

THE TRANSITION TEMPERATURE

The transition temperature is now calculated from the equality of the free energies.

Because of the high temperatures involved, the free energies can be computed from two expressions of the form

$$F = -NU + 3RT \ln h\nu_m/kT + 3RT \ln h\nu_r/kT,$$

where ν_m and ν_r are the acoustic and optical frequencies, h is Planck's constant and k the gas constant per molecule.

The temperature at which the free energies are equal is given by

$$T = \frac{(U_1 - U_2)}{3k \ln (\nu_m \nu_r)_1 / (\nu_m \nu_r)_2}, \quad (16)$$

where the subscripts 1 and 2 refer to the CsCl type and NaCl type lattices, respectively.

By using the frequencies calculated for 0°K, the transition temperatures obtained are 810°K for CsCl and 700°K for NH₄Cl, as compared with the experimental values, 718° and 457°. These

results must be regarded as satisfactory in view of the small accuracy to be expected. Slightly better values are obtained if the corrections for the electron polarization are not made.

In calculating the transition temperatures from Eq. (16), the frequencies used should be those corresponding to the temperature T .

Because of the rapid decrease of ν_m for the CsCl type lattice as indicated in the values of Table VI, no transition point is obtained if the temperature dependence of the frequencies is considered. It appears quite probable that it is the temperature dependence of the frequencies that is incorrect rather than the values found for absolute zero.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Professor K. F. Herzfeld and to Dr. Maria Goeppert-Mayer for suggesting the present problem and for rendering much assistance during its solution.

AUGUST 15, 1937

PHYSICAL REVIEW

VOLUME 52

Coercive Force in Single Crystals

K. J. SIXTUS

Research Laboratory, General Electric Company, Schenectady, New York

(Received June 7, 1937)

The coercive force H_c of ten single crystal disks of silicon-iron has been measured in different directions in their planes. In any one disk, H_c changes with the direction; it is mainly determined by the angle α_3 between the field and the [001] axis nearly normal to the disk, and has a minimum value when that angle is 90°. The angle α_1 between the field direction and another cubic axis which lies nearly in the plane of the disk and close to the field direction has a smaller effect on H_c . The relation H_c

$= A/\cos \alpha_1 + B \cos \alpha_3$ represents very closely the curves taken on well annealed disks; A and B are constants with values close to 0.1 and 0.4, respectively. The effect on H_c of varying the disk shape and of increasing the internal strains by carburization has been studied. Finally it has been shown that H_c values calculated from the empirical relation are in good agreement with data on single crystal wires and strips (Kaya, Ruder).

1. INTRODUCTION

MAGNETIC theory can at present account satisfactorily for the behavior of ferromagnetic material near technical saturation. Our understanding, on the other hand, of what happens in low fields in general, and of the phenomenon "coercive force" in particular, is still very limited and vague. It was recognized early that internal strains in a ferromagnetic

material caused by cold work or by impurities increased the coercive force. This was proved systematically by Kussmann and Scharnow.¹ Contributions from the theoretical side were made by R. Becker, N. Akulov and by F. Bloch. Bloch² in referring to experiments by K. J.

¹ A. Kussmann and B. Scharnow, *Zeits. f. Physik* **54**, 1 (1929).

² F. Bloch, *Zeits. f. Physik* **74**, 295 (1932).

Sixtus and L. Tonks³ assumed that only inhomogeneous internal strains affect the coercive force H_c and gave an atomic picture in which he showed qualitatively how local variations in atomic spacing by their effect on the exchange integral determine the energy necessary for reversal of magnetization and thus H_c .

One could expect that a study of H_c in single crystals might yield new and useful information. Sizoo⁴ has measured a number of iron and nickel crystals without finding a relation between coercive force and crystal orientation. The spread of H_c values for crystals with similar orientation betrayed the presence of different strains in those crystals. Kaya⁵ also made measurements on iron single crystals, in wire form, but gave no relation for H_c . The first evidence of a definite dependence of H_c on crystal orientation is contained in a paper by Ruder.⁶ Kaya's and Ruder's results will be discussed later in the light of our findings.

In the present investigation⁷ it was decided to use single crystal specimens in the form of disks. This shape makes it possible to obtain a dependence of H_c on orientation, within certain limits, in one specimen by applying the field in various directions in the plane of the disk. It eliminates, at the same time, all doubt as to variations in strain state which arises when several different specimens are compared. Since H_c can be

measured directly without applying corrections in samples of any shape, there are no difficulties due to the high demagnetizing factor of disks.

2. MATERIAL

The crystals were produced in iron-silicon sheets by a strain-anneal method consisting of a two percent extension of hot rolled strips followed by a two-hour anneal at 1300°C. The crystals were carefully cut from the sheet on a lathe, polished and reannealed at 1100°C in pure dry hydrogen. In a few disks very fine crystals had grown on the circumference because of excessive strain developed during cutting. These small crystals were cut off in a lathe with greater precautions than before and no new crystal growth was visible after another 1100° anneal. Chemical analysis gave the following elements besides iron (by weight percentage): Si: 2.8; C: 0.02; Mn: 0.10; S: 0.021; P: nil. The diameters of the disks were between 2 and 2.5 cm; the original thickness ranged around 0.05 cm.

Table I gives dimensions and orientations of the 10 disks used. The orientations were determined from Laue patterns, with an accuracy of $\pm 1^\circ$ and are referred to an arbitrary line along a diameter of the disk. Crystals No. 1M and No. 5M were omitted because they each contained a small included crystal which affected the results considerably.

3. METHOD OF MEASUREMENT

The coercive force was measured directly as that value of applied field at which the induction I became zero. A coil, 17.5 cm long with a constant of 99.0 oe./amp. supplied the field in which the single crystal disk could be so adjusted that the reference line drawn on it made any angle (azimuth) with the field direction while its plane was always horizontal and therefore always in the direction of the field. A search coil of 4500 turns fitted closely around the center of the disk; it could be moved away from the disk parallel to itself and to the field. The earth's magnetic field was, at the place of the disk, compensated by a pair of Helmholtz coils. For convenience the magnetizing field was applied, and H_c was measured, in a direction at right angles to the horizontal component of the earth's field.

TABLE I. Data for single crystal disks. ϑ is the angle between an axis and its projection on the disk, φ the angle between this projection and an arbitrary disk diameter used as reference line.

No.	DIAMETER IN CM	THICKNESS IN CM	[100]		[010]		[001]	
			φ_1	ϑ_1	φ_2	ϑ_2	φ_3	ϑ_3
2M	2.35	0.043	317	19.5	224	9	20	68.5
3M	2.35	.047	23	12	291	11	156	73.5
4M	2.30	.048	2	15	268	17	129	67
6M	2.38	.047	132	38.5	44	2.5	320	51
7M	2.20	.035	250	10	158	9	27	76.5
8M	2.33	.046	277	4	187	12	19	77
9M	2.14	.044	17.5	5.5	286	9.5	133	79
10M	2.35	.049	25.5	3.5	294	23.5	122	66.5
11M	2.35	.048	321	23	226	12	109	63
12M	2.77	.048	307	17	215	5	110	72

³ K. J. Sixtus and L. Tonks, Phys. Rev. **37**, 930 (1931).

⁴ G. J. Sizoo, Zeits. f. Physik **56**, 649 (1929).

⁵ S. Kaya, Zeits. f. Physik **84**, 705 (1933).

⁶ W. E. Ruder, Trans. Am. Soc. for Metals **22**, 1120 (1934).

⁷ A short abstract has appeared in Phys. Rev. **50**, 395 (1936).

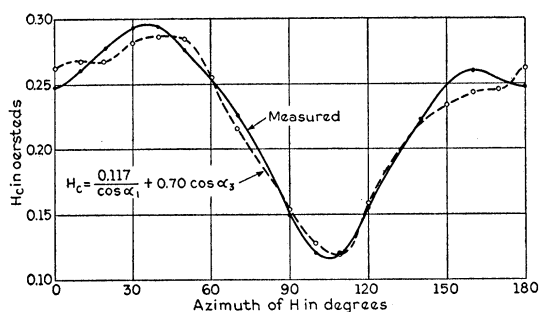


FIG. 1. Coercive force vs. azimuth in single crystal disk No. 8M.

The sample was first magnetized to 1000 oersteds which brought it to a point on the reversible part of the magnetization curve near saturation. The field was then slowly reduced to zero and increased in the opposite direction until vanishing deflection in the galvanometer circuit upon withdrawal of the coil from the sample indicated that the coercive force had been reached. The whole procedure was repeated every time in opposite field direction; a disagreement between the measured values of coercive force in the two directions would then reveal the presence of a stray field with a component in the measuring direction.

It was found at the start of the investigation that fields of even several times the strength of the earth's field did not affect H_c as long as they were applied perpendicular to the direction in which H_c was measured. Although this finding eliminated the necessity for compensating the earth's field, all measurements were made with compensation.

The measured values of H_c could be reproduced consistently within one percent if mechanical and magnetic shocks were avoided. The latter condition was fulfilled by reducing the field current gradually from its maximum value to zero with a potentiometer.

4. RESULTS

In Figs. 1, 2 and 3 curves for three disks are given whose surface normal made increasing angles with the $[001]$ axis which was most nearly normal to the surface. (No. 8M: 13° , No. 10M: 23° , No. 6M: 39° .) In each disk the coercive force shows considerable variation with azimuth of H . The range of variation obviously

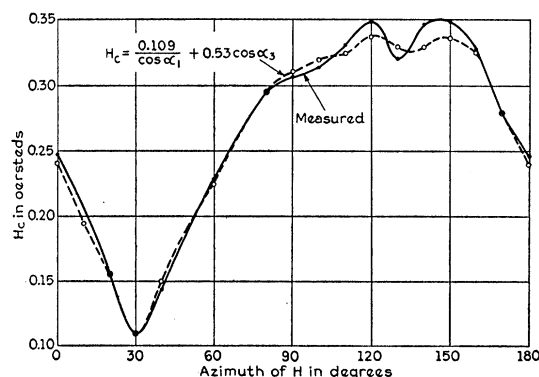


FIG. 2. Coercive force vs. azimuth in single crystal disk No. 10M.

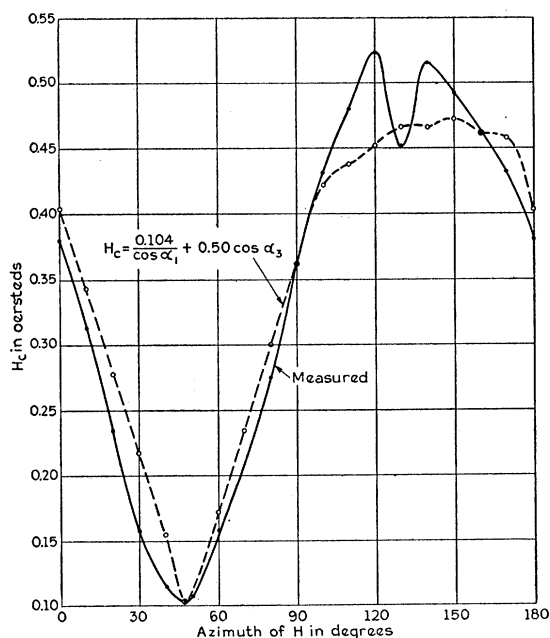


FIG. 3. Coercive force vs. azimuth in single crystal disk No. 6M.

increases with the angle between $[001]$ and the surface normal. The minimum of H_c occurs in every disk at that azimuth, where H was at right angles to $[001]$. This made it evident at once that the main factor in determining the shape of H_c curves was the $[001]$ axis while the orientation of the other two cubic axes lying more nearly in the surface had a smaller influence (Fig. 4).

An analytical expression for the curves was derived by trial and error. Satisfactory fits even with regard to detail were found by taking into account only the angles between H and the

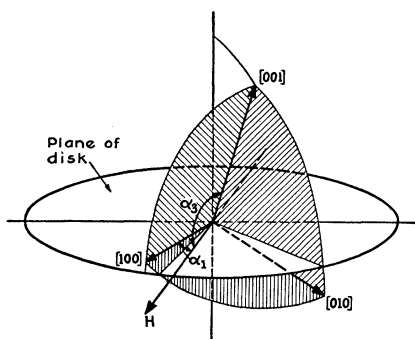


FIG. 4. [100] and [010] are cubic axes lying nearly in the plane of the disk, [001] is nearly perpendicular to it. Measurements show that α_3 has a large, α_1 only a small, influence on the coercive force.

nearest cubic axis (α_1) and between H and the [001] axis nearly normal to the surface (α_3), always measured as acute angle, and combining them in the following equation:

$$H_c = A/\cos \alpha_1 + B \cos \alpha_3. \quad (1)$$

This approximation could be expected to give the best agreement when α_1 was close to 0 and α_3 close to 90°, because only in that case was the omission of the third axis really justified. In Figs. 1 and 2, the calculated and observed curves agree quite closely, but in Fig. 3 where α_3 assumes values as low as 51° the agreement is less satisfactory. In the second term one might have expected—from symmetry considerations—a second power rather than a first power law. Such a law was actually found in one disk where H_c had been increased by diffusion of carbon (Section 6).

The constants A and B in Eq. (1) are given in Table II. The small variation from disk to disk indicates that the basic state of strain in the different disks was approximately the same and justifies comparisons between H_c values taken on different disks. On this basis we can illustrate the decisive influence of the direction of the [001] axis expressed in Eq. (1) by a striking example. We compare the coercive force in a direction as close as possible to the dodecahedral axes in disks No. 8M and 6M. In the first case where the surface is nearly parallel to a cubic plane, these values are 0.27 oe. and 0.22 oe., respectively; in the second, where the surface lies approximately in a dodecahedral plane, the value is 0.5 oe.

5. REDUCTION IN DIAMETER AND THICKNESS

The following experiments were undertaken in order to obtain the variation of the constants A and B in Eq. (1) with changes in dimensions.

Disk No. 12M was reduced on the lathe from a diameter of 2.56 cm to 2.04 cm, thus lowering its diameter to thickness ratio from 58 to 42. The constants A and B , measured after anneal, were negligibly larger. They had increased from 0.119 to 0.124, and from 0.40 to 0.42, respectively.

Etching in concentrated nitric acid with following anneal was chosen as the most suitable method of reducing the thickness. The etching left the surface smooth and even, and any absorbed hydrogen was presumably driven off during the anneal. Table III gives the variation of constants A and B for decreasing thickness in disks No. 2M and 4M. Both constants increase, A at a greater rate than B .

The observations on disk No. 12, together with the results on wires and strips reviewed in Section 7, indicate that the shape of samples may be varied within certain limits without affecting the correctness of Eq. (1) and even without much effect on the constants A and B . An extreme case for which Eq. (1) would obviously change into another one, symmetrical with respect to α_1 , α_2 , and α_3 , would be met with in a sphere. The value of A and B , but not the form of Eq. (1), changes when the thickness of the samples decreases below 0.2 mm. Our results on disks No. 2M and 4M indicate that H_c for any given azimuth begins to increase considerably when the disks are thinned down below this value. The same effect has been noted before in polycrystalline material although the critical thickness was found to be smaller. This is presumably due largely to the presence of high internal strains in the materials used in those investigations.⁸

TABLE II. The constants A and B in Eq. (1) for different disks.

Disk No.	2M	3M	4M	6M	7M	8M	9M	10M	11M	12M
A	0.096	0.119	0.109	0.104	0.108	0.117	0.113	0.109	0.130	0.119
B	.43	.43	.30	.50	.50	.70	.68	.53	.42	.40

⁸ Cf. W. Elenbaas, Zeits. f. Physik **76**, 829 (1932).

6. CARBURIZATION

The question arose whether the variation of coercive force would persist in crystals with large internal strains and accordingly high absolute values of coercive force. If the strain energy exceeded the lattice energy by a large amount and if the strains were isotropic, one should expect that the anisotropy of magnetic properties would disappear.

Chemical hardening rather than a plastic deformation of the material appeared most likely to produce strains of a random character. Disk No. 12M was heated in a mixture of charcoal and sodium carbonate for six hours at a temperature of 785° which kept it just below the γ -range for any amount of carbon which it might take up. At that temperature 0.06 percent C can be absorbed in solid solution. During slow cooling to room temperature where only 0.03 percent C can be held in solution under equilibrium conditions the excess carbon will precipitate as carbide. Quenching will preserve the high temperature condition and therefore produce a state of strain in the material.

The original H_c curve and the curves after slow cooling from 785° and after quenching in water from that temperature are shown in Fig. 5. Curve 3 obviously follows a simpler law than curve 1; the hump at 160° which is quite evident in 1 does not appear in 3. Accordingly an equation of the type of Eq. (1) no longer represents the experimental findings satisfactorily. The following expressions were found to give the best fit:

$$\text{Curve 1: } H_c = 0.124/\cos \alpha_1 + 0.42 \cos \alpha_3$$

$$\text{Curve 2: } H_c = 0.186 + 5.0 \cos^2 \alpha_3$$

$$\text{Curve 3: } H_c = 0.93 + 6.1 \cos^2 \alpha_3$$

TABLE III. Variation of A and B (Eq. (1)) with reduction in thickness.

Disk No. 2M			Disk No. 4M		
THICKNESS IN MM	A	B	THICKNESS IN MM	A	B
0.43	0.096	0.43	0.48	0.109	0.30
0.30	0.114	0.43	0.30	0.138	0.33
0.18	0.159	0.47	0.16	0.184	0.45
0.13	0.254	0.53			
After Anneal 0.13	0.298	0.60			

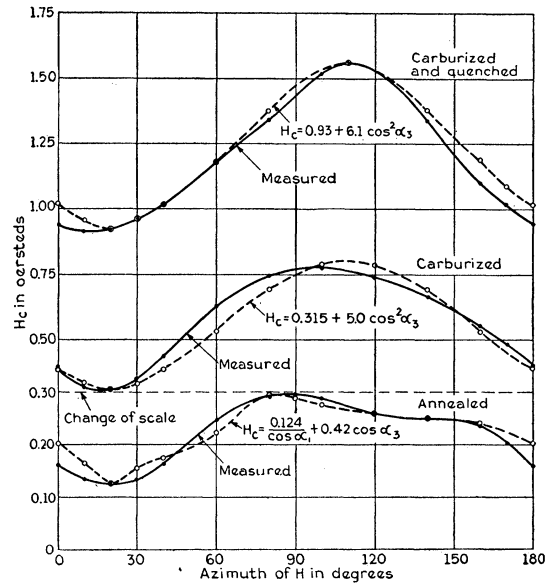


FIG. 5. The effect of carbon on H_c in disk No. 12M.

The fact that the influence of the $[100]$ and the $[010]$ axis on H_c has been eliminated while the effect of the $[001]$ axis persists can be explained in two ways. First, the carbon may diffuse into the lattice in such a fashion as to set up an anisotropic strain condition. Secondly, the strain may still be insufficient to entirely overcome the original anisotropy of the lattice. The second cause appears more plausible; a decision could very likely be made with crystals of nickel whose magnetic crystal energy is only about one-tenth that of iron.

Incidentally, an anneal first at 785° and then at 1100° in pure dry hydrogen returned the crystal to its original condition. The values of H_c in this final state did not differ more than five percent from those plotted in Curve 1.

7. DISCUSSION

The generality of Eq. (1) has been further tested by applying it to Kaya's⁵ and Ruder's⁶ data on the coercive force of single crystal wires and strips. Kaya's data on wires of electrolytic iron are given in Table IV, together with H_c values calculated from the equation $H_c = 0.08/l + 0.4n$. l , m and n in Tables IV and V stand for $\cos \alpha_1$, $\cos \alpha_2$ and $\cos \alpha_3$, respectively; α_1 being the smallest, α_3 the largest of the angles which the

TABLE IV. Coercive force of single crystal wires of electrolytic iron as measured by Kaya, compared with calculated values (wire thickness 0.2 cm).

No.	l	m	n	H_c (OERSTEDS)	
				MEAS.	CALC.
1	0.901	0.416	0.130	0.19	0.14
2	0.926	0.374	0.045	0.14	0.11
3	0.855	0.432	0.284	0.20	0.21
4	0.718	0.696	0.039	0.11	0.13
5	0.665	0.612	0.425	0.21	0.29
8	0.779	0.627	0.001	0.11	0.11
10	0.996	0.065	0.054	0.10	0.10
16	0.901	0.334	0.277	0.24	0.20
18	0.796	0.527	0.296	0.22	0.22
19	0.754	0.598	0.275	0.22	0.22
21	0.894	0.441	0.067	0.12	0.12

three {100} axes make with the wire or strip axis. Ruder's data on strips of 3.5 percent silicon iron could not be used for our purpose in their original form since his H_c values were obtained from loops with a maximum induction of only 10,000 gauss. Mr. Ruder kindly supplied us with those strips which were still available (N series) and some additional new ones (O series). They were reannealed, their H_c measured after saturation, and their orientation determined more accurately from x-ray patterns. Table V contains the new data which differ not materially from the old ones and the H_c values calculated from $H_c = 0.1/l + 0.4n$. It should be noted that n does not refer to the cubic axis most nearly perpendicular to the width of the strip but to that axis most nearly perpendicular to the axis of the strip. The agreement between calculated and measured values in Tables IV and V is, in general, satisfactory; the discrepancy in the case of No. 5, Table IV and No. 18- O , Table V is accounted for by the large values of n , for which our empirical equation cannot be expected to hold.

A complete theory would have to explain, in

TABLE V. Measured and calculated values of coercive force for Ruder's single crystal strips. Dimensions of the N -series: $1.55 \times 0.054 \times 25.0$ cm³; O -series: $1.35 \times 0.054 \times 25.0$ cm³.

No.	l	m	n	H_c (OERSTEDS)	
				MEAS.	CALC.
1- N	0.857	0.500	0.087	0.15	0.15
2- N	0.743	0.656	0.191	0.21	0.21
3-1- N	0.799	0.588	0.191	0.16	0.20
4- N	0.819	0.500	0.242	0.20	0.22
5- N	0.914	0.423	0.122	0.13	0.16
5-1- N	0.914	0.423	0.122	0.13	0.16
6- N	0.707	0.695	0.105	0.17	0.18
7- N	0.927	0.391	0.070	0.15	0.14
9- N	0.934	0.358	0.000	0.12	0.11
10- N	0.982	0.156	0.122	0.12	0.15
8- O	0.966	0.259	0.052	0.14	0.12
13- O	0.755	0.602	0.259	0.21	0.23
17- O	0.961	0.292	0.052	0.13	0.12
18- O	0.719	0.643	0.326	0.22	0.27

the first place, the particular type of relation between the variables expressed in Eq. (1). While the dependence of H_c on α_1 is obviously due to the fact that only the field component in the direction of the [100] axis is operative in reversing the magnetization along that axis, its dependence on α_3 could be accounted for only after an analysis of the distribution of elementary districts together with a consideration of their demagnetizing fields.

In connection with the constants of Eq. (1) which a theory also has to deal with we want to mention here only the remarkable agreement between the values of A and B found with three different kinds of samples as given above. Considering only A —which measures H_c along a cubic axis—this may imply that H_c is approaching a lower limit. On the basis of a nucleus concept of coercive force⁹ such a limiting value would follow naturally from the presence of minimum size nuclei.

⁹ K. J. Sixtus, Phys. Rev. **48**, 425 (1935).