to 4.9. For fields above about 1,000 oersteds the agreement with the theoretical expression is extremely good. It may be noted that over the wide range nearly linear in  $1/H$  the coefficient  $a$  increased with decreasing density from about 50 to 300. There can be little doubt that the long-standing problem presented by the  $a/H$  term first given by Weiss as long ago as 1910 in an empirical expression for the approach to saturation has at last, in principle, been satisfactorily resolved. This does not mean that a physical explanation of the magnitude of the hardness coefficient,  $a$ , found for any particular material can immediately be given; but the direction in which to look is now clear.

*Remanence.* On the implicit assumptions that magnetic interaction between the individual crystals may be neglected, and that the change from saturation to remanence occurs only by reversible rotational processes, Gans calculated the remanence of random aggregates of crystals of the iron, nickel and cobalt types in the paper (1932) to which reference has been made above. Writing  $j_r$  for  $I_r/I_0$ , the results, which do not appear to be widely known, are as follows:

(a) For cubic crystals with cube edges as easy directions (e.g. iron),

$$j_r = (3/\pi)2^{1/2} \tan^{-1} 2^{-1/2} = 0.8312.$$

(b) For cubic crystals with cube diagonals as easy directions (e.g. nickel),

$$j_r = 3^{1/2}/2 = 0.8660.$$

(c) For hexagonal crystals with the hexagonal axis as the easy direction (e.g. cobalt),

$$j_r = 0.5.$$

The value under (c),  $j_r = \frac{1}{2}$ , would apply quite generally for randomly orientated crystals with a single easy axis of magnetization, such as might arise even in cubic crystals as a result of stresses. For aggregates with preferential orientations the reduced remanence might have any value from zero to unity, as illustrated by the curves of Figure 4.3. For unstrained cubic crystals, with  $K_4$  positive, the values of the remanence for special orientations are indicated by Figure 2.1 (see also I, pp. 57, 59).

For materials under applied stress of such magnitude that  $\lambda Z$  exceeds  $K$  the experimental results are, on the whole, in good accordance with the simple theory. For example, the value of  $j_r$  for a wire under increasing tension approaches unity if  $\lambda$  is positive, zero if  $\lambda$  is negative. For annealed materials in which the state of random orientation of the individual crystals would be expected to be closely approached the  $j_r$  values differ widely. For both iron and nickel, from data collected by Bozorth (1948), the  $j_r$  values range from about 0.3 to 0.7. The values are almost invariably lower than those given under (a) and (b) above, and are usually lower than 0.5.

The effect of magnetic interactions on remanence does not appear to have been explicitly discussed, though the curve and figures given by Néel (1947 a, pp. 325, 329) indicate, in place of the  $j_r$  value of 0.5, as given under (c), the higher value 0.7. Bozorth, on the other hand, suggests that the demagnetizing field of any single domain will tend to decrease the magnetization in it by a process involving reversal of part of the domain and the formation of a boundary wall. Such a process would clearly be favoured by small values of the crystal or strain anisotropy, and Bozorth sees here a possible explanation of the very low remanence of iron-nickel and other alloys which have been well annealed and have low crystal anisotropy. It is, of course, far from clear under what circumstances the 'negative' self-demagnetizing field of a domain would outweigh the intercrystalline field, which the treatment of Holstein and Primakoff and of Néel indicates to be positive and large.

From an experimental standpoint the inadequacy of a treatment based on the assumption that only reversible rotational processes occur from saturation to remanence is not surprising. In general the descending curve is not closely retraced when the field is increased from zero (in other words, the irreversible susceptibility is an appreciable fraction of the differential susceptibility) and, connected with this, the Barkhausen effect becomes marked well before remanence is reached on the descending curve. This is clearly illustrated, for a fairly representative material, in the curves of Figure 3.18. Reversible boundary movement may, of course, also occur, and it should be mentioned that a tentative theoretical treatment has been given of the relation between the initial susceptibility and the reversible susceptibility at remanence assuming that only 90° boundaries are involved, though no clear-cut conclusions can be drawn from such comparisons with experiment as have been made (BD, pp. 160–62).

The analysis of a magnetization curve in the remanence region presents a very complex problem. A theoretical treatment based on the assumption of pure rotations does not provide a complete answer to the question of just what is taking place inside the material; but it does provide a sufficient part of the answer to point the way clearly to some of the further experimental and theoretical investigations which are required.

## 4(iv). Rotational Processes and Hysteresis

In materials which have been developed for permanent magnets (§ 5(iv)), coercivities exceeding 500 oersteds have been obtained with values of the remanence  $B_r$  exceeding  $10^4$  gauss. Such a combination of characteristics could not be accounted for in terms of domain boundary movements on the basis of the Becker-Kersten theory (nor, it may be added, on the basis of Néel's much more general disperse field theory, though this can account satisfactorily for much higher coercivities than can the earlier strain theory), and a different type of mechanism seemed to be indicated. Investigation of the alloy of approximate composition  $\text{Fe}_2\text{Ni Al}$ , which is the prototype of an important group of permanent magnet alloys, by x-ray and other methods (I, pp. 107-8) showed that high coercivity is developed by a heat treatment intermediate between that required to retain the high temperature single-phase state (quenching) and that required to give a complete breakdown into a two-phase state (very slow cooling). The suggestion made by Bradley and Taylor (1938 a, b), and generally accepted, was that the alloy then contained iron-rich 'islands', too small to be regarded as a precipitated phase in the usual sense, and the high coercivity was tentatively attributed to immense local stresses set up. In view of the suspected inadequacy of the stress interpretation, it appeared desirable to carry out a quantitative theoretical investigation of the magnetic behaviour of small particles of a ferromagnetic embedded in a non-ferromagnetic matrix. In such particles, if they are below a certain critical size, depending on shape, no domain boundaries could be formed (§ 3(iv)); they would be single-domain particles, uniformly magnetized, and change of direction of the magnetization vector could occur only by the rotational process. Preliminary calculations, made in 1939, showed that very high coercivities could arise in this way in an aggregate of single-domain, magnetically anisotropic particles. The magnitudes of these coercivities are comparable with the values earlier estimated as upper limits with magneto-crystalline or strain anisotropy, but which were regarded as physically unrealizable owing to boundary movement effects (BD, p. 110). With shape anisotropy even higher values are possible. It was not until much later that a detailed systematic investigation of the general problem could be made (Stoner and Wohlfarth 1947, 1948). In the interim, a considerable amount of work had been carried out in France on the development of iron powder materials for permanent magnets, in which Néel and his collaborators played a large part. The theoretical considerations which served as a guide in this work, as outlined in three short papers published later by Néel (1947 b, c, d), were essentially the same as those indicated above, and, although no elaborate numerical calculations appear to have been undertaken, the estimated values for certain key quantities are in good agreement with those obtained in the more detailed treatment. Further reference is made to the powder magnet work below (§ 5(iv)). Investigations by Guillaud had also shown that high coercivities could be obtained with finely divided ferromagnetic materials, and that, in the materials he studied, the effects could be attributed to single-domain particles with anisotropy primarily of magneto-crystalline origin. Guillaud's work in this field was not widely known, and even now no full account of it is generally available; but in a recent note Guillaud (1949) outlines what had been done, and gives references to his earlier publications. The basic ideas arise naturally from the outlook which was developing in 1939, and may well

have occurred to others than those mentioned. The following outline of the theoretical treatment of rotational processes in single-domain particles and of the physical bearing of the results is based on the paper of Stoner and Wohlfarth (1948), which should be consulted for further details.

Assuming first that the magnetic anisotropy is due purely to shape, it is convenient to consider a single-domain uniformly magnetized particle in the form of a prolate spheroid, for which it may be shown that  $I_0$  lies in the plane defined by  $H$  and the polar axis. The relevant part of the total energy  $E$ , equivalent here to the free energy  $F$ , is then the sum of the demagnetizing field energy  $E_D$  and the external field energy  $E_H$ . With the symbols of Figure 4.2,

$$E = E_D + E_H = \frac{1}{2} I_0^2 (N_a \cos^2 \psi + N_b \sin^2 \psi) - H I_0 \cos \phi, \quad \dots \dots (4.23)$$

where  $N_a$  and  $N_b$  are the demagnetization coefficients along the polar and equatorial axes.

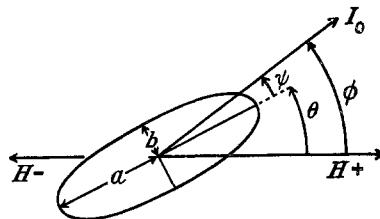


Figure 4.2. Symbols for prolate spheroid in magnetic field.

After some manipulation, an expression for the variable part of a suitably reduced energy may be obtained in the form

$$\eta = -\frac{1}{4} \cos 2\psi - h \cos \phi, \quad \dots \dots (4.24)$$

where

$$\eta = \frac{E}{(N_b - N_a) I_0^2} - \frac{1}{4} \frac{N_b + N_a}{N_b - N_a},$$

and

$$h = H / \{(N_b - N_a) I_0\}. \quad \dots \dots (4.25)$$

Information is first required as to how the angle,  $\phi$ , between the magnetization vector,  $I_0$ , and the positive direction of the field (or, more usefully, the reduced resolved magnetization,  $I_H/I_0$ , equal to  $\cos \phi$ ) varies with the field  $H$  (or the reduced field  $h$ ) for a given orientation,  $\theta$ , of the spheroid in the field. It is better, therefore, to rewrite (4.24) as

$$\eta = -\frac{1}{4} \cos 2(\phi - \theta) - h \cos \phi. \quad \dots \dots (4.26)$$

For given values of  $\theta$  and  $h$ , stationary values of  $\eta$  are given by

$$\partial \eta / \partial \phi = \frac{1}{2} \sin 2(\phi - \theta) + h \sin \phi = 0, \quad \dots \dots (4.27)$$

and these correspond to minima, points of inflection, or maxima for

$$\partial^2 \eta / \partial \phi^2 = \cos 2(\phi - \theta) + h \cos \phi \geq 0. \quad \dots \dots (4.28)$$

Although the general character of the change of  $\phi$  with  $h$  may in part be obvious physically (e.g. as  $h$  changes from a large positive value to zero,  $\phi$  changes from 0 to  $\theta$ ) the precise course of the change, and whether or not discontinuities occur, can be determined only by obtaining the solutions of (4.27) which, in the light of (4.28), are physically relevant. Analytical expressions relating  $h$ ,  $\phi$  and  $\theta$  can be derived corresponding to critical values of  $h$  at which discontinuities in magnetization occur, but in general solutions of the equation (4.27) must be obtained

numerically. Detailed numerical results for an effectively complete range of fields and orientations are given in the original paper. The general character of these results is illustrated in a physically significant form in the curves of Figure 4.3, which, with the caption, is self-explanatory.

The magnetization curve for an assembly of prolate spheroids orientated at random is shown in Figure 4.4. The integrations involved in obtaining precise numerical values for the mean magnetization for values of  $h$  from  $-0.5$  to  $-1.0$  on

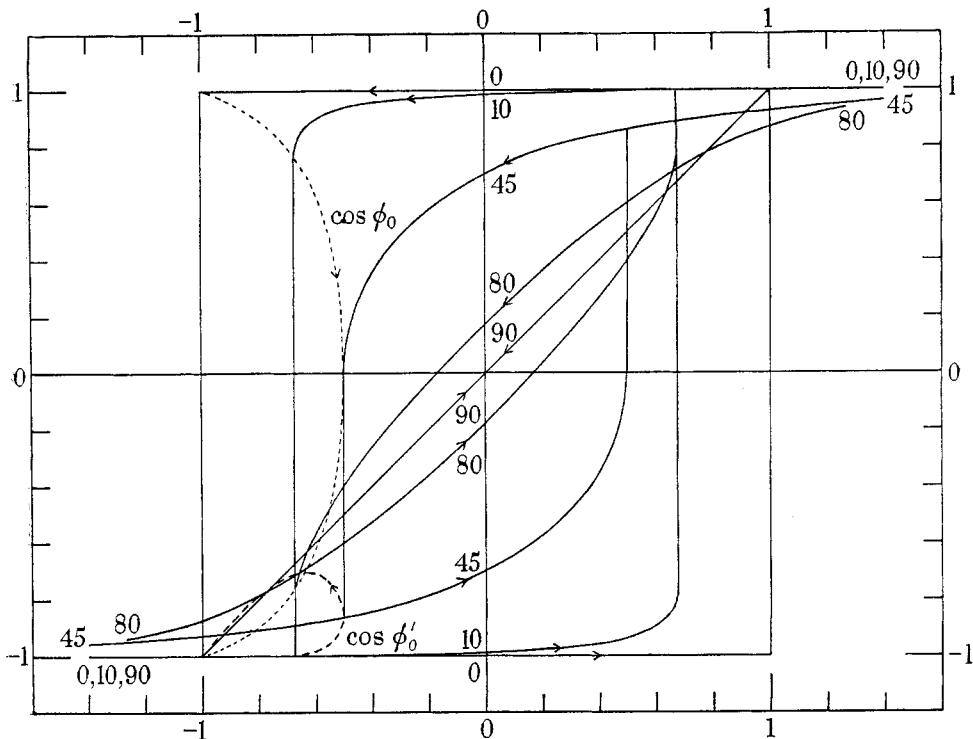


Figure 4.3. Magnetization curves for uniformly magnetized prolate spheroids.

The resolved magnetization in the positive field direction is  $I_0 \cos \phi$ . The field  $H$  is given by  $H = (N_b - N_a)I_0h$ . The angle,  $\theta$ , between the polar axis and the field is given, in degrees, on the curves. The dotted curves give  $\cos \phi_0'$  and  $\cos \phi_0$ , where  $\phi_0$  and  $\phi_0'$  are the angles made with the positive field direction by the magnetization vector at the beginning and end of the discontinuous change at the critical value,  $h_0$ , of the field. (Stoner and Wohlfarth 1948.)

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the descending curve are very troublesome. In drawing the curve of Figure 4.4 the original numerical values, at intervals of  $0.1$  in  $h$ , have been supplemented by further values, due to Rhodes (1948), at intervals of  $0.02$  over the range from  $-0.5$  to  $-0.6$ ; the discontinuity in the slope of the curve at  $h = -0.5$  is clearly shown. It is to be noted that there are no discontinuous changes on the descending (or ascending) branch of the curve until  $|h|$  exceeds the ‘mean coercivity’ value,  $|h_c| \approx 0.479$ . In Figure 4.4 the magnetization curve for an assembly of oblate spheroids is also shown. For ellipsoids in the special form of oblate spheroids there is no hysteresis, but a discontinuity in magnetization occurs at  $h=0$ . As the field decreases through zero, the magnetization vector can leave the plane defined by the field and the polar axis, and rotate through  $180^\circ$  in the

equatorial plane from the equilibrium direction appropriate to a small positive field to that appropriate to a small negative field. For the general ellipsoid the relations, which have been considered in less numerical detail, are very complicated, but it is clear that the mean magnetization curves would be intermediate between those for prolate and oblate spheroids.

The initial curve for the prolate spheroid assembly shown in Figure 4.4 is the mean of the ascending and descending branches of the hysteresis curve. It corresponds to a definite initial demagnetized state in which, for spheroids orientated within any angular range, the magnetization vector for one half is along the polar axis in one sense (e.g.  $\phi = \theta$ ), and for the other half in the opposite sense ( $\phi = \pi + \theta$ ).

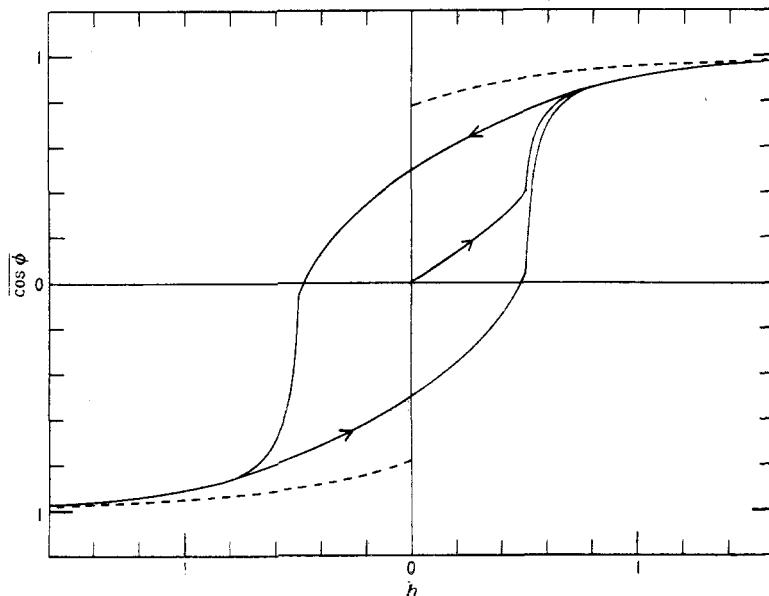


Figure 4.4. Magnetization curves for prolate (full curves) and oblate (broken curves) spheroids orientated at random.

The mean resolved magnetization per spheroid in the positive field direction, or the resultant magnetization in this direction of the assembly, is proportional to  $\cos \phi$ .  $H = (|N_b - N_a|)I_0 h$ .

(After Stoner and Wohlfarth 1948, and Rhodes 1948.)

If the anisotropy of the particles is due entirely to shape, then, from (4.25), the maximum coercivity, corresponding to  $h=1$  (see Figure 4.3), for prolate spheroidal particles orientated parallel to the field is equal to  $(N_b - N_a)I_0$ . For random orientation of the particles, the 'mean coercivity',  $h_c = 0.479$ , corresponds to a value of  $H_c$  a little under half as great. The upper limit of  $N_b - N_a$  for needle-like particles is  $2\pi$ . Thus the upper limit to coercivity due to shape anisotropy is

$$(H_c)_{\max} = 2\pi I_0, \quad \dots \quad (4.29)$$

giving values of about 11,000, 3,000 and 9,000 for iron, nickel and cobalt respectively. These are extreme values, but the values are high even for comparatively slight deviations from a strict spherical form; for a dimensional ratio as low as 1.2, for example, the corresponding values of  $(H_c)_{\max}$  are about 1,530, 430 and 1,260. It should be noted that if the particles are embedded in a non-ferromagnetic matrix,  $I_0$  is the saturation intensity for the material of the particles,

not the mean value for the aggregate. The field, in all the relations, is that 'applied to' the particle, and this may differ significantly from the field acting on the specimen containing the particles, whether before or after 'correction' for the demagnetizing field of the specimen as a whole; in applications it is essential that this should be taken into account (cf. Néel 1947 c, Weil 1947).

The basic equation (4.27) has been derived with specific reference to shape anisotropy. Precisely the same equation is obtained for spherical particles subject to tension (for  $\lambda$  positive) or compression ( $\lambda$  negative), and for which the magneto-strain anisotropy is of the type corresponding to the energy expression (cf. (3.19), (4.1))

$$E_Z = \frac{3}{2}\lambda Z \sin^2 \psi, \quad \dots \dots (4.30)$$

the relation between  $H$  and  $h$  then being

$$H = (3\lambda Z/I_0)h. \quad \dots \dots (4.31)$$

Without considering the physical question of how such magneto-strain effects might arise, it may be noted that, with  $Z$  expressed in kg.mm<sup>-2</sup>, the values of  $(H_c)_{\max}/Z$  are about 3, 30 and 4 for iron, nickel and cobalt respectively. With the mechanism under consideration very high coercivities could, therefore, hardly be accounted for primarily in terms of magneto-strain effects for particles of iron or cobalt; these effects may, however, be of great importance for nickel particles.

Magneto-crystalline anisotropy of the type corresponding to the energy expression (cf. (2.2))

$$E_K = K \sin^2 \psi \quad \dots \dots (4.32)$$

again leads to equation (4.27), with the same consequential results, but with the relation between  $H$  and  $h$  now given by

$$H = (2K/I_0)h. \quad \dots \dots (4.33)$$

For cubic crystals with magneto-crystalline energy expressions of the type of (2.1) the field-orientation-resolved magnetization relations, which would be much more complex than when the anisotropy is of the uniaxial type, have not been investigated in detail. For iron, however, for which the anisotropy coefficient  $K_4$  is positive, the maximum coercivity is the same as that derivable from (4.33), namely  $(H_c)_{\max} = 2K/I_0$ . For iron and cobalt the values indicated for  $(H_c)_{\max}$  are about 500 and 6,000, and for nickel the value is hardly likely to exceed 200.

For aggregates containing iron particles, coercivities appreciably exceeding 500, such as have been obtained with iron powder magnets (Néel 1947 b), must almost certainly be attributed to shape anisotropy. Analyses of Guillaud's results on the compound MnBi by Kittel (1948), and of those on Mn<sub>2</sub>Sb by Guillaud (1949), show that here the high coercivities are connected with magneto-crystalline anisotropy. In most cases, however, definite conclusions cannot be drawn as to the type of anisotropy primarily involved purely from a consideration of the magnitudes of the observed coercivities. Further investigations are necessary, among which it is obvious that an examination of the temperature variation of the coercivity, such as has been made by Weil *et al.* (1947, 1948) for some of the powder magnet materials, may be of great value (see § 5 (iv)).

The three types of materials to which the treatment outlined seems to be particularly relevant are, as indicated in the original paper, (a) metals and alloys containing ferromagnetic impurities, (b) powder magnets, and (c) high coercivity

alloys of the dispersion hardening type. It is clearly impossible to discuss the various materials *in extenso* here, though reference will be made to some of them below (§5(ii), (iv)). It may perhaps be appropriate to draw attention to an interesting application of the general ideas to the interpretation of the characteristics of magnetic recording wire (Hobson and Osmond 1948). The most frequently used wire material is chromium-nickel stainless steel which, after the cold working and heat treatment found appropriate, has a coercivity of the order of 500, and contains ferromagnetic ferrite particles dispersed in a non-ferromagnetic austenitic matrix. From a determination of the relative amount of ferrite present, and an examination of the range of undistorted amplitude and frequency response, Hobson and Osmond have made estimates, admittedly rough, of the mean lengths and cross sections of the ferrite particles. The ratio of length to diameter is found to be about 10, and the diameter about  $10^{-5}$  cm. or less. These values are completely consistent with the theoretical estimates (§3(iv)) of the particle sizes below which boundary formation cannot occur. Probably the most extensive field of application of the theoretical treatment is to dispersion hardening alloys, and the survey made of the earlier work on these alloys left little doubt as to the value of the new approach to the interpretation of the magnetic characteristics. Most of these alloys, however, are extremely complex, and, in general, there is little likelihood of being able to explain their magnetic properties in terms of one type of elementary process. The possibilities and limitations of explanations in terms of rotational processes in single-domain particles will become clearly apparent only when much further experimental work has been carried out on these remarkable alloy systems.

It may finally be remarked that the single-domain particle mechanism is not so sharply distinct in character from other mechanisms which have been considered (§4(ii)) as may at first appear. If the particles were larger than those considered, domain boundary formation would occur within them, and the behaviour of the particles, or segregates, would become similar to that of ferromagnetics in bulk. A clear-cut simplicity is given to the theoretical treatment by limiting it to single-domain particles, a limitation which appears to correspond closely to the physical conditions in many types of materials characterized by high coercivity. Sharply defined particles, however, correspond to an extreme form of fluctuation in composition, with the associated fluctuation in magnitude of the intrinsic magnetization, and the disperse fields which are consequentially developed are here the demagnetizing fields of the particles themselves. It may be noticed that the importance of purely magnetostatic effects, the recognition of which has already been mentioned as characterizing so much of the more recent theoretical work on ferromagnetism, is again very evident in the whole of the treatment of hysteresis associated with rotational processes in single-domain particles.

#### 4(v). Magneto-thermal Effects

The magneto-thermal effect to be discussed here is the change of temperature accompanying a change of field applied to a ferromagnetic under adiabatic conditions. It is often convenient to consider, instead of the change of temperature,  $\Delta T$ , the corresponding 'heat developed',  $\Delta Q'$ , per unit volume of the material, related to  $\Delta T$  by

$$\Delta Q' = C\rho\Delta T, \quad \dots\dots (4.34)$$

where  $C$  is the specific heat and  $\rho$  the density. By far the best known of all magneto-thermal effects is the heat developed, commonly known as the hysteresis loss, when a ferromagnetic is taken through a magnetization cycle. This loss may be accurately determined by well-known methods, although the actual temperature change for a single cycle is usually very small, of the order of  $10^{-4}$  deg. c. for soft magnetic materials. It is hardly necessary to discuss hysteresis loss as such here, for although it is, technologically, an important characterizing magnitude for certain types of material, it is clearly not a primary characteristic. It is sufficient to recall that it may be determined from the area of an  $I, H$  or  $B, H$  loop, and that it corresponds to the aggregate of the irreversible thermal changes as the cycle is traversed. In contrast to the irreversible changes contributing to the hysteresis loss, the changes of temperature with field in high fields are purely reversible. The temperature change may be small at room temperature, but in the Curie point region changes of more than  $1^\circ$  are observed in nickel, and more than  $2^\circ$  in iron for field changes of the order of  $10^4$  oersted. These temperature changes may be associated with changes in intrinsic magnetization (I, pp. 50, 77, 81), and the effect is essentially similar in origin to that utilized in obtaining very low temperatures by the adiabatic demagnetization of paramagnetic salts. The main experimental investigations are those of Weiss and Forrer (1926) on nickel, and of Potter (1934) on iron, and theoretical discussions of the results are given by these authors and also by Stoner (1936). The high-field effect is not distinct in character from that in lower fields, and it is misleading to refer to it, as is sometimes done, as *the magneto-caloric effect*.

In low and moderate fields the change of temperature with change of field is, like the change of magnetization, far from linear. The difficulty of investigating the adiabatic temperature changes in these fields is that if any detailed information is to be obtained as to the course of the changes as the magnetization curve is traversed, the field changes must be made in small steps; the changes in temperature to be measured are then small fractions of the extreme range of the temperature change, which itself is often much less than  $10^{-3}$  deg. Since the pioneer work of Adelsberger (1927), the experimental methods have been refined, and measurements made on representative materials by Constant (1928), Honda, Okubo and Hirone (1929), Ellwood (1930), Townsend (1935), Okamura (1936) and Hardy and Quimby (1938). More recently comprehensive investigations, surveyed in a lecture by Bates (1949), have been made on iron, nickel and cobalt and a number of alloys by Bates with Weston (1941), Healey (1943), Edmondson (1947) and Harrison (1948 a, b). The experimental arrangements which have been adopted differ in such things as the form of the test sample (single specimen, or built-up multiple specimen), the number and manner of attachment of the thermocouples, the way of connecting them to the galvanometer, and the method of calibration. For convenience and range of applicability a single specimen method is much to be preferred. In the method developed by Bates (1941), the specimen is a rod or stout wire; to this is attached one junction of each of some twenty thermocouples, the other junction being close to, but thermally insulated from, the rod; each couple is in series with its own primary on a mu-metal spiral core, and the low-resistance secondary of many turns is in series with a specially designed galvanometer. The overall sensitivity obtained by the different workers is much the same, ranging from about 200 to 900 erg.cm<sup>-3</sup> per scale division (100 erg.cm<sup>-3</sup> corresponds, for iron, to  $2 \cdot 8 \times 10^{-6}$  deg.), and it.

seems not improbable that the consistency and reliability of the results obtained depend much more on meticulous attention to details in avoiding or eliminating ‘spurious’ effects than on the more obvious features of the different methods. An objective test of the reliability of the results is provided by a comparison of the hysteresis loss from the measured heat developed in traversing a cycle, and from the area of the hysteresis loop. In the work of Bates, and of Hardy and Quimby, the agreement is remarkably close, usually within a few per cent.

Examples of the experimental results are shown in the curves labelled  $Q'$  in Figures 4.5 and 4.6. These curves give the heat developed in traversing the ascending branch of a hysteresis loop. The aggregate heat developed is half the hysteresis loss. It is to be noticed that the  $Q'$  curve for iron (Figure 4.5) is completely different from that for cobalt (Figure 4.6). There is a remarkable diversity in the course of the temperature changes for different materials, as shown in the many curves given by Bates and his collaborators. (If the curves given by different investigators are examined, an equally remarkable diversity is sometimes apparent for effectively the same material, which may suggest that little significance can be attributed to any of these results; but it may be said at once, without implying that all, or even most, of the earlier results are unreliable, that there is no doubt of the substantial accuracy of the results obtained in the work of Bates and of Hardy and Quimby.) Although consideration has been given to the interpretation of the experimental results in some of the papers referred to (e.g. Bates and Weston 1941) and elsewhere (BD. pp. 267–70), the first detailed quantitative theoretical treatment of the analysis of the magneto-caloric data is that recently given by Stoner and Rhodes (1949).

Four interrelated questions have been discussed. The first is how far the ‘magneto-caloric properties’ of a material may be coordinated with other properties, known or determinable from experiment, involving essentially a thermodynamic treatment. The second is that of the magneto-thermal characteristics of the various elementary magnetization processes, boundary movement, rotation, and change of intrinsic magnetization, which requires consideration of the ‘atomic’ character of the processes. The third is the application of the general principles to the analysis of the experimental results, that is the determination, as far as may be possible, of just what sequence of elementary processes underlies the observed sequence of temperature changes. The fourth is the question of whether, or to what extent, new or supplementary information might be obtained about the processes occurring as the magnetization changes, which could not be obtained, or not obtained so readily, in other ways. It is possible here to indicate only a few particular points in the treatment, more particularly some of those immediately relevant to the third of the above questions. It may perhaps first be mentioned that the thermodynamics of magnetization often appears extremely involved when it is approached via the relations for a completely general electromagnetic system (Guggenheim 1936, Lives 1945–48); the very simple treatment which is possible when the ‘system of interest’ is particular magnetizable material in an external magnetic field (Stoner 1935, 1937) is, however, all that is required in the present connection.

The basic equation defining an internal energy function,  $E$ , referred to unit volume, of a body in a magnetic field may be taken as

$$dE = dQ + H dI, \quad \dots \dots (4.35)$$

where  $dQ$  is the heat transferred to the body. For an adiabatic change  $dQ$  is zero. A change in internal energy,  $\Delta E$ , may be divided into two parts, one associated with change of temperature,  $\Delta E_T$ , measured directly by the heat developed,  $\Delta Q'$ , given by (4.34), and the other with change of magnetization,  $\Delta E_M$ . The 'magnetic' energy change is then given by

$$\Delta E_M = \Delta E - \Delta E_T = \int H dI - \Delta Q', \quad \dots \dots (4.36)$$

a relation which has been widely used in the presentation of the experimental results. The equations (4.35) and, for adiabatic changes, (4.36) apply whether or not the changes are reversible; they involve only the first law of thermodynamics. If the changes are reversible, the internal energy function satisfies the relation

$$dE = T dS + H dI, \quad \dots \dots (4.37)$$

where  $dS$  is the change of entropy. Other thermodynamic functions can then be obtained in the usual way, and among the numerous thermodynamic relations which may be derived, the most important, in the present connection, is

$$\left( \frac{\partial T}{\partial H} \right)_S = - \frac{T}{\rho C_H} \left( \frac{\partial I}{\partial T} \right)_H, \quad \dots \dots (4.38)$$

or, using (4.34),

$$dQ' = -T(\partial I/\partial T)_H dH. \quad \dots \dots (4.39)$$

By these equations the change in temperature (or in heat developed) with change of field under isentropic conditions is related to the change of magnetization with change of temperature at constant field. The equations may be applied not only in correlating the immediate observations, where only reversible changes are involved, but also in dealing with the magneto-thermal characteristics of particular types of elementary magnetization process.

Considering only the effects associated with changes in intrinsic magnetization, and changes due to rotations of the magnetization vectors, it is found, by a somewhat lengthy argument, that the heat developed is given by

$$\Delta Q' = a \int d(IH) + b \int H dI, \quad \dots \dots (4.40)$$

where

$$a = -\frac{T}{I_0} \frac{dI_0}{dT}, \quad b = \frac{T}{k} \frac{dk}{dT},$$

$I_0$  being the spontaneous magnetization (or, sufficiently closely, the saturation magnetization) and  $k$  the modulus of the effective anisotropy coefficient. Since  $dI_0/dT$  and  $dk/dT$  are, in general, both negative,  $a$  and  $b$  are of opposite sign. Increase of intrinsic magnetization is accompanied by a positive contribution to the temperature change on adiabatic magnetization, increase of magnetization due to rotation of the magnetization vectors against the anisotropy field by a negative contribution. An 'explanation' of the first effect, which is satisfactory in principle if not in quantitative detail, can be given in terms of the atomic theory of intrinsic magnetization (I, pp. 65-78); any such explanation of the second effect is at present little more than speculative owing to the incomplete state of development of the atomic theory of anisotropy (§ 2(iv)). The first term in (4.40) is a generally valid expression for the heat developed owing to changes in intrinsic

magnetization, and the coefficient  $a$  is known with reasonable accuracy at least for the ferromagnetic elements. The second term is valid only over reversible ranges of magnetization. If the material consists of an aggregate of effectively unstrained crystalline grains, the value of  $b$  can be estimated to the degree of accuracy with which the magneto-crystalline anisotropy coefficients and their temperature coefficients are known, but from the account given earlier (§ 2(ii)) it is clear that even in the most favourable cases the ideal magnitude of  $b$  is much more uncertain than that of  $a$ . If the crystal grains are strained, the values of

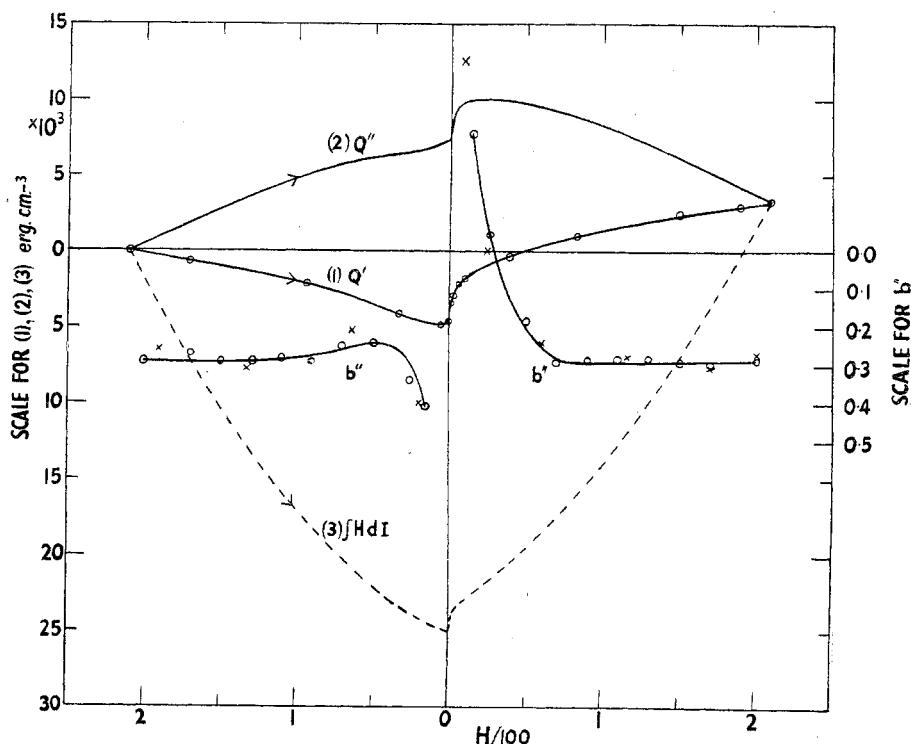


Figure 4.5. Magneto-caloric effect in annealed Armco iron.

Data for curves (1) and (3) from Hardy and Quimby (1938).

$Q'$ , heat developed. ( $\Delta T \approx 2.8 \times 10^{-8} \Delta Q'$ )

$Q''$ , heat developed less than due to change in intrinsic magnetization.

$b''$ ,  $\Delta Q''/\Delta \int H dI$ . Circles, values derived from smoothed curves; crosses, values from experimental points. (Stoner and Rhodes 1949.)

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$k$  and  $b$  are modified, but it would be difficult to determine the magnitude of the modification for, say, a given average value of a tensile or compressive stress, even if the necessary basic data were available. For nickel, for which measurements on the temperature variation of the saturation magnetostriction have been made (Döring 1936), a very rough calculation indicated that for a stress of  $1 \text{ kg.mm}^{-2}$  there would be an increase in the effective value of  $k$  and a decrease in that of  $b$  by about a quarter. The relative effect would be smaller for iron and cobalt, for which the magneto-crystalline anisotropy coefficients are larger.

It is now appropriate, before considering other magnetization processes, to turn to the experimental results. A convenient procedure is to express the experimentally observed heat developed in the form

$$Q' = a \int d(IH) + \int b'' H dI, \quad \dots \dots (4.41)$$

where the  $\Delta$  is dropped in the interest of economy of symbols, the first term on the right is the same as that in (4.40), and  $b''$  is to be regarded as a possibly variable coefficient to be determined from the experimental results. Denoting the heat

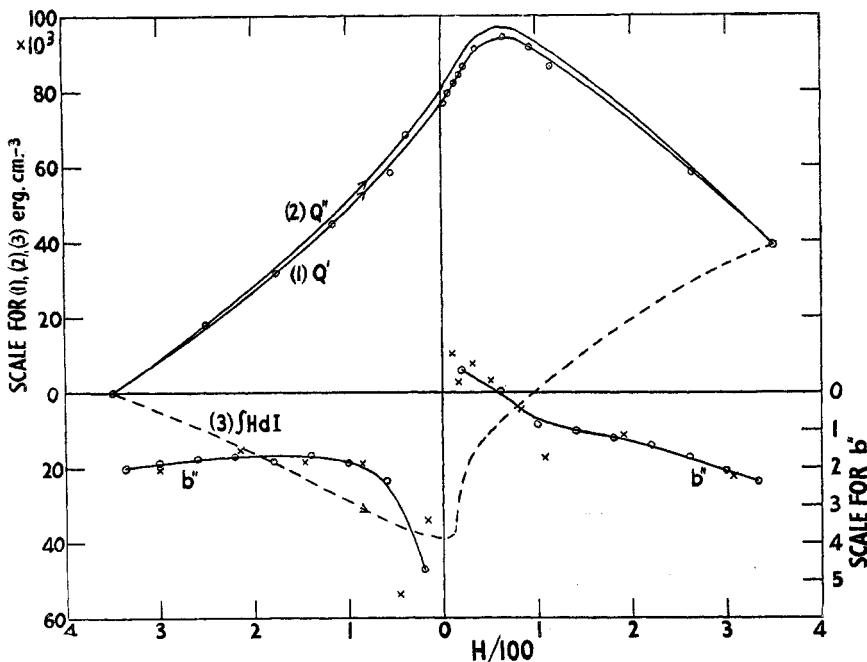


Figure 4.6. Magneto-caloric effect in annealed cobalt.

Data for curves (1) and (3) from Bates and Edmondson (1947).

For symbols, see Figure 4.5. ( $\Delta T \approx 2.6 \times 10^{-8} \Delta Q'$ ). (Stoner and Rhodes 1949.)

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developed additional to the reasonably accurately calculable part due to change in intrinsic magnetization by  $Q''$ ,

$$Q'' = Q' - a \int d(IH) = \int b'' H dI. \quad \dots \dots (4.42)$$

Curves showing  $Q''$ , and  $b''$  as obtained from (4.42) are given in Figures (4.5) and (4.6) for iron and cobalt respectively. A perhaps unexpected point which is brought out by the calculation of the coefficients  $a$  and  $b$  in (4.40) is that, although the change in intrinsic magnetization in low and moderate fields may be negligible in its contribution to the change in apparent magnetization, the associated contribution to the magneto-caloric temperature change may be relatively large. The contribution to the heat developed is given by the difference between the  $Q'$  and  $Q''$  curves, and it is apparent from Figure 4.5 that for annealed iron the absolute value of this contribution exceeds the absolute value of the aggregate

effect. In cobalt, in contrast, the intrinsic magnetization contribution is relatively small ( $dI_0/dT$  is some five times smaller than for iron). When allowance is made for the intrinsic magnetization effect, the residual  $Q''$  curve bears a similar quasi-symmetrical relation to the  $\int H dI$  curve in both cases.

For iron, the values of  $b''$  for the larger fields are fairly constant at about  $-0.3$ . This agrees as to order of magnitude with the rather uncertain estimated value, from (4.40), for the rotational effect in completely strain-free polycrystalline material of about  $-0.6$ . For cobalt the numerically much higher value of  $-2.0$  for  $b''$  (Figure 4.6) again agrees as to order of magnitude with the estimated value of  $-1.3$  for  $b$ . It is the agreement as to order of magnitude between the observed and calculated values which should be stressed at this stage rather than the numerical discrepancies, though these may later prove to be significant. At present no definite conclusion can be reached as to whether they are due wholly or in part to errors in the magneto-caloric measurements themselves, to shortcomings in the basic data from which the theoretical values of  $b$  are derived, to the effects of residual stresses in the annealed materials, or to the occurrence of processes other than rotations and changes in intrinsic magnetization even in the higher fields.

In the lower field regions there is no question of constancy of the  $b''$  values. The form of the curve, with the marked decrease as zero field is approached, the discontinuity, and the subsequent decrease from a high value to approximately the same value as initially, brings out in a very striking way the effect of those processes not taken into account in the derivation of (4.40). It is, in fact, possible to account qualitatively for the course of the curve in the low field region in terms of the irreversible processes which are there superposed on the reversible processes. In the original paper the magneto-thermal characteristics of irreversible (and also reversible) boundary movement processes are considered in some detail. As far as the analysis of the experimental  $Q'$  curves are concerned, however, it is concluded that little further progress is possible until a clear-cut separation can be made of irreversible and reversible effects along the course of a magnetization curve. To this end, the most practicable method appears to be by measurements of the reversible susceptibility along the initial and cyclic magnetization curves over a range of temperatures. From the temperature variation of reversible susceptibility, conclusions might be drawn, using the appropriate thermodynamic relations, as to the magneto-caloric temperature changes associated with the reversible processes, and by subtracting these from the total observed changes, the course of the contributions from irreversible processes could in principle be determined. In recent years comparatively few detailed experimental studies of reversible susceptibility have been made, the most extensive being those of Kirkham (1937) and Kahan (1938). The usual methods of measurements are, however, extremely tedious, and it is hoped that a new rapid oscillographic method developed by Tebble and Corner (1950) will greatly facilitate studies of this kind. It is, of course, essential, particularly in dealing with low field properties, that specimens as nearly as possible of magnetically identical material should be used in related investigations.

With regard to irreversible processes it is perhaps worth while to state that the mere fact of their being irreversible does not necessarily mean that no information can be derived theoretically about their thermal characteristics. If the mechanism of the process is known (the relevant information might be conveyed by curves similar to that in Figure 4.1(a)) the thermal effects can in

principle be calculated. Thus, precise calculations have been made of the energy changes and thermal effects associated with the sequence of reversible and irreversible processes along the theoretical magnetization curve of Figure 4.4 (Rhodes 1948). In general, for actual ferromagnetics, far too little is known about the mechanism or the sequence of the irreversible processes for any theoretical calculation of the associated thermal changes to be possible.

In summary, the reversible temperature changes accompanying adiabatic magnetization, which usually play a larger part in determining the general overall form of the experimental curves (the  $Q'$  curves) than the irreversible changes, can be accounted for, in the main, as arising from a superposition of two effects, of opposite sign, one associated with rotational changes, the other with changes in intrinsic magnetization. In cobalt (Figure 4.6) the rotational effect predominates; in some of the alloys studied by Bates and Harrison (1948 a), such as monel metal, with a Curie point not greatly above room temperature, the relatively very large temperature changes, opposite in sign to those in cobalt, are almost entirely due to the intrinsic magnetization effect. In iron and nickel, the magnitudes of the two effects are comparable, and the aggregate effect is small; moreover, since it corresponds to a difference between two numerically larger quantities, relatively large differences may be found in the curves for particular materials subjected to not widely different thermal and mechanical treatments. Although the general features of these curves are now better understood, it cannot be said that any of the curves have been accounted for in quantitative detail. There are two main requirements for further progress in the analysis of these curves: the first is the unambiguous separation of the reversible and irreversible effects, the second the accurate determination of the basic magnetic characteristics of the materials under investigation. If these two requirements could be more nearly met, far more information could be derived from the study of magneto-caloric effects than is at present possible, not only about rotational changes and changes in intrinsic magnetization, but also about boundary movements, and possibly even about boundary formation. The successful surmounting, in recent experimental work, of the many difficulties in the way of obtaining reliable measurements of the very small temperature changes in low and moderate fields is a considerable achievement. It has opened up a new and potentially most valuable method of attack on the numerous unsolved problems which are encountered whenever an attempt is made to give a detailed analysis of magnetization curves.

## § 5. MAGNETIC MATERIALS

### 5 (i). *Introductory*

It is obviously impracticable in a report of this kind to present in any detail the information which has been obtained in recent years in investigations of the low- and moderate-field characteristics of innumerable ferromagnetic materials. Moreover, a partial compilation of data in tabular form, such as might have been included, would serve little useful purpose, when full compilations of data on magnetic materials generally, and on particular types of material, are readily available. A very large proportion of the time and effort given to research in the general field with which this report is concerned is, however, occupied with the study of the magnetization curves of particular materials. Further, the value of the more fundamental experimental and theoretical investigations discussed in

preceding sections lies, in large part, in their relevance to the whole range of ferromagnetic materials. It seems desirable, therefore, to draw attention in the text, as is done below, to some of the books and articles in which fuller information is collected together, and also at least to 'introduce' some of these interesting materials and the problems which arise in connection with them. Accordingly, after a survey of the general field, with particular reference to the interrelation between what may be called the scientific and technological approaches (§ 5 (ii)), a hurried glance is taken at some of the more recent work on a few illustrative materials falling in the categories loosely described as magnetically soft (§ 5 (iii)) and magnetically hard (§ 5 (iv)).

The 'primary' information about magnetic materials is widely scattered in scientific and technological journals, in technical reports (usually restricted in circulation, and often, in varying degrees, 'confidential'), and in patent specifications. The secondary sources, in the form of books, review articles, and reports of conferences are, therefore, almost indispensable as guides; it may be remarked, too, that the term 'secondary', as applied to them, often does less than justice in its implications. In seeking for information about particular materials, almost invariably, except of course where very recent papers are required, the approach may most expeditiously be made via one or other of these secondary sources. The books and articles mentioned below are included in the references at the end of this report.

Books dealing primarily with ferromagnetic materials are those of Messkin and Kussmann (1932) on the ferromagnetic alloys, the monumental compilation on iron and its alloys by v. Auwers (1938) in *Gmelins Handbuch*, and the short but most informative book by Brailsford (1948). Mention may also be made of a forthcoming book by Hoselitz (1950). The book by Snoek (1947) on recent work in Holland on ferromagnetic materials is naturally much narrower in its scope, but it is particularly useful for the account given of the ferrites. Bitter's *Introduction to Ferromagnetism* (1937) contains a long chapter contributed by Yensen on magnetic materials and their preparation, and Becker and Döring's *Ferromagnetismus* (1939) includes a substantial section (pp. 382–435) on technical magnetic materials and their application. Most of the more general books on magnetism (e.g. Stoner 1934, 1948) have sections on ferromagnetic materials.

Among the more comprehensive review articles dealing with ferromagnetic materials generally are those of Kussmann (1935, 1939) and Webb (1938). Soft materials are surveyed by Yensen (1939, 1948), and hard by Hoselitz (1946). A recent most valuable review of progress on magnetic materials by Brailsford *et al.* (1948) contains sections on electrical sheet steels (Brailsford 1948), permanent-magnet materials (Oliver and Hadfield 1948) and magnetic powder cores (Polgreen 1948). Finally, a very clear and concise account of magnetic materials is given in an Encyclopaedia article by Bozorth (1947). All the above articles include compilations of data in tabular form, diagrams of magnetization curves and associated characteristics of the materials, and, except the last, extensive references.

### § 5 (ii). General Survey

*Technological requirements.* This survey may appropriately be opened by a few remarks on points connected with the technological application of ferromagnetic materials. Most of the work on the preparation of these materials, and on the measurement of their magnetic properties, unlike the corresponding work on

dia- and paramagnetics, has been stimulated, directly or indirectly, by technological requirements. Even a slight acquaintance with the technological background leads to some understanding of the unevenness of distribution over the range of ferromagnetic materials of the vast amount of information which has been accumulated, of the diversity in scientific quality of this information, and of the scientifically unrevealing form in which it is not infrequently presented; at the same time it may lead to a greatly enhanced appreciation of achievements which might be entirely overlooked in a too purely scientific approach to work in this field.

Varied in application though magnetic materials are, their immediate purpose, whether in heavy electrical machines, in transformers large or small, in communication and in general electronic equipment, in electromagnets or in permanent magnets, is to produce magnetic flux more conveniently and more economically than is possible with currents alone. The economic factors are complex, and it is sufficient to note here, with regard to initial costs, that iron is much cheaper than nickel, and nickel than cobalt, so that, other things being approximately equal, preference would be given to materials containing iron as the main constituent. With regard to running costs (leaving aside permanent magnets, whose running costs would ideally be zero), these are less, in 'copper losses', the smaller the applied field necessary to produce the required induction, i.e. the higher the permeability over the relevant range; and when changing, and in particular alternating, fields are involved, they are less, in 'iron losses', the smaller the magnetic hysteresis and eddy current heating.

An upper limit to the induction in the material, and roughly to the external field, due to the ferromagnetic material itself is  $4\pi I_0$  (the maximum value of the 'ferric induction') which has values of about 21,600, 6,100 and 17,840 for iron, nickel and cobalt respectively. (It may be noted in passing that there is little purpose in using an iron core in electromagnets for fields much larger than 25,000 oersteds, say for fields of the order of  $10^5$  oersted, for most of the field must be produced directly by currents. Air core coils are used with heavy currents of short duration (Kapitza) or, for continuous fields, with elaborate cooling arrangements (Bitter).) A fair relative measure of the potential range of application of a ferromagnetic material is therefore given by its saturation magnetization,  $I_0$ . The values of  $I_0$ , as fundamental characterizing magnitudes of ferromagnetics, have already been fully discussed (in I) in relation to elements and alloys. The value of  $I_0$  for iron is appreciably exceeded only in some of the alloys in the iron-cobalt system (cf. I, p. 92); it is the combination of high saturation intensity and very low cost which gives to iron its outstanding technological importance as the basic ferromagnetic material.

Within the limits imposed in the choice of materials by the maximum induction required, the general desiderata (except in permanent magnet materials) are low hysteresis and, over the relevant range of field or induction, high permeability. This report has largely been concerned with the fundamental factors on which these depend. The characteristic magnitudes which are important are the crystal anisotropy (directly, and also indirectly in connection with the effects of inclusions) and the magnetostriction (mainly indirectly in connection with the effects of internal stresses). Alloys give a much wider scope than the elements for obtaining suitable combinations of characteristics, mechanical and electrical as well as magnetic. For many applications their often much higher resistance than that of

pure metals is an immediate advantage in reducing eddy current losses. The use of materials in special forms or states of aggregation (e.g. laminations, 'dust' cores) should not be overlooked as a means of obtaining effective electrical and magnetic characteristics which more nearly meet particular requirements. (For a recent review of the applications of powder metallurgy to magnetic materials see Pfeil *et al.* 1947.)

*Pure iron.* The sensitivity of the low-field properties of a ferromagnetic to small disturbing influences is well brought out by the work of Yensen, extending over many years, Cioffi and others on the effect of further purification (by high temperature treatment *in vacuo*, or in a suitable atmosphere) on already pure iron, say 99.9 per cent Fe. (For general references, see § 5(i).)

Studies on very pure single crystals have been made by Cioffi, Williams and Bozorth (1937). The initial material, an almost spectroscopically pure sample of carbonyl iron, was heat treated in hydrogen at  $1,500^{\circ}\text{C}$ ., cooled to  $880^{\circ}\text{C}$ . and maintained at that temperature to permit the growth of large crystals. From the sheet a picture frame crystal (cf. § 2(ii)), approximately 1 cm. square in outside dimensions, was cut, with sides parallel to a [100] direction. Magnetization curves were obtained with this specimen after further annealing. The maximum measured permeability was  $1.43 \times 10^6$  at  $B = 17,500$ , corresponding to the attainment of 80 per cent of the saturation intensity in a field of 0.012 oersted. This is the highest permeability so far recorded. Surprisingly, the measured coercivity,  $H_c = 0.15$ , was considerably higher than values which have been obtained for less pure polycrystalline iron (cf. Bozorth 1937).

For polycrystalline iron, a maximum permeability of  $2.8 \times 10^5$  is given for hydrogen-annealed Armco iron by Cioffi (1934), but the highest values obtained in the many very pure specimens prepared and investigated by Adcock and Bristow (1935) and by Cleaves and Hiegel (1942) are about  $3 \times 10^4$  and  $9 \times 10^4$  respectively. These values are all considerably higher than the normal value of about  $6 \times 10^3$  for dynamo sheet. There are many sources of uncertainty in the determination of high permeabilities in very low fields. Moreover, although measurements of maximum permeability,  $\mu_{\max}$ , may be somewhat less uncertain than those of the initial permeability,  $\mu_0$ , the quantity itself depends on so many factors that it has no clear-cut theoretical significance. The values that have been quoted serve to show that very high permeabilities are not a prerogative of special alloys, but can occur equally in a pure, strain-free ferromagnetic element.

High initial and maximum permeabilities and low coercivity are almost invariably associated, and the values of any or all of these give a measure of what is qualitatively referred to as the magnetic 'softness' of the material. Pure iron itself, quite apart from its costliness in production, would be of very limited technological value as a magnetic material, for the magnetic softness is associated with mechanical softness and low electrical resistance, and also with defects of a chemical character. Alloying does not improve the magnetic softness; but in alloys comparable magnetic properties may be obtained much more readily than by intensive purification, and in combination with other required characteristics.

*Alloys.* Alloys are broadly classified as homogeneous (single-phase) or heterogeneous. The classification is generally convenient, but difficulties arise in connection with 'traces' of impurities. On practical grounds, Yensen (1937, p. 72) prefers to place in the heterogeneous class only alloys containing microscopically visible inclusions (of volume greater, say, than  $10^{-16}\text{ cm}^3$ ). From a

magnetic standpoint such a classification would be misleading, for the magnetic effect of sub-microscopic segregates may be enormously different from that of the same number of atoms uniformly distributed in strict solid solution. Leaving aside the various special problems which arise in this way, it may be said that over a single-phase range starting from a ferromagnetic element the variation of magnetic properties proceeds smoothly not only in respect of such basic characteristics as the saturation magnetization (cf. I), the crystal anisotropy (cf. § 2(ii)) and magnetostriction, but also in respect of the softness characteristics,  $\mu_0$ ,  $\mu_{\max}$  and  $H_c$ . Transition to a heterogeneous state (e.g. in passing a solubility limit) is in general marked by a rapid change in these latter characteristics. Little can be said that is both concise and general, however, about the low field properties of heterogeneous alloys, for these properties depend so much on the character of the phase segregation, and hence on the details of the thermal treatment to which the alloys are subjected. Each alloy raises its own complex of problems. There is little doubt that, with the advance of magnetic theory, magnetic investigations will contribute more and more towards the solution of problems which are regarded as primarily metallurgical. This is well illustrated by the work of Gerlach (1938) on the effect of different thermal treatments on the coercivity of dispersion-hardening alloys (Ni-Au, Ni-Be, Fe-Cu), and by that of Sucksmith (1939) on the saturation magnetization and its temperature variation in alloys in the iron-nickel-aluminium and other systems (cf. I, pp. 106-9) and more recently on the low field properties of a series of heterogeneous alloys (see § 5(iv)).

Among the soft magnetic materials by far the most important technologically are the iron-silicon alloys and the nickel-iron alloys (see § 5(iii)). The former alloys came into use soon after the beginning of the century, and the latter in the early twenties. The earlier, and very largely the later, 'discoveries' of alloys with good magnetic qualities are in the main due to systematic empirical investigations. It is only in comparatively recent years that 'theory', in providing at least partial explanations of known properties of particular alloys, has, to a corresponding extent, served as a guide to methods of 'improving' existing alloys, and, to a much smaller extent (since at least the economically favoured range of alloys has been well covered empirically), to the discovery of new ones. A scientific approach to this problem is well illustrated by some work of Snoek and Went (Snoek 1947, pp. 14-20). Magnetic softness is favoured by low magnetostriction and low magneto-crystalline anisotropy. In binary alloy systems there may be zero- $\lambda$  and zero- $K$  compositions, but it is unlikely that  $K$  and  $\lambda$  will be zero at the same composition. In ternary alloys the zero points become zero lines. An investigation of the course of these lines may indicate whether or not alloys of outstanding qualities in softness are likely in the ternary range. Snoek and Went investigated (or supplemented previous investigations on) the variation of  $\lambda$  and  $K$  with composition of eleven binary iron alloys in the single-phase body-centred range. A zero- $\lambda$  composition was found only in the Fe-Si system (at about 6 per cent Si by weight) and zero- $K$  compositions only in the alloys with Si, Al, Co. This suggests that coincidence of zero  $\lambda$  and zero  $K$  might occur in the ternary systems Fe-Si-Al and Fe-Si-Co. The course of the zero lines in these systems could be determined sufficiently closely by examination of a fairly small number of ternary alloys. The lines do not intersect in the Fe-Si-Co diagram, so that no alloys with unusually high permeability are to be expected in this ternary system. In the Fe-Si-Al diagram the curves intersect roughly at

the composition Fe84, Si10, Al6. It happens that the high permeability ( $\mu_{\max}$  up to  $1.6 \times 10^5$ ) and low hysteresis loss of alloys in this composition region had already been found in a most extensive investigation of this ternary system by Masumoto (1936) (the alloys, which, under the name of 'sendust', are used in powder cores, have been further investigated by Selisski and Zaimovski (1941)), so in one sense nothing new had been discovered; the newness is in the method of approach, which is of a kind which may well be more widely applied in the future. The importance of the  $\lambda$ ,  $K$  factors will be further exemplified below (§ 5 (iii)). Other factors than these are, however, involved; in the iron-silicon alloys neither  $\lambda$  nor  $K$  is unusually small.

Heterogeneity seems to be a necessary condition for magnetic hardness (essentially, high coercivity, though other characteristics are also required for permanent-magnet materials). In the martensitic carbon steels (almost universally used for permanent magnets prior to 1910), and the tungsten and chromium magnet steels, there is little doubt that inhomogeneity of internal stress is the major factor determinative of the coercivity ( $H_c$  values up to about 80) through its direct or indirect effect on the positional variation of domain boundary energy (§ 4 (ii)). In the many alloys developed from the iron-nickel-aluminium prototype since 1931, with much higher coercivities ( $H_c > 500$ ), stress and inclusion effects may be involved, but it seems probable that the single-domain mechanism (§ 4 (iv)) is a more important factor. Some of these alloys are considered below (§ 5 (iv)) and also the 'micro-powder' magnet materials (which, it may be noted, are in one sense heterogeneous alloys with air, or a non-ferromagnetic binding material, as the second phase). The commercial magnet alloys are usually very complex in composition, and for a scientific investigation of the underlying processes taking place other alloys may be much more suitable. Examples are the binary Ni-Au, Ni-Be and Fe-Cu alloys already mentioned, and Fe-Mo alloys studied by Sucksmith and Margerison (1949), in which there is a one-phase state at high temperatures, which may be retained by quenching, and a well defined equilibrium two-phase state at ordinary temperatures, so that the extent and character of the precipitation may be controlled by appropriate heat treatment.

Many ferromagnetic binary and ternary alloys are now known which contain no ferromagnetic element. The saturation magnetization,  $I_0$ , is seldom higher than that of nickel, but some of the alloys, after appropriate heat treatment, have striking low field characteristics. Thus the Heusler type alloy 'silmanal' (Ag 86, Mn 9, Al 5) has a remanence,  $B_r$ , of 550, and a coercivity,  $I_H$ , of 6000 ( $BH_c = 540$ ). The main interest of these alloys, however, is in their intrinsic magnetization characteristics, and since the problem of their low field properties is similar in kind to that of other more fully investigated alloys, they will not be considered here. (For references, see Bitter (1937), Brailsford *et al.* (1948), Sucksmith (1949 a).)

*Non-metallic ferromagnetics.* Although far less work has been carried out on the non-metallic than on the metallic ferromagnetics much of it is of such a character that an account of it sufficiently detailed to be useful could not conveniently be incorporated in the present or the earlier report (cf. I, p. 109). Mention must be made, however, in a section on magnetic materials, of the intensive investigation of the ferrites carried out by Snoek, Boeke, Louwerse and others largely during the period 1940-45, and described by Snoek (1947, pp. 20-24, 68-99). The ferrites have the general formula  $MO \cdot Fe_2O_3$ , and those

of cubic structure which were primarily studied, with Mg, Zn, Cu, Fe, Co and Mn for M, form mixed crystals in any proportion. For most of these ferrites the saturation intensity is of the same order as that for nickel. Zinc ferrite is exceptional in that it is not ferromagnetic at room temperature, the Curie temperature being lower. The technological stimulus to this work is due to these materials having a very high specific resistance (of the order  $2 \times 10^4$  ohm cm.) compared with metals, so that in this respect they have very favourable properties for core materials, particularly for high frequencies. The initial permeability of the simple ferrites, as ordinarily prepared is, however, rather low (e.g. less than 100 for a carefully prepared sample of magnetite,  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ , and usually less than 10 for an ordinary sample). It was found that greatly increased values of  $\mu_0$  (and associated low values of  $H_c$  and of hysteresis loss) could be obtained in mixed crystals with zinc ferrite as one of the components. With the non-ferromagnetic component, the Curie point in the mixed crystal can be reduced to a temperature not far above room temperature, so that the usual maximum in the  $(\mu_0, T)$  curve is brought into the room temperature region. At the same time the effective anisotropy and magnetostriction are reduced to zero or to very small values. Values of  $\mu_0$  up to 4,000 have been obtained in the nickel-zinc ferrites, which may be compared with typical values of a little over 100 for nickel-iron alloy powder material, and of well under 100 for most iron powders. Detailed investigations were made of the effects of different heat treatments and of the proportions of simple ferrites required to give optimum properties for various purposes. In the preparation of homogeneous mixed crystals many difficulties were encountered, which were overcome by the development of carefully controlled sintering processes. For a full account of many interesting details of this work, in which science and technology are so happily blended, and which has led to the production of various types of 'ferroxcube', already widely applied, particularly in high frequency work, reference may be made to Snoek's book.

### 5 (iii). Iron-Silicon and Nickel-Iron Alloys

A general understanding of the magnetic characteristics of the iron-silicon and nickel-iron alloys may perhaps be facilitated by a brief qualitative restatement of the main factors which, in the light of both theory and experiment, appear to be determinative of magnetic softness. This depends essentially on the freedom of movement of domain boundaries. The freedom is checked (as fully discussed in § 4(ii)) by inhomogeneities of composition and of internal strain. Internal strains of mechanical origin can be minimized by appropriate annealing treatments. Beyond this, more and more complete removal of impurities enhances the permeability and decreases the coercivity, as exemplified in the work on very pure iron (§ 5(ii)). The effect of variations in composition (in particular those corresponding to the presence of inclusions, either non-ferromagnetic or less ferromagnetic than the matrix) is less the smaller the magneto-crystalline anisotropy; the effect of internal stresses (whether arising from lattice distortion due to the presence of impurities, or as a result of thermal and mechanical treatment) is less the smaller the magnetostriction. Small values of  $K$  and  $\lambda$  are thus favourable to magnetic softness, and the actual values set a limit to the values of the permeability (or at least of the initial permeability) that are attainable, for there is always some degree of heterogeneity of stress resulting from magnetostrictive changes as the material cools down from the Curie point (cf. I, p. 65). This limit is usually

very much higher than the values ordinarily obtained; within this limit, the main controlling factor appears to be the amount of impurity present, and, of course, its character, and form of aggregation.

In brief commentaries on various alloy systems detailed references to original papers would be out of proportion, and only a few supplementary references are given. Much more extensive accounts of these systems, with full references, are readily available in the books and papers listed above (5 §(i)), among which attention may be particularly directed to the book and review article by Brailsford (1948).

It is impracticable to include magnetization curves of all the materials mentioned in the present account, but an appreciation of the significance of the numerical values quoted may be assisted by the representative curves for soft magnetic materials shown in Figure 5.1 (based on a figure given by Stoner (1944)).

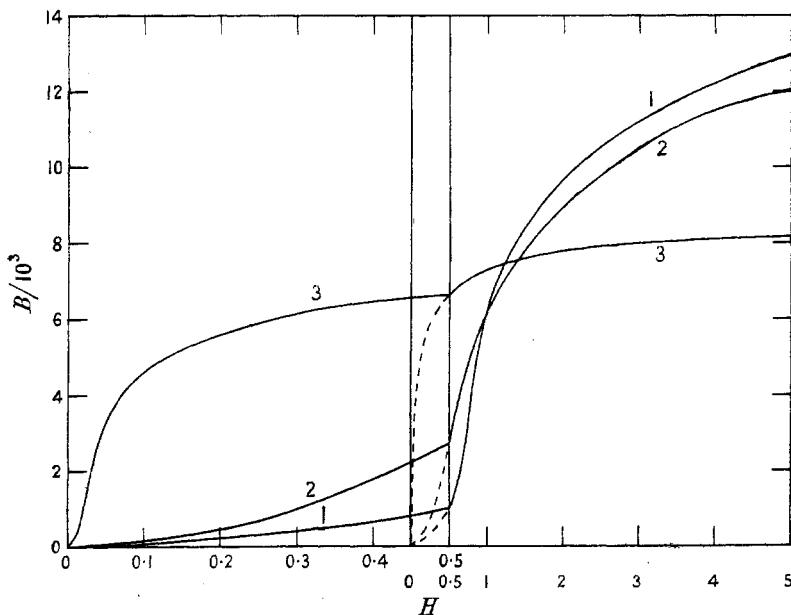


Figure 5.1. Representative magnetization curves for soft magnetic materials.

1. Swedish iron, annealed (C 0.027, Mn 0.030).  $4\pi I_0$ , 21,200.  $H_c$ , 0.8.  $\mu_0$ ,  $0.47 \times 10^3$ .  $\mu_{max}$ ,  $6.4 \times 10^3$ .
2. Silicon sheet steel, hot rolled (Si approx. 4.0).  $4\pi I_0$ , 19,500.  $H_c$  (for  $B_{max}$  10,000), 0.5.  $\mu_0$ ,  $1.25 \times 10^3$ .  $\mu_{max}$ ,  $6.5 \times 10^3$ .
3. Permalloy C (approx. Ni 78.5, Fe 18.0, Mo 3.0, Mn 0.5).  $4\pi I_0$ , 8,200.  $H_c$  (for  $B_{max}$  5,000), 0.03.  $\mu_0$ ,  $2 \times 10^4$ .  $\mu_{max}$ ,  $7 \times 10^4$ .

*Iron-silicon.* The solid solution range of silicon in iron extends to about 15 per cent silicon (by weight), but the brittleness of the alloys increases rapidly with silicon content above about 4 per cent. Alloys with above 6 per cent are seldom used, the usual range in electrical sheet steels being up to about 4.5 per cent. The high-temperature face-centred region (or  $\gamma$ -phase, extending in iron from about  $910^\circ$  to  $1390^\circ$  c., cf. I, p. 83) is diminished by addition of silicon; alloys with more than about 2.5 per cent Si are single-phase body-centred over the whole temperature range up to the melting point, and large-grained material can be readily obtained. (For recent work on the phase diagram, see Guggenheim

(*et al.* 1948). As illustrative of the effect of alloying, for a 4 per cent alloy,  $I_0$  is about 10 per cent smaller than for pure iron, the anisotropy coefficient about 40 per cent smaller (cf. § 2(ii)), and the specific resistance about six times as great (about 55 as compared with 9.6 microhm cm.). The magnetostriction does not appear to have been studied for single crystals. The available data indicate that the mean  $\lambda$  passes from positive to negative between 6 and 7 per cent Si. The reduction in eddy current losses due to the addition of silicon is readily intelligible. It does not seem, however, that the increased permeability and lower coercivity (and lower purely magnetic hysteresis loss) as compared with iron containing similar impurities can be accounted for purely in terms of the not greatly lower  $K$  and  $\lambda$  values. It is usually attributed to the 'scavenging' action of silicon on oxygen impurities, and to the effect of dissolved silicon on carbon impurities; these tend to precipitate as graphite, which has a less harmful magnetic effect than finely dispersed cementite. The losses may also be reduced to some extent by the increased grain size obtainable. Part of the hysteresis loss is usually attributed to a grain boundary effect, and some of the results obtained suggest (though this is a controversial issue) that in otherwise similar materials, this contribution to the loss is proportional to the grain boundary area. The loss does appear to decrease with increasing grain size, but a limit is set to improvement in this direction by deterioration in the workability of thin sheet material if the linear size of the grains approaches the sheet thickness. The effect of impurities and grain size has been discussed by Richer (1938) who concluded that, with the minimum impurities present in commercial 4 per cent silicon steel, the lower limit to the total loss (estimated at 0.95 watt kg<sup>-1</sup> at 50 cycles, corresponding to about 1,500 erg cm<sup>-3</sup> per cycle, for  $B_{\max} = 10,000$ ) was not far below that obtained in practice (about 1.3 watt kg<sup>-1</sup>). The type of commercial silicon steel referred to here is that produced by a hot-rolling process, and of which the qualities, according to Brailsford (1948, p. 528), 'have remained unchanged over a long period of years'.

Sheet steel of considerably better quality has been successfully produced commercially (under the name of 'Hipersil') by a combination of two methods. The first is essentially a reduction of impurities, particularly of carbon, by a high temperature anneal in pure dry hydrogen. This operation is preceded by an appropriate sequence of cold-rolling and annealing processes, by which sheets are obtained with a preferential orientation of the crystal grains, approaching that in which the [100] directions are in the rolling directions, and the [110] directions at right angles in the plane of the sheet. The sheet is anisotropic with an easy direction along the rolling direction (the magnetization curves are similar to, but less sharp than, those for single crystals of iron, as shown in Figure 2.1); for magnetization in this direction, the induction is higher for a given field than for isotropic sheets, and the losses lower. The improvement is considerable. Thus the total iron loss for cold-rolled sheet containing about 3 per cent Si, under the conditions given above, is about 0.6 of the loss for the corresponding hot-rolled isotropic sheet. In unfavourable directions the losses may be greater than for isotropic sheets, but for transformers, the main application, almost full advantage may be taken of the greatly improved qualities along the rolling direction. In the country of its origin cold-rolled sheet is rapidly replacing hot-rolled, so it would seem that the greater initial cost is more than compensated by the lower running cost of the finished transformers.

The mechanism by which cold rolling gives rise to preferential orientation in subsequent recrystallization is still very obscure, but such effects are not, of course, peculiar to ferromagnetic alloys (cf. Barrett 1943, pp. 395-434). That preferential orientation should give rise to improved magnetic qualities in the sheet may seem, at first, readily intelligible. Quantitatively, however, there are many unsolved problems, perhaps more in connection with eddy current losses than with the actual shapes of the magnetization loops, and investigations on these questions are in active progress (see, for example, Lawton, Shoenberg and Stewart 1947, De Barr 1949). The orientational distribution of crystals in sheets may be determined by x-ray, optical and other methods. In certain cases the degree of preferred orientation can be rapidly estimated by the torque curve method (cf. § 2(ii)). The possibility of estimating the distribution from the magnetization curves themselves has been explored by Richer (1944, 1947). Such a method, suitably developed, might give valuable supplementary information, but the 'unknowns' at present are far too numerous (as pointed out by De Barr in 1948, unpublished) for an unambiguous determination to be made by this method alone.

*Nickel-iron alloys.* A general survey of the magnetic properties of the nickel-iron alloys and their applications, with extensive data in tabular and graphical form, has recently been published by the Mond Nickel Company (see Anon., 1949). This forms an admirable introduction to the more detailed discussions of particular questions in the books and review articles already mentioned, as well as to the accounts of original work. The phase diagram of the binary alloys has already been discussed (I, pp. 104-6). The alloys to be considered here are exclusively those in the single-phase face-centred range extending from about 35 per cent to 100 per cent nickel. The saturation intensity,  $I_0$ , starting from nickel, increases almost linearly from about 485 for Ni to about 1230 for 50 Ni 50 Fe, and subsequently decreases rapidly. These alloys do not compete with iron-rich alloys in transformers and power equipment owing to their much lower saturation magnetization (for iron,  $I_0 \approx 1720$ ), but where high permeability and low losses are required at low and moderate inductions they have found innumerable applications.

The earlier investigations, notably by Arnold and Elmen (1923), showed that very high permeabilities could be obtained in alloys in the range 75-80 Ni by suitable heat treatment. (The binary alloys will be specified by the percentage of nickel by weight unless otherwise stated.) Annealing at about 1000°C. and slow cooling is ineffective, but subsequent heating to 600°C. followed by air-quenching gives high permeability with a fairly well defined maximum at about 78.5 Ni ( $\mu_0 \approx 1.2 \times 10^4$ ,  $\mu_{\max} \approx 9.0 \times 10^4$ ). (It may be noted, to prevent misunderstanding, that although 'permalloy' is strictly a trade name for a series of alloys of this basic composition, the high permeability nickel-iron alloys generally are sometimes referred to as 'the permalloys'.) The saturation magnetostriction,  $\lambda$ , of the iron-nickel alloys passes from positive to negative in this region, and it was suggested by McKeehan (1925) that the high value of  $\mu_0$  might be associated with the low value of  $\lambda$ . This suggestion was later made more precise by Kersten's relation for the maximum value of  $\mu_0$  (cf. I, p. 65), namely

$$(\mu_0)_{\max} - 1 = 4\pi(\kappa_0)_{\max} = \frac{8\pi}{9} \frac{I_0^2}{\lambda^2 E}, \quad \dots\dots (5.1)$$

where  $E$  is Young's modulus. The work of Lichtenberger (1932), however, shows that the mean value of  $\lambda$  and the values along the main crystal directions all pass through zero at approximately 82 Ni. At 78·5 Ni, the magnetostriction is, in fact, comparable with that for iron. The high permeability is not, therefore, to be explained solely in terms of the magnetostrictive characteristics of the material. The magneto-crystalline anisotropy must also be considered. The leading anisotropy coefficient,  $K_4$ , passes through zero at about 75 Ni (see Figure 2.5) from the results of Kleis (1936), confirmed by the more detailed work of Grabbe (1940). It may be that, with a minimization of impurity precipitation by the air-quenching treatment, the maximum  $\mu_0$  at about 78·5 Ni is to be explained mainly as resulting from an optimum combination of low values of both  $K$  and  $\lambda$ .

It has often been suggested (e.g. Becker and Döring 1939, p. 412) that the possible formation of a superlattice at and near the composition  $\text{Ni}_3\text{Fe}$  (75·9 Ni) might have some connection with the high permeability of alloys in this range. Although the character of the dependence of many of the properties on thermal treatment suggests that an ordering process may be involved, the definite establishment of its occurrence by x-ray methods is difficult owing to the similarity in scattering power of iron and nickel. It was first accomplished, using cobalt  $K\alpha$  radiation, by Leech and Sykes (1939), who obtained films showing all the superlattice lines with a specimen annealed for 500 hours in the temperature range 490° to 370°C. Among the many investigations of the effect of ordering on magnetic, electrical and thermal properties (e.g. Kaya 1938, Haworth 1938, Grabbe 1940, Källbäck 1948, Sucksmith 1949 b), mention may be made particularly of the work of Grabbe, who, using single crystals, measured the magneto-crystalline anisotropy (cf. § 2(ii)) and other properties of a series of alloys in the range from 65 to 80 Ni, both in the quenched state and after prolonged annealing. It may be said at once that ordering, or the thermal treatment required to produce ordering, so far from increasing the permeability, decreases it enormously, as would be expected from the earlier work. Grabbe suggests, very plausibly, that the lower permeabilities resulting from slow cooling, as opposed to air-quenching, are due to the heterogeneity arising from small ordered regions in an otherwise disordered lattice. The change in the anisotropy coefficient,  $K_4$ , on ordering is greatest (from 0 to  $-2\cdot3 \times 10^4$  erg. cm<sup>-3</sup>) at about 75 Ni. The composition at which  $K_4$  is zero in the ordered alloy is between 65 and 68 Ni, as compared with about 75 Ni for the disordered alloy. This, as pointed out by Snoek (1941) and others, may be relevant to the explanation of the effect of magnetic annealing.

It was found by Dillinger and Bozorth (1935) that the maximum permeability of a certain range of alloys in the iron-cobalt-nickel system could be considerably increased by annealing in a magnetic field. The largest effects are produced when the field is applied over the temperature range from 500° to 400°C., and the Curie point must be substantially above the lower of these temperatures, which may be identified with that at which plastic flow begins to occur. In the binary nickel-iron alloys the greatest change is produced for compositions between 65 and 70 Ni, where the Curie temperature rises to a maximum of about 600°C. A typical increase in  $\mu_{\max}$  for a 65 Ni alloy is from  $5 \times 10^3$  to  $3 \times 10^5$ , and for one specimen, which was given a preliminary prolonged high temperature anneal, the change was from  $2 \times 10^4$  to  $6 \times 10^5$ . With a single crystal, in hollow rectangle form, of similar material, Cioffi, Williams and Bozorth (1937) obtained a change

in  $\mu_{\max}$  along the [100] direction from  $1.8 \times 10^4$  to the enormous value of  $1.33 \times 10^6$ , nearly as great as that obtained in a single crystal of pure iron (see also Bozorth 1937). The magnetically annealed alloys are strongly anisotropic. In one particular specimen,  $\mu_{\max}$  along the direction in which the field had been applied was greater by a factor of 150 than that at right angles. The tentative qualitative explanation of these effects suggested by Dillinger and Bozorth is simple. As the spontaneous magnetization increases on cooling below the Curie point, magnetostrictive stresses are set up, which may be relieved by deformation if the cooling over the plastic range is sufficiently slow. The deformation is such as to make the energy a minimum for the actual direction of magnetization over any uniformly magnetized region, whether this is an entire single crystal grain or a smaller domain. When the material has 'hardened' at lower temperatures, these actual directions become relatively easy directions of magnetization compared with others which, in an unstrained crystal, are equivalent. Ordinarily, these easiest directions will be distributed at random among the equivalent easy directions of the crystals constituting the polycrystalline aggregate; but if a field is applied during the cooling, the easiest directions will be those most nearly parallel to the applied field. In the demagnetized state the domain magnetization vectors would then be approximately parallel or antiparallel to the previously applied field, and change of magnetization in this direction could occur readily by the movement of  $180^\circ$  boundaries, giving a high initial and maximum permeability; a transverse change of magnetization would involve a turning of domain magnetization vectors from the easiest to more difficult directions, and the permeability would be correspondingly low. It is maintained by Becker and Döring (1939, pp. 418–22) that this treatment breaks down quantitatively, and they suggest speculatively that a change of crystal structure from cubic to tetragonal may be involved; whether or not this is so, there can be little doubt that the basic process is much as envisaged by Dillinger and Bozorth. It may be noted that a value of  $\lambda$  different from zero is essential for the magnetic annealing effect to occur at all; on the other hand, the smaller the value of  $K$ , the greater is the effect likely to be, as the directions of easiest magnetization developed during cooling are more completely controlled by the direction of the applied field. The relevance of Grabbe's discovery of the shift of the zero  $K$  region in the ordered nickel–iron alloys at once becomes apparent. It also becomes understandable that only a very small change is produced in the permeability of iron and iron–silicon, with their relatively high  $K$  values.

The cold-rolling process, described in connection with the iron–silicon alloys, was first applied with success to the nickel–iron alloys. The details, however, cannot be described here. Short accounts of the work are given by Brailsford, and representative papers are those of Snoek (1935, 1936), Randall (1937) and Scholefield (1949). For accounts of the many interesting ternary alloys, such as those in the Fe–Co–Ni system which include the 'perminvars', with effectively constant permeability over a low field range, reference may be made first to the books and articles already mentioned. A number of the technologically valuable alloys, although they have more than two components, are perhaps best regarded as nickel–iron alloys 'modified' by the replacement of some of the nickel or iron by other elements to obtain better magnetic characteristics for particular purposes, to increase resistivity, to improve workability, or to simplify commercial production by, for example, decreasing the strictness of control necessary in heat treatment.

Examples are the chromium and molybdenum permalloys (78.5 Ni, 17.7 Fe, 3.5 Cr or Mo), mumetal (76 Ni, 17 Fe, 5 Cu, 2 Cr), and '1040' (72 Ni, 11 Fe, 14 Cu, 3 Mo). Finally mention may be made of a recent new material of high permeability, described by Boothby and Bozorth (1947), to which the name 'supermalloy' has been given. The composition is about 79 Ni, 15 Fe, 5 Mo, 0.5 Mn. By a combination of hot and cold rolling, high temperature (1300° c.) annealing in pure dry hydrogen, and cooling at a critical rate over the range 600° to 300°, values of  $\mu_0$  from  $5 \times 10^4$  to  $1.5 \times 10^5$ , and of  $\mu_{\max}$  from  $6 \times 10^5$  to  $1.2 \times 10^6$  have been obtained. The coercivity ranges from 0.002 to 0.005, and the hysteresis loss per cycle at  $B=5,000$  is less than 5 erg. cm<sup>-3</sup>. The remarkable properties are believed to be due on the one hand to a minimization of the usual impurities, and on the other, though this has yet to be confirmed, to a combination of small  $\lambda$  and small  $K$ , resulting from a critical degree of ordering controlled by the rate of cooling. The figures given refer not to a laboratory specimen, but to a material which has been made in considerable quantities and used in the form of thin tape for the cores of communication transformers. The development of supermalloy illustrates again how the meeting of technological requirements may be assisted by a scientific approach to the problems involved.

#### 5 (iv). Permanent-magnet Materials

##### *Required characteristics.*

It is perhaps desirable to introduce permanent-magnet materials by a few remarks on the criteria used in assessing them. The most useful single number criterion of the suitability of materials for permanent magnets is the maximum value of the product  $BH$  on the descending branch of the hysteresis loop, as shown in Figure 5.2 (based on a figure given by Stoner (1944)).

By a readily proved general theorem, in the absence of currents,

$$\int BH dv = 0, \quad \dots \dots (5.2)$$

where the integral is taken over all space (or, approximately, over a volume at the boundary of which the field is approximately zero). For a single magnet,

$$\int H^2 dv_o = - \int BH dv_i, \quad \dots \dots (5.3)$$

where the subscripts o and i refer to the space outside and inside the magnet. A somewhat artificial but often useful distinction may be made between the useful flux (e.g. in a pole gap) and the leakage flux. Denoting the volume of the magnet by  $V$ , the effective volume of the gap by  $v$ , and the field in the gap by  $H_g$ ,

$$-(\overline{BH}) V = \int H^2 dv_o = q \overline{H_g^2} v, \quad \dots \dots (5.4)$$

where  $q$  is a 'leakage' factor necessarily greater than, and in practice usually much greater than, unity. It will be clear from these equations, first, that the greater the value of  $(BH)_{\max}$  the greater the potential efficiency of the material for magnets (i.e. the smaller the volume required to produce a given effect) and, secondly, that if full advantage is to be taken of the properties of the material the magnet should be so designed that the mean working point on the demagnetizing curve is at or near the  $(BH)_{\max}$  point. The mechanical properties of a material and its cost must be taken into account in assessing its overall efficiency; but apart from these, if the shape of the magnet is determined in part by other than

purely magnetic considerations (e.g. that it must fit conveniently into the general assembly design of a piece of equipment), the material of highest  $(BH)_{\max}$  value which is available is not necessarily the most efficient.

*Dependence of  $(BH)_{\max}$  on remanence and coercivity.*

High  $(BH)_{\max}$  values are ordinarily associated with high values of both the remanence,  $B_r$ , and the coercivity,  $H_c$ , but it must be borne in mind that the relevant coercivity is the value of  $H$  at which  $B$  is reduced to zero,  ${}_B H_c$ , and not the value, which may be much higher, at which  $I$  is reduced to zero,  ${}_I H_c$ . In the

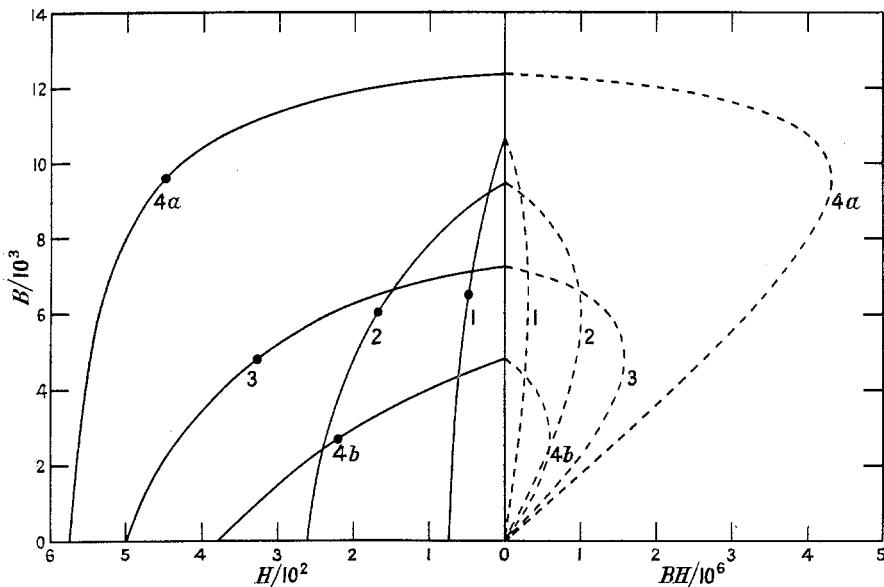


Figure 5.2. Representative demagnetizing and  $BH$  curves for permanent-magnet materials.

1. Tungsten steel (W 5.5, C 0.6).
2. Cobalt steel (Co 35, Cr 6, W 4, C 0.8).
3. Alnico (Ni 18, Co 12.5, Al 10, Cu 6).
4. Alcomax (Co 25, Ni 11, Al 7, Cu 6).

Alcomax is anisotropic. The curves show typical characteristics along (4 a), and at right angles to (4 b), the direction of the field applied during cooling. The  $(BH)_{\max}$  points are marked on the curves.

remainder of this section, unless otherwise stated,  $H_c$  or 'coercivity' refers to the value  ${}_B H_c$ . The shape of the descending  $(B, H)$  curve is important, and is sometimes roughly indicated by a 'fullness factor',  $\gamma$ , defined by

$$\gamma = (BH)_{\max} / (B_r H_c). \quad \dots \dots (5.5)$$

Estimates may be made of the highest  $(BH)_{\max}$  values ideally attainable, following a method of treatment of the geometry of demagnetizing curves developed in detail by Hoselitz (1944). The highest values would occur if the intensity of magnetization,  $I$ , remained constant at the remanence value,  $I_r$ , as the field increased negatively. The induction would then be

$$B = 4\pi I_r - H = B_r - H,$$

and a limit to  $(BH)_{\max}$  is given by

$$(BH)_{\max} \geq \frac{1}{4} B_r^2. \quad \dots \dots (5.6)$$

If, however,  $H_c$  is less than  $\frac{1}{2}B_r$ , simple consideration shows that

$$(BH)_{\max} \geq H_c(B_r - H_c). \quad \dots \dots \quad (5.7)$$

Throughout this section it will be convenient to express  $(BH)_{\max}$  values in units of  $10^6$  erg. cm<sup>-3</sup>. There are now available commercial materials for which the  $(BH)_{\max}$  values approach 6. It follows at once from (5.6) that such values cannot be exceeded by materials for which  $B_r$  is less than about 5,000. Thus for the Heusler type alloy silmanal already mentioned (§ 5(ii)), the  $B_r$  value is about 550, and in spite of the enormous  $H_c$  value 6,000, the maximum possible value of  $(BH)_{\max}$  is 0.076, which is practically attained (the observed value is, in fact, given as 0.08). For most of the permanent magnet alloys,  $H_c$  is much less than  $\frac{1}{2}B_r$ , and the limit for  $(BH)_{\max}$  is that given by (5.7). This limit is approached only by the anisotropic alloys of the alcomax type. Thus for one of the alloys of the alcomax series, with  $B_r$  12,500,  $H_c$  550, the observed value of  $(BH)_{\max}$  is 4.3 as compared with the limiting value of 6.6, a ratio of 0.65. For isotropic alloys the ratio is smaller. For alnico, for example, the ratio is about 0.48.

#### *Ideal permanent-magnet material.*

A rough estimate of an ideal upper limit to  $(BH)_{\max}$  is obtained by taking  $B_r$  as  $2 \times 10^4$  in (5.6), which gives a value of 100, more than 10 times as great as that for any of the materials available at present. The increase in field for a given ratio of magnet volume to gap volume would be by a factor of about 3, the improvement being comparable with that from tungsten steels to present-day magnets. For such a value to be attained, however, a material would be required with a remanence equal to the saturation magnetization of iron, a rectangular ( $I, H$ ) loop, and a coercivity of  $10^4$  oersted. Consideration has been given to a highly idealized magnetic material on the one hand to show that considerable improvement may still be made on materials now available, and on the other to make it clear that even the ideally possible improvement (which greatly exceeds any 'theoretically possible' improvement which has so far been envisaged) is not nearly so great as is sometimes supposed.

The characteristics of actual permanent-magnet materials are so comprehensively tabulated in the articles already mentioned, particularly in that of Oliver and Hadfield (1948), that no more than a bare indication of them is given here, and in view of earlier references (§ 4(iv), § 5(ii)) to the possible theoretical interpretations of these characteristics, only a very brief survey is necessary.

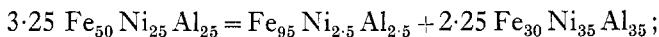
*Alloys.* The permanent magnet alloys which were brought into use before 1930 were all of the quench-hardened type, and usually contained about 1 per cent of carbon. This applies to the carbon, tungsten, chromium and cobalt steels, with  $(BH)_{\max}$  values of up to about 0.2, 0.3, 0.3 and 1.0 respectively. The alloys have a complex martensitic structure, and it may reasonably be presumed that there are large heterogeneities of internal stress with which the relatively high coercivities (ranging from about 50 for carbon steel to 250 for 35 cobalt steel) compared with those of annealed materials may be associated. There are, however, so many uncertainties and difficulties that no quantitative correlation of the magnetic properties with the structural characteristics has yet been made.

The discovery by Mishima (1931) that carbon-free iron-nickel-aluminium alloys of approximate composition Fe<sub>2</sub>Ni Al, suitably heat treated, had a coercivity of about 500 opened a new era in the history of permanent-magnet materials.

Additions of cobalt and copper were found to improve the properties, and an alloy introduced in 1934 under the name 'alnico' (Al 10, Ni 18, Co 13, Cu 6), with a  $(BH)_{\max}$  value of 1·6, remained as the 'best' commercial material until the introduction some years later of a number of anisotropic alloys, produced by cooling in a magnetic field. These alloys contain more cobalt than ordinary alnico. The trade varieties (alcomax, ticonal, alnico, with sub-varieties designated by letters or numbers) all contain Fe, Ni, Al, Co and usually Cu, with various additions, such as titanium and, recently, niobium. Alcomax II, of which demagnetizing curves are shown in Figure 5·2, is reasonably typical, with approximate composition Al 7, Ni 11, Co 25, Cu 6. The  $(BH)_{\max}$  values range from about 3·5 to 5·5 as averages, which may be exceeded in individual specimens. All these alloys are brittle, and must be cast and ground; alternatively, and with advantages for some purposes, the sintering techniques of powder metallurgy may be used, and are said to give magnetic properties within 10 per cent of those of the equivalent cast alloy. A number of malleable and ductile materials have been produced, among which cunife (60 Cu, 20 Ni, 20 Fe) and vicalloy (52–57 Co, 8–14 V, bal. Fe) may be mentioned, with  $(BH)_{\max}$  values of about 1·5, and up to 3·5 respectively.

The various alloys are, of course, only in part specified by the approximate composition. The phases present in alloys with optimum magnetic properties have been determined in a few cases by x-ray and other methods, but even here the knowledge is usually incomplete, and definite knowledge of the states of aggregation of the phases is almost entirely lacking. The fuller specification of the alloys is, therefore, necessarily indirect, through statements, in sufficient detail, of the heat treatments (which may include cooling in a magnetic field) and other treatments (e.g. cold reduction) which are required for the development of the specified magnetic properties.

The x-ray and magnetic work by Bradley and Sucksmith respectively on the ternary Fe–Ni–Al alloys has already been summarized (§ 4(iv) and I, pp. 106–8). The equilibrium state of the alloy of approximate composition  $\text{Fe}_2 \text{Ni Al}$  at high temperatures is single-phase, at room temperature two-phase, the two phases both being body-centred but of slightly different lattice spacings. The phase separation may be represented by



the two phases, it may be noted, are approximately Fe and Fe Ni Al. The specific saturation intensity of the iron-rich phase is about 212, that of the second phase about 61. The single-phase state is retained by quenching, and the two-phase state is produced by long annealing. Neither of these treatments results in an alloy of high coercivity, for which an intermediate rate of cooling is necessary. In the intermediate state, it was suggested (Bradley and Taylor 1938 b) that there was an incipient precipitation of the iron-rich phase, with the formation of sub-microscopic iron-rich regions. The evidence is consistent with the formation of more strongly ferromagnetic islands, below the critical size for domain boundary formation to be possible, in a less ferromagnetic matrix, and, as discussed by Stoner and Wohlfarth (1948) (cf. § 4(iv)), high coercivities can then be accounted for readily in terms of the rotational processes occurring in anisotropic single-domain particles. Whether shape, magneto-crystalline or strain anisotropy is predominant must at present be left open, and it must be remembered that, since the matrix is itself ferromagnetic and some of the islands formed may be

relatively large, processes other than rotations in single domains are involved. None the less, it seems probable that the single-domain processes, which have been fully examined theoretically, play a centrally important part in determining the high-coercivity characteristics of many permanent-magnet alloys of the dispersion hardening type. It should be noted that although the proposed mechanism requires that the individual particles segregated should be small, the aggregate volume occupied by them may be a large fraction of the total volume.

In more recent work Bradley (1949 a, b) has made a comprehensive microscopic study of alloys in the Fe-Ni-Al system. A comprehensive x-ray and metallographical study of this system has also been made by Kiuti (1941), with results in substantial agreement with those of Bradley.

The anisotropic alloys which have been most fully studied are probably those of the alcomax type (see Figure 5.2). The heat treatment required to give optimum properties has been fully investigated by Oliver and Hadfield (1946). For a particular alcomax alloy (11.5 Ni, 7.5 Al, 25.0 Co, 6.0 Cu, bal. Fe) the best properties are obtained by cooling from a 'solution temperature' (in the range 1200° to 1300° c. or 875° to 925° c.) at a controlled rate (about 1.6 deg. sec<sup>-1</sup>) in a magnetic field of about 4500 oersteds (which must be maintained from above the Curie temperature at about 875° c. to about 650° c.), and subsequently tempering at about 600° c. for 15 hours or more. It may be noted that any considerable deviation from the temperatures stated, say by 50°, results in a very large deterioration of the final properties. (These technical details are given here to illustrate that much more is needed in the barest specification of a magnetic material than a statement of its composition.) A very extensive 'exploratory' x-ray study of these alloys has been made by Oliver and Goldschmidt (1947), the phase structure having been examined after a wide variety of heat treatments. The x-ray work indicates that the development of high coercivity is associated with incipient segregation in a metastable phase as in the simpler ternary alloys, but the totality of structures and transformations revealed as possible in the system is of bewildering complexity. The significance of many of the findings will hardly become clear until a better understanding is gained of the simpler ternary and binary systems.

The effect of cooling in a magnetic field is that in the direction in which the field has been applied the remanence, coercivity, and 'fullness' are all increased, and in a perpendicular direction decreased. The demagnetizing curves in the favoured direction and at right angles to it (see Figure 5.2) bear a remarkably close resemblance to those which would arise with single domain particles with easy axes approximately parallel to the field (say the curves for 10° and 80° in Figure 4.3, as compared with the mean curve in Figure 4.4). On the basis of the single-domain mechanism, it is suggested that cooling in a magnetic field favours energetically the formation of segregates with an easy direction of magnetization parallel to the field, independently of how the anisotropy arises (Stoner and Wohlfarth 1947, 1948, Néel 1947 d). Whether or not a field is applied, there must, however, be some relation between the orientation of the segregate and that of the crystal in which it is formed. Measurements of magnetostriction of alcomax by Hoselitz and McCaig (1949) are consistent with the view that, after cooling in a magnetic field, the easiest directions of magnetization (i.e. the directions of the domain magnetization vectors in the absence of a field) are along or near the cube-edge directions which are nearest to the anisotropy axis of the specimen. This is

supported by later measurements of McCaig (1949) on samples with 'columnar' crystals, that is polycrystalline samples in which all the crystals have one axis parallel to a given direction. This particular work has no direct bearing on the question of the detailed mechanism giving rise to high coercivity, but it does provide important additional information which must be taken into account in any attempt to explain more fully the totality of magnetic properties of these alloys.

Since the details of the process of phase segregation have such an important bearing on magnetic properties, mention should be made of some x-ray work by Daniel and Lipson (1943, 1944), following earlier observations by Bradley, on an alloy of approximate composition Cu<sub>4</sub>Ni Fe<sub>3</sub>, which, when suitably heat-treated, develops permanent-magnet characteristics. Quenched from 1,000° c., this alloy is single-phase, and gives sharp x-ray diffraction lines. On prolonged annealing at 650° c. it segregates into two distinct face-centred phases with different lattice spacings, and the original lines are doubled. With short annealing periods the sharp lines characteristic of the single-phase state are flanked by diffuse but strong 'side-bands'. It is shown that these side-bands, characteristic of the initial stages of segregation during which the coherence of the original lattice is retained, can be accounted for as arising from a periodic variation of the lattice spacing. The spacing increases where the concentration of the copper atoms increases and conversely. The dependence of the wavelength and amplitude of the variation on the time of annealing was studied in detail. Preliminary magnetic measurements by Sucksmith have indicated that as the wavelength increases (up to something over 100 lattice spacings) the remanence at first increases rapidly, and then falls off slowly, and the coercivity increases more gradually to a fairly well defined maximum (Anon. 1946, Sucksmith 1949 a). These effects have usually been attributed to a variation of internal stress associated with the spacing variation, on the general basis of the Becker-Kersten strain theory (§ 4(ii)), but no quantitative treatment of the problem appears to have been published. Further work is, however, in active progress on the side-band effect, the importance of which is, of course, not confined to ferromagnetic materials.

A number of illustrative examples have been given of the bearing of x-ray investigations, additional to the purely structural studies, on magnetic problems. It is, however, impracticable to deal adequately here with this theme. For a survey of x-ray work on metals and alloys generally, much of which is directly or indirectly relevant to questions considered in this section, reference may be made to the book by Barrett (1943), and for more recent work to a comprehensive review article by Douglas (1949).

The permanent-magnet alloys which have been considered have been almost exclusively ternary or more complex alloys, most of them being alloys (or prototypes of alloys) of technological interest. Relatively high coercivity is also developed in a number of binary (or nominally binary) alloy systems. Among these are alloys of platinum, which are of particular scientific interest (cf. I, p. 92), even though their commercial development as permanent-magnet materials is somewhat improbable. The platinum-iron alloys have been studied by Graf and Kussmann (1935). For an alloy of composition Pt 78 Fe 22, which corresponds to equal atomic percentages,  $(BH)_{\max}$  values as high as 3 are obtained ( $B_r$  5800,  $H_c$  1570). Microscopic and x-ray studies of this alloy, after various heat treatments, have been made by Lipson, Shoenberg and Stupart (1941), who conclude, in disagreement with Graf and Kussmann, that the structure is tetragonal. In the

high coercivity state the microstructure shows crystal grains crossed by sets of parallel bands, which are interpreted as twinning bands due to the breakdown of the high-temperature face-centred cubic structure. For the equiatomic platinum-cobalt alloy, Pt 77 Co 23, coercivities as high as 4,000 have been obtained (Jellinghaus 1936), and values of  $(BH)_{\max}$  greater than 4 are quoted (cf. Hoselitz 1944, Oliver and Hadfield 1948, see also Douglas 1949, Sucksmith 1949 a). From what is known about the structure of the platinum alloys in the high-coercivity state, the occurrence of large internal-stress variations seems reasonably certain; but whether these stress variations alone can account for the coercivity through the disperse field effect (§ 4(ii)) is still an open question.

Investigations have recently been made of binary alloys of a different type in the iron-molybdenum system by Sucksmith and Margerison (1949). Over the range of compositions from Mo 8 to Mo 35 the alloy at high temperatures consists of a solid solution of Mo in Fe, which is retained by quenching. Subsequent heat treatment causes the precipitation of a non-magnetic phase of approximate composition  $\text{Fe}_3\text{Mo}_2$ . The alloys studied contained Mo 10, 15 and 20. Through the development of a method of determining magnetization and hysteresis curves at temperatures up to over  $800^{\circ}\text{C}$ ., it was possible not only to examine the magnetic properties of the alloys at room temperature after various heat treatments, but also to follow the manner in which the saturation magnetization, the remanence and the coercivity varied with temperature. From other evidence it is probable that the non-magnetic phase precipitates in the form of plate-like structures, giving layer-like or cell-like non-magnetic boundaries to the thus separated regions of the more abundant ferromagnetic phase. If it is assumed that the fairly high coercivities (up to over 100) are due to stress variations, an approximate theoretical estimate of the magnitudes of these can be made; the values so obtained appear to be considerably higher than is compatible either with the sharpness of x-ray diffraction lines, or with the small effect of prolonged heating at  $700^{\circ}\text{C}$ . on the value of the coercivity. It is therefore suggested that rotational hysteresis in single-domain regions contributes to the observed effects, and also, since over a considerable range there is a linear variation of  $H_c$  with  $I_0$ , that shape anisotropy is primarily involved. On this basis, a qualitative explanation can be given of some of the main effects observed. It would not be expected that the experimental results would agree, in any completeness, with the theoretical results (§ 4(iv)) for an assembly of non-interacting single-domain particles. It is, indeed, remarkable that the unelaborated theoretical treatment applies as closely as it appears to do to an alloy in which the aggregate volume of the ferromagnetic 'particles' considerably exceeds that of the matrix, and in which only a proportion of the particles are likely to be single-domain. Further experimental investigations, such as are in progress, on alloys of the iron-molybdenum type, and of complementary alloys in which the precipitation of a ferromagnetic phase from a non-ferromagnetic solid solution can be controlled, offer great promise of leading to a better understanding of the phenomena underlying the development of high coercivity in alloys.

*Micro-powder magnets.* Reference has already been made (§ 4(iv)) to the experimental and theoretical work of Néel and his collaborators on magnetic materials made up of very fine particles, which may be presumed to be mainly single-domain, and to the development of these materials for permanent magnets. The materials are essentially different from powder agglomerates such as sintered alcomax, with constituent grains neither isolated nor, necessarily, very small.

The distinctive description of the new materials as 'micro-powder' or 'ultra-fine powder' materials is therefore appropriate. Methods of preparation which have been described in patent specifications include the precipitation of suitable salts (such as formates, acetates and oxalates), or mixed salts (e.g. ferrous iron and cobalt salts) from solution, followed by decomposition of the salts at temperatures lower than 600° c., treatment in various atmospheres (reducing in one process, oxidizing in another), and compression, with or without a binding agent, of the powder so formed. Information about the commercial products is not readily accessible, but Oliver and Hadfield (1948) give for micro-powder iron (with 15 per cent  $\text{Fe}_3\text{O}_4$ ) a  $(BH)_{\max}$  value of 1·0 ( $B_r$  5000,  $H_c$  600), and for iron-cobalt (Fe 37, Co 26,  $\text{Fe}_3\text{O}_4$  22·5) a value of 1·7 ( $B_r$  7500,  $H_c$  500). The values are comparable with those for ordinary alnico.

Extensive investigations of these micro-powder materials have been made by Néel, Weil and others. No full collected account of this work seems to have been published, but various aspects of it are presented in a number of short notes. In the first of these to which reference has already been made (§ 4(iv)), Néel (1947 b) considers the critical size for single-domain particles, and examines the properties of assemblies of such particles with magneto-crystalline characteristics similar to those of iron. He shows that if the anisotropy were of magneto-crystalline origin, the mean coercivity,  $I_H_{cm}$ , for random orientation, would be approximately  $0.64K/I_0$ , that is about 160 for iron. Since coercivities of about 1000 have been observed, he concludes that shape anisotropy is also involved. In a second paper (1947 c) shape anisotropy is further considered, and the effect of the mutual magnetic interaction of the particles is discussed. An important relation is given, though not derived in detail, for the mean coercivity of a powder, namely

$$I_H_{cm} = (I_H_{cm})_0 \{1 - (\rho/\rho_0)\}, \quad \dots \dots (5.8)$$

where  $\rho$  is the density of the powder,  $\rho_0$  that of the metal in bulk, and  $(I_H_{cm})_0$  a limiting coercivity for effectively non-interacting particles ( $\rho \rightarrow 0$ ). With shape anisotropy alone for an assembly of randomly orientated similar prolate spheroids  $(I_H_{cm})_0$  has the value  $0.48(N_b - N_a)I_0$ , the maximum value being  $0.96\pi I_0$  (cf. § 4(iv)). For a particular, somewhat artificial, distribution of eccentricities of the spheroidal particles, which, however, probably gives a fair representation of an actual powder, Néel obtains the result

$$(I_H_{cm}) = 0.26\pi I_0. \quad \dots \dots (5.9)$$

The relation (5.8) has been verified experimentally with fair approximation by Weil (1947) for non-agglomerated powders (held in paraffin) of iron and iron-cobalt with effective values of  $\rho/\rho_0$  ranging from about 0·5 to 0·1. The extrapolated limiting values of  $I_H_{cm}$  were about 670 and 1000 for the iron and iron-cobalt powders respectively, as compared with  $(I_H_{cm})_0$  values, from (5.9), of about 1400 and 1540. With specially prepared powder materials actual  $I_H_c$  values of up to and about 1080 and 1230 have been obtained for iron and iron-cobalt respectively.

The actual size of the iron powder particles has been estimated by Weil (1948 a) from the 'heat of wetting' in organic liquids, as compared with that measured for coarser carbonyl-iron powders whose particle sizes are determinable microscopically. The estimated mean diameter of  $4.5 \times 10^{-6}$  cm. is regarded

as an upper limit (in view of the tendency of the particles to cohere in groups), and is rather larger than the value indicated by x-ray measurements (about  $3.0 \times 10^{-6}$ ). These values are satisfactorily consistent with the theoretical estimates of size for single-domain particles (§ 3(iv)).

Measurements of the variation with temperature of the coercivity of these materials are of value as giving some indication of the origin of the anisotropy. If the anisotropy is primarily of magneto-crystalline origin,  $I_H$  should vary as  $K/I_0$  and, if it is primarily due to shape, as  $I_0$ . Work on nickel powders (Weil and Marfoure 1947, Weil 1949) covering in all a temperature range from about  $-250^{\circ}\text{C}$ . to the Curie point (about  $360^{\circ}\text{C}$ .) indicates that at very low temperature the magneto-crystalline effect is predominant (i.e.  $I_H$  varies approximately as  $K/I_0$ ), but that over most of the range shape anisotropy is equally or more important. For cobalt powders, examined by Weil, Marfoure and Bertaud (1948), the effects are complicated by the presence of both hexagonal and cubic forms. The interesting results obtained indicate that, at room temperature, in hexagonal cobalt the magneto-crystalline and shape effects are of comparable importance, and in cubic cobalt the shape effect predominates. Four ferronickel powders, with from 10 to 50 per cent Fe, have been investigated by Weil (1948b) over a range of effective densities as for the iron powders. For these powders the anisotropy is due almost entirely to shape. The coercivity varies with density in the way indicated by (5.8), and the ratio of the limiting value of  $I_H$  to  $I_0$  was approximately 0.5 in all cases, the limiting values of  $I_H$  ranging from about 320 to 630.

Further investigations on micro-powder materials are in active progress. This brief summary of the published work must suffice to give a general impression of what has been achieved. From a theoretical standpoint it would seem that permanent-magnet characteristics appreciably better than those that have been specified might be obtainable, but the practical difficulties are formidable. Whether or not these materials eventually acquire a value for technological applications comparable with that of the more recent permanent-magnet alloys, they are of outstanding scientific interest in many ways, particularly in relation to the account given here of permanent-magnet materials generally, in manifesting so directly the occurrence of rotational hysteresis effects in single-domain particles.

#### § 6. CONCLUSION

In this report an account is given of scientific work over a period of some sixteen years on the behaviour of ferromagnetic materials in low and moderate fields, and in particular of those investigations, both experimental and theoretical, which have contributed to a better knowledge and understanding of just 'what is happening inside a ferromagnetic when it is magnetized'. Ten years ago it would have been easy to gain the impression from much that was written on ferromagnetism that, except for a few refinements, a neat co-ordination, almost a codification, had been effected of all those properties summarized in magnetization and hysteresis curves. Such an impression will hardly have been given by this report. The diversity of the magnetic behaviour of ferromagnetics cannot be unified by a few relatively simple formulae, as has been made abundantly clear by the more recent work which has been reviewed. At the same time, notably

through the work on domain structure and boundary movement processes, the foundations have been laid for a proper analysis and interpretation of the very varied sequences of changes of magnetization accompanying changes of field in different materials, and for a much more satisfactory co-ordination of ferromagnetic characteristics than was previously possible.

It is unnecessary to give here a summary of the report; it is adequately summarized by the table of contents and the outline in the Introduction. The report is long, reflecting the amount of work which has been carried out during the period under review, but neither in fact nor in intention is it exhaustive. Little space has been devoted to work on magneto-mechanical effects, for example, for reasons mentioned earlier (§ 4(i)), but frequent reference has been made to the results obtained in their bearing on the interpretation of magnetic properties. Some of the later work on magneto-mechanical effects is surveyed by Bates (1950), who also discusses magneto-electric effects; these have not been considered here, as little more would have been possible than an isolated summary of some of the experimental results. The main omission, however, is an account of work on time effects in magnetization, except incidentally in connection with the Barkhausen effect (§ 3(iii)), and in a few other places. An adequate account would have made the report considerably longer, without adding appreciably to an elucidation of the main problems under consideration. Time effects include those diverse phenomena which have been studied under such names as magnetic viscosity, magnetic after-effect, and magnetic ageing. A discussion of these and other relaxation effects is given by Becker and Döring (1939, pp. 242–67), and there is a tentative analysis of some of them in the book by Snoek (1947); among recent papers in which new contributions are made, and which may also serve as an approach to the earlier work, are those of Snoek (1949) and of Street and Woolley (1949). The effect of macroscopic eddy currents on the time sequence of the change of magnetization after application or removal of a field is usually regarded as in principle calculable, and eddy current effects (including the skin effect) in alternating fields are treated in detail in many standard works. With increasing frequency, microscopic eddy current effects, depending on the details of the localized elementary processes of change of magnetization, become increasingly important; and considerable attention has been devoted recently both to the experimental study, and the theoretical interpretation of the variation with frequency of the reversible permeability, as measured in an alternating field, with or without a superimposed steady field. Although there are a number of unsolved problems in connection with the low-frequency effects, it is the high-frequency behaviour, in particular in the centimetre wavelength range, which is of central interest in relation to the questions discussed in this report. Some account of this work is given by Becker and Döring (1939, pp. 228–42), and there is a comprehensive review by Allanson (1945) of methods of measurement, results obtained, and ‘explanatory hypotheses’. Among recent papers may be mentioned those of Birks (1948, 1950), Johnson and Rado (1949) and Millership and Webster (1950).

This report is intended to be reasonably self-explanatory, and in consequence, like the earlier report, it overlaps to some extent books and general articles written during the period under review. A substantial part of the work considered, mainly but not entirely that since about 1939, has, however, not been previously

reviewed in any detail, or had not, at the time of writing. The balance aimed at would have been destroyed if material had been selected merely on the ground that it had not been reviewed before; but in general no more than summary accounts have been given of work of which adequate reviews are readily available. The books on magnetism and on ferromagnetism which are listed in section A of the References provide, it need hardly be said, a much fuller account of the background, and in many cases a fuller account of topics which have only been touched on here. The indebtedness to Becker and Döring's *Ferromagnetismus* (1939) will be apparent from the many references which have been made to it. The debt is not lessened by the fact that more recent work has thrown doubt on the adequacy of the co-ordinating scheme which is so convincingly maintained in that remarkable book, with its wealth of information and illuminating commentary on almost every aspect of the magnetization-curve side of ferromagnetism. In section B of the references, review articles are distinguished by quotation of their titles. Reference has already been made to all of these articles, some of which may be found useful as giving shorter general surveys of the field, and others as giving more detailed reviews of special topics. For collections of data, the review articles on magnetic materials are an indispensable complement to this report (see § 5(i)). In the references to original work, an attempt has been made to include all the more substantial papers in the field dealt with, and also the most recent papers of any closely related series. Preliminary communications and notes have been excluded except in special cases. It is believed that practically all the original work will be found at not more than one remove from the papers listed.

In closing this second and concluding report on ferromagnetism, the hope may be expressed that the two reports will enable those who are relatively unfamiliar with the field to gain a clear and reasonably detailed impression of its many-sided interest. The interest is not localized in ferromagnetic materials; for the conclusions drawn as to the internal structure (crystalline, sub-crystalline or atomic) of these materials from a study of the readily investigated ordinary magnetic characteristics may often be relevant to the structure of solids generally. The reports may also be useful to those actively engaged in the investigation of ferromagnetism, and in the development and application of ferromagnetic materials. That the reports are long is partly due to there having been no previous articles concerned exclusively with ferromagnetism in the *Reports on Progress in Physics*. The background provided may make less formidable the task of future writers of reports in this general field in enabling them to deal more readily with particular aspects of the subject, or with recent advances in those directions in which notable progress may have been made.

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