

VIII

FERROMAGNETISM

8.1. The Weiss model

THE term ferromagnetism is applied to a magnetic behaviour of which iron is a typical example and which also is found in cobalt and nickel, and in certain alloys and compounds.

It was recognized by Weiss that the properties of these substances can be understood if one assumes that they consist of small domains, each of which is usually magnetized. In an apparently non-magnetic piece of iron, the directions of magnetization of the domains are distributed at random, so that the total moment is zero. The process of magnetization consists in altering the directions of the magnetization in the domains, without altering the intensity of magnetization in each. It is therefore clear that the magnetization of a domain or 'intrinsic magnetization' at any temperature is one of the most fundamental properties of a ferromagnetic.

Weiss also realized that the existence of such an intrinsic magnetization must be due to a strong interaction of the elementary magnetic moments contributed by the different atoms. This interaction must have a tendency to make the moments take the same direction.

Such an interaction is, in principle, caused by magnetic forces, but these depend sensitively on the external shape of the body, and, above all, they are, as we shall see, much too weak to explain an intrinsic magnetization except at very low temperatures. Weiss therefore postulated the existence of a 'molecular field' of unknown origin which was proportional to the magnetization, and acted on each individual magnet like a strong magnetic field.

It is now known from measurements of the gyromagnetic effect, i.e. of the ratio of mechanical angular momentum to magnetic moment, that the elementary magnets are electron spins. For the present purpose I shall assume that we may regard each magnet as a single spin, which is therefore capable of two orientations. In this case (which, of course, is not precisely the picture used by Weiss) we may then say that the spin will have a different energy according to whether it is in the direction of prevalent magnetization, or opposite to it. The energy is

$$E = \pm \mu H_m, \quad (8.1)$$

where H_m is the Weiss molecular field. The distribution of spins over the two directions is then given by Boltzmann's factor, so that

$$\frac{N_+}{N_-} = e^{2\beta\mu H_m}. \quad (8.2)$$

The total moment is therefore

$$M = \mu(N_+ - N_-) = \mu N \frac{e^{\beta\mu H_m} - e^{-\beta\mu H_m}}{e^{\beta\mu H_m} + e^{-\beta\mu H_m}} = N\mu \tanh \frac{\mu H_m}{kT}. \quad (8.3)$$

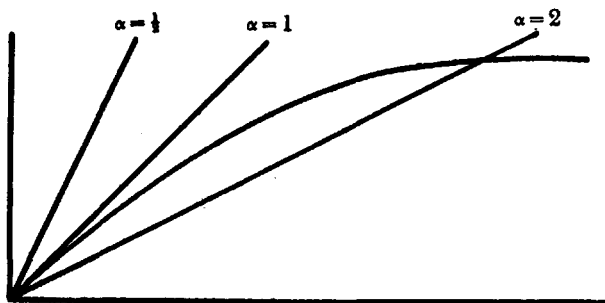


FIG. 15.

We now assume that the molecular field is proportional to the magnetization, so that

$$H_m = \frac{C(N_+ - N_-)}{N}. \quad (8.4)$$

Combining (8.3) and (8.4) we have the equation

$$\frac{M}{M_0} = \tanh \alpha \frac{M}{M_0}, \quad (8.5)$$

where

$$M_0 = N\mu; \quad \alpha = \frac{\mu C}{kT}. \quad (8.6)$$

Fig. 15 shows $y = x/\alpha$ and $y = \tanh x$ for several values of α .

An intersection represents a solution of (8.5), and the ordinate is M/M_0 . It is evident that no intersection with $M \neq 0$ exists, if $\alpha \leq 1$, i.e. if

$$T \geq \frac{\mu C}{k} = \Theta. \quad (8.7)$$

This determines the 'Curie point' Θ , above which the spontaneous magnetization vanishes. Below Θ there always exists a solution, which for decreasing temperature rapidly approaches saturation. It is easily seen that, for temperatures just below Θ ,

$$\left(\frac{M}{M_0}\right)^2 = 3 \frac{\Theta - T}{\Theta}, \quad (8.8)$$

whereas at very low temperatures

$$\frac{M}{M_0} = 1 - 2e^{-\Theta/T}. \quad (8.9)$$

Equation (8.8) shows that the magnetization disappears continuously, but has an infinite temperature derivative at the Curie point. This sharply defined temperature is a characteristic feature of a 'co-operative' phenomenon, in which the simultaneous interaction of very many particles plays a part.

In quantitative detail (8.5), and the limiting laws (8.8) and (8.9), are not in good agreement with observation, but they do show the right qualitative behaviour. In order to account for the order of magnitude of the Curie point, which in iron is about $1,000^\circ$, μC , the energy of one spin when all others are parallel, should be of the order of 0.1 eV. If the molecular field was a magnetic effect, this would therefore require a field of the order of $1.5 \cdot 10^7$ gauss, which is much too high.

The correct explanation was given by Heisenberg. He pointed out that an effect of just this kind would be provided by electron exchange effects. In any electronic system containing two electrons in different orbital states, we may have the electron spins either parallel or opposite. In the first case we have to form the antisymmetric, in the second the symmetric combination of the orbital wave functions. The two belong to different spatial distributions of the electrons and in the case of parallel spin the electrons are less likely to be very close to each other, with a corresponding reduction in their interaction energy. The same cause is responsible for the separation between different multiplet terms in atomic spectra. Of several multiplets with the same configuration (i.e. the same individual levels for the separate electrons) the one with the highest multiplicity, and therefore the largest resultant spin, in general has the lowest energy, and the energy differences are of the order of an eV and therefore sufficient for the effect here required.

The electron exchange provides therefore a mechanism that can explain the existence of ferromagnetism. This opens the way, in principle, to a quantitative treatment. In the next few sections we shall consider two methods that have been applied to this problem in the past, starting from different approximations. These are known, respectively, as the theory of spin waves, and the collective electron theory. Of these the latter follows more closely the lines of the approximation to a metal which we have used in previous chapters, but is the more difficult one mathematically, and little is known as yet about the properties of its

solutions. It will therefore be more convenient to discuss the spin-wave theory first.

8.2. The spin-wave theory. One dimension

It is evident that ferromagnetism depends on the interaction between the electrons and that we therefore must not neglect the interaction between electrons, as we have mostly done up to now. We must therefore consider the whole system of ions and electrons, and one simple way of doing this is to start from neutral atoms. We imagine that N neutral atoms, each for simplicity containing one valency electron, are brought together to form a crystal.

If we may still regard the atoms as well separated, and each electron strongly bound to its atom, the situation is similar to that of the strong-binding approximation of § 4.2. However, in that case we took the electrons as moving independently, so that the chance of finding two electrons in the same atom would be no less than that of finding them in two different places. The electron interaction will reduce the likelihood of having two electrons located in the field of the same ion, and for simplicity we exaggerate this by assuming that it may never happen. In that case each atom contains just one electron, and the only freedom we have is in arranging their spins.

This model, which is the same as that used in the Heitler-London theory of the hydrogen molecule, cannot give any conductivity, since it assumes that the electrons cannot pass over each other, and the probability of a whole column of electrons making a simultaneous quantum jump is extremely small.

To employ such a model in the case of a metal is not as inconsistent as might appear at first sight. Mott and Jones (1936) have shown that in the ferromagnetic metals, in which the atomic $3d$ and $4s$ levels lie very close together, one must regard both these states as partly filled. If one considered only the $3d$ states, they would give rise to a very narrow band, since the overlap of neighbouring wave functions is small, whereas the $4s$ states by themselves give rise to a wide band. If we constructed Bloch wave functions by the method of § 4.2, suitably amended to include several different atomic states, we would find that the wave functions are in general mixtures of the d and s states, but there will be only a small region within the conduction band in which the $3d$ states will play a prominent part. It is therefore a reasonable approximation to distinguish $3d$ and $4s$ electrons even in the crystal, and Mott and Jones also show that it is mostly the $3d$ electrons which are responsible for the

magnetism, whereas the $4s$ electrons, which form a wider band, and therefore have greater velocities, would be expected to be responsible for the conductivity. The Heitler–London model would then be intended to describe only the $3d$ electrons.

To explain the procedure, we assume that there is only one electronic state per atom, and we consider the case of a linear chain of atoms.

If the atoms were well separated, the state of the system would have to be described by means of the atomic wave function $\phi_n(x)$ of the n th atom, in which only the coordinate x of the valency electron is shown explicitly, and a spin function χ_μ of that electron, where μ indicates some component of the spin and may equal $\frac{1}{2}$ or $-\frac{1}{2}$. We may now specify the state by writing down the spin component of each atom, i.e. by a set of numbers $\mu_1, \mu_2, \dots, \mu_N$. For brevity we shall use the symbol $\{\mu\}$ for the whole set of numbers.

The wave function belonging to this set is then

$$\Phi\{\mu\} = \frac{1}{\sqrt{(N!)}} \begin{vmatrix} \phi_1(x_1)\chi_{\mu_1}(1) & \phi_2(x_1)\chi_{\mu_2}(1) & \dots & \phi_N(x_1)\chi_{\mu_N}(1) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N)\chi_{\mu_1}(N) & \phi_2(x_N)\chi_{\mu_2}(N) & \dots & \phi_N(x_N)\chi_{\mu_N}(N) \end{vmatrix} \quad (8.10)$$

where x_1, x_2, \dots, x_N are coordinates of the N electrons, $\chi_{\mu_1}(1)$ is the spin function of the first electron having component μ_1 . This function is antisymmetric in the electrons as required by Pauli's principle, and the factor in front of the determinant secures the correct normalization.

If the atoms are now placed at a finite distance from each other, (8.10) is no longer an energy eigenfunction, since it ignores the interaction of each electron with the field of other atoms and the electrons in them. We therefore look for the best combination of functions of the class (8.10) which will approximate to an exact solution, and to do this we proceed as in § 4.2 to minimize the expectation value of the total energy.

We define a combination

$$\Psi = \sum_{\{\mu\}} A\{\mu\} \Phi\{\mu\} \quad (8.11)$$

and we determine the coefficients by minimizing the energy

$$E - E_0 = \frac{(\Psi^*(H - E_0)\Psi)}{(\Psi^*\Psi)} = \frac{\sum A^*\{\mu\} A\{\mu'\} (\Phi^*\{\mu\} (H - E) \Phi\{\mu'\})}{\sum A^*\{\mu\} A\{\mu'\} (\Phi^*\{\mu\} \Phi\{\mu'\})}, \quad (8.12)$$

where H is the Hamiltonian, and the brackets imply an integration over all electron coordinates and summation over spin variables. E_0 is the

energy of N single atoms. This expression is stationary if the A satisfy the equation

$$\sum_{\{\mu'\}} [(E - E_0)(\Phi^*\{\mu\} \Phi\{\mu'\}) - (\Phi^*\{\mu\}(H - E_0)\Phi\{\mu'\})A\{\mu'\}] = 0. \quad (8.13)$$

Now in forming the product of two functions (8.10) we obtain a number of terms containing the product of two different atomic wave functions

$$\phi_n^*(x)\phi_{n'}(x). \quad (8.14)$$

For $n \neq n'$ these products are always small, since in the spirit of the approximation we take the atomic distance as rather larger than the atomic radius, so that the overlap between the wave functions is small. The largest terms will therefore be those in which we take corresponding terms from the two determinants, so that the electron which occurs in one factor in the n th atom is in the same atom in the other factor. Such terms, however, occur only if $\mu_{n'} = \mu_n$, since otherwise the spin functions are orthogonal. The largest contribution to (8.13) therefore comes from the term in which $\{\mu'\} = \{\mu\}$. In that case the large terms give

$$(\Phi^*\{\mu\}\Phi\{\mu\}) = 1, \quad (8.15)$$

$$(\Phi^*\{\mu\}(H - E_0)\Phi\{\mu\}) = \sum_{n \neq n'} \alpha_{n,n'}, \quad (8.16)$$

where

$$\alpha_{n,n'} = \iint |\phi_n(x)|^2 |\phi_{n'}(x')|^2 [U_n(x) + \frac{1}{2}V(x, x') + \frac{1}{2}W] dx dx' \quad (8.17)$$

is the mean energy change of the n th electron due to the presence of the atom n' . $U_n(x)$ is the potential of the core of the atom n' , as in § 4.2, $V(x, x')$ is the interaction between the two electrons, and W that of the cores. The factor $\frac{1}{2}$ in the last two terms is there because otherwise the interaction between any two particles would be counted twice. The integral $\alpha_{n,n'}$ depends only on the distance between n and n' and decreases rapidly with that distance. We neglect all terms except those for adjacent atoms. If we write α for $\alpha_{n,n+1}$, then (8.16) is $2N\alpha$.

We now go one step further and include terms with overlap factors of the type (8.14), provided they do not contain more than two such factors, and we allow only overlap between adjacent atoms. In the diagonal term $\{\mu\} = \{\mu'\}$, we then get a further contribution by multiplying two products from the determinant (8.10) in which two adjacent electrons with the same spin have been interchanged. (If the spins are different, the product vanishes because of the orthogonality of the χ .) This contributes to (8.15) the term $-r|\beta|^2$, where

$$\beta = \int \phi_n^*(x)\phi_{n+1}(x) dx \quad (8.18)$$

and r is the number of pairs of adjacent parallel spins. The contribution to (8.16) is $-r\gamma$, where

$$\gamma = \iint \phi_n^*(x) \phi_{n+1}^*(x') [U_n(x') + U_{n+1}(x) + V(x, x') + W] \times \\ \times \phi_n(x') \phi_{n+1}(x) dx dx'. \quad (8.19)$$

In the bracket of the 'exchange integral' the first two terms are negative, whereas the other two are positive. The factors outside the bracket taken together are positive when $x = x'$, but, if the wave function has nodes, will be negative in other parts. We shall for the present take γ as positive, since this is the case in which we shall find ferromagnetic behaviour.

Terms of the order β and γ now appear also when $\{\mu\}$ and $\{\mu'\}$ are not identical, but differ merely by interchanging two opposite spins. In that case

$$\left. \begin{aligned} (\Phi^*\{\mu\} \Phi\{\mu'\}) &= -\beta^2 \\ (\Phi^*\{\mu\} (H - E_0) \Phi\{\mu'\}) &= -\gamma \end{aligned} \right\}. \quad (8.20)$$

Combining all these results, we find that (8.13) takes the form

$$[(E - E_0)(1 - r\beta^2) - 2N\alpha + r\gamma] A\{\mu\} = \sum_{\{\mu'\}} [(E - E_0)\beta^2 - \gamma] A\{\mu'\} \quad (8.21)$$

provided it is understood that the sum on the right includes only those spin arrangements which differ from $\{\mu\}$ by the exchange of two adjacent opposite spins.

It is now plausible that we are justified in neglecting β^2 , which appears always multiplied by $(E - E_0)$, which is itself of the first order in the small quantities α , β^2 , γ , since without the interactions and overlap evidently $E = E_0$. We also note that $N - r$ is the number of adjacent pairs of unlike spins, which is just the number of terms on the right-hand side.

With the abbreviation

$$\epsilon = E - E_0 - 2N(\alpha - \gamma/2) \quad (8.22)$$

the equation for the A is finally

$$\epsilon A\{\mu\} = \gamma \sum_{\{\mu'\}} (A\{\mu\} - A\{\mu'\}). \quad (8.23)$$

Here the sum is to be understood with the same restriction as before. It therefore, in particular, does not connect spin arrangements which have different values of the total component

$$m = \sum_n \mu_n. \quad (8.24)$$

(This is true quite generally and not merely to the approximation used here.) We may therefore consider each m value separately. The

simplest case is $m = N$, when all spins are parallel. Then the sum in (8.23) is empty, and $\epsilon = 0$.

Next take $m = N - 1$, i.e. one spin reversed. If its position is denoted by n , we may use n to identify the spin arrangement $\{\mu\}$, and (8.23) becomes

$$\epsilon A_n = \gamma(2A_n - A_{n+1} - A_{n-1}) \quad (8.25)$$

with the solution

$$A_n = \text{constant} \times e^{i\epsilon a n}, \quad \epsilon(g) = 2\gamma(1 - \cos ga). \quad (8.26)$$

Here we have again included the atomic distance a in the definition of the phase factor for the convenience of later generalization. In analogy with §§ 1.5 and 4.2 it follows again that g must be real and a multiple of $2\pi/Na = 2\pi/L$, where L is the length of the chain, and that it will be convenient to assume it to lie between $-\pi/a$ and π/a . The energy values form a practically continuous band from $\epsilon = 0$ to $\epsilon = 4\gamma$.

This result shows up one of the important qualitative differences between the Weiss model and the present picture. Whereas in the Weiss model the energy required to reverse a spin from the completely saturated state is equal to the constant quantity $4k\Theta$, we now find a continuous distribution of energy values. This tends to increase the number of 'wrong' spins at low temperatures. In fact, as we shall see, in the one-dimensional case it is so easy to reverse a spin that one does not get any ferromagnetic behaviour at all.

Consider now the case $m = N - 2$. Then we characterize the spin arrangement by stating the positions n_1, n_2 of the two spins which are 'wrong'. We therefore have an amplitude $A(n_1, n_2)$ which is defined only when $n_1 \neq n_2$ and we may also assume that $n_1 < n_2$. Then (8.23) takes the form

$$\epsilon A(n_1, n_2) = \gamma[4A(n_1, n_2) - A(n_1 + 1, n_2) - A(n_1 - 1, n_2) - A(n_1, n_2 + 1) - A(n_1, n_2 - 1)] \quad (n_2 \neq n_1 + 1), \quad (8.27a)$$

$$\epsilon A(n, n + 1) = \gamma[2A(n, n + 1) - A(n - 1, n + 1) - A(n, n + 2)]. \quad (8.27b)$$

The right-hand side of (8.27a) is a sum of two operators, of which the first acts only on n_1 , the second only on n_2 , and consequently we can find a solution of this equation in the form of a product

$$e^{i\alpha(g_1 n_1 + g_2 n_2)}, \quad (8.28)$$

but this will not satisfy (8.27b). We can, however, meet this second requirement by combining two solutions of this type with suitable coefficients. This situation is to be interpreted as follows. (8.28) describes two separate 'wrong spins' or 'spin waves' travelling along the chain. We may form an almost stationary state by building wave packets for

each of the two spins, and, if they are well separated, the amplitude $A(n_1, n_2)$ vanishes near $n_1 = n_2$, and therefore (8.27 *b*) does not arise. However, the two wave packets will travel with a velocity which will obviously be the group velocity

$$v(g) = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial g} = \frac{2\gamma a}{\hbar} \sin ga \quad (8.29)$$

for each. These will in general be different, and so the two spin waves will meet after some time. The correction required by (8.27 *b*) then results in scattering. In this scattering process the translational invariance of the problem will, in complete analogy with previous collision problems, lead to the equation

$$g'_1 + g'_2 - g_1 - g_2 = K, \quad (8.30)$$

where K in this linear case is either 0 or $2\pi/a$.

However, solutions of the form (8.28) with real g_1, g_2 are not the only solutions of (8.27 *a*) which are physically reasonable. This is because by definition $n_2 - n_1$ is positive, and if we give to g_1 and g_2 equal and opposite imaginary parts, this may lead to a solution which decreases exponentially as $n_2 - n_1$ is large. This leads to a solution of the form

$$A(n_1, n_2) = \text{constant} \times e^{iGa(n_1+n_2) - ba(n_2-n_1)}, \quad (8.31)$$

where b has a positive real part. Inserting this in (8.27), some simple algebra gives the relations

$$\begin{aligned} \cos Ga &= e^{-ba}, \\ \epsilon &= 2\gamma \sin^2 Ga. \end{aligned} \quad (8.32)$$

There is thus just one solution for each value of G ; its energy is positive, but less by a factor $\cos^2 \frac{1}{2}Ga$ than the least energy of two separate spin waves whose wave vectors add up to $2G$; the latter by (8.26) is $8\gamma \sin^2 \frac{1}{2}Ga$.

The solution (8.31) has been called a 'spin complex' by Bethe (cf. Bethe and Sommerfeld, 1933). It represents a state in which the two wrong spins are bound together. Since adjacent spins have a preference for being parallel, it is plausible that it should take less energy to produce two wrong spins if they are kept together. But since there are altogether N possible values for G , and therefore N such bound states, they are statistically negligible compared to the 'free' spin-wave solutions (8.28), whose number is practically N^2 .

For still smaller values of m , i.e. more wrong spins, we find again states with only free spin waves, which scatter each other on collision, and spin complexes of varying size which may also scatter each other and the single spins. Bethe has shown how to construct the general solution, but since it has not proved possible to generalize this solution to two or three dimensions we shall not discuss the details here.

All the solutions we have found have $\epsilon \geq 0$, i.e. energies not lower than that of the fully magnetized state $m = N$. This suggests that there exists no level with negative ϵ . This conjecture can be confirmed by the following argument. Suppose there were one level with negative ϵ . In the corresponding state function (8.11), choose the coefficient with the greatest modulus. This must exist, since the number of coefficients is finite. If several coefficients have equal modulus, we may choose any one of them. Let this belong to the arrangement $\{\mu^{(1)}\}$. Then (8.23) says that

$$A\{\mu^{(1)}\} \left[1 - \frac{\epsilon}{(N-r)\gamma} \right] = \bar{A}, \quad (8.33)$$

where $N-r$ is, as before, the number of pairs of adjacent opposite spins, and \bar{A} denotes the arithmetic mean of all coefficients occurring on the right-hand side of (8.23). If ϵ is negative, the factor on the left is greater than unity, and hence

$$|\bar{A}| > |A\{\mu^{(1)}\}|.$$

There must therefore be some coefficient which occurs in the average, and which exceeds $A\{\mu^{(1)}\}$ in modulus. This is a contradiction. We conclude that no state has lower energy than that with $m = N$. (The same argument shows that no state can have $\epsilon > 2N\gamma$.)

We can also find easily the mean energy of all states. A well-known theorem states that the mean of all eigenvalues of the set of equations (8.23) is equal to the diagonal sum of the coefficients on the right, which is γ times the mean value of $N-r$ over all spin arrangements. This is

$$\bar{\epsilon} = \frac{1}{2}N\gamma. \quad (8.34)$$

8.3. Spin-wave model and ferromagnetism

We now turn to the case of a three-dimensional crystal, with one atom per cell, but otherwise keep all our simplifying assumptions.

It is then evident that we again obtain equation (8.23), where $\{\mu\}$ now means an arrangement of spins, each $\pm \frac{1}{2}$, over all lattice points, and $\{\mu'\}$ is an arrangement differing from it by the exchange of any two adjacent opposite spins. ϵ now has to be defined as

$$\epsilon = E - E_0 - zN(\alpha - \frac{1}{2}\gamma), \quad (8.35)$$

where z is the number of neighbours which each atom has in the lattice. Again the state $m = N$ has $\epsilon = 0$, and the argument that no lower energy is possible applies directly. For one 'wrong' spin, we obtain in place of (8.26) a solution

$$A_{\mathbf{a}} = \text{constant} \times e^{i\mathbf{g} \cdot \mathbf{a}_1}, \quad (8.36)$$

with the energy $\epsilon(\mathbf{g}) = \gamma \sum_{\mathbf{l}} (1 - \cos \mathbf{g} \cdot \mathbf{a}_1), \quad (8.37)$

the sum to be extended over the z lattice vectors \mathbf{a}_i which join a given atom to its neighbours. For more than one 'wrong' spin we again have to consider combinations of spin waves which will scatter each other, and there may be spin complexes in which any number of wrong spins may be bound together.

Now we expect, and the calculations will confirm, that in statistical equilibrium at low temperatures most of the spins will be parallel, so that the number of wrong spins is a small fraction of N , and that the existing spin waves will all have small \mathbf{g} . In that case we may neglect the scattering of the spin waves by each other, and also neglect the spin complexes.

That the latter is justified is not quite trivial, since the spin complexes represent, for each given total wave number, the state of lowest energy. However, we saw in (8.32) that for given total wave number $2G$ the energy of the spin complex differed from the state of two free spin waves by a factor $\cos^2 \frac{1}{2}Ga$, which for small G means a correction of higher order. This situation has been discussed for the one-dimensional case by Bethe.

We may then assume the spin waves independent, and introduce the number $n(\mathbf{g})$ of spin waves of wave vector \mathbf{g} as variable. We may apply Bose-Einstein statistics to these and find in the usual way that

$$\bar{n}(\mathbf{g}) = \frac{1}{e^{\epsilon(\mathbf{g})/kT} - 1}, \quad (8.38)$$

and for low temperatures we need to know $\epsilon(\mathbf{g})$ for small \mathbf{g} . In that case, expanding the cos in (8.37),

$$\epsilon = \frac{1}{2}\gamma \sum_i (\mathbf{g} \cdot \mathbf{a}_i)^2,$$

which for cubic symmetry may be replaced by

$$\epsilon = \frac{1}{2}\gamma z d^2 g^2,$$

where d is the distance between nearest neighbours. For a simple, body-centred, or face-centred cubic lattice of cube side a this comes to

$$\gamma a^2 g^2. \quad (8.39)$$

With this result, and using the fact that the density of permissible values of \mathbf{g} in reciprocal space is $1/(2\pi)^3$ per unit volume, we find for the total number of spin waves per unit volume

$$\frac{1}{(2\pi)^3} \int \frac{4\pi g^2 dg}{e^{\gamma a^2 g^2/kT} - 1}. \quad (8.40)$$

When $kT \ll \gamma$, the integrand is small for g values comparable with the size of the basic cell, and we may therefore integrate to infinity. (At

higher temperatures the approximations made previously would not be justified.) Then the proportion of 'wrong' spins is

$$\frac{1}{2\pi^2\nu} \left(\frac{kT}{\gamma} \right)^{\frac{3}{2}} \int_0^{\infty} \frac{x^2 dx}{e^{x^2} - 1}, \quad (8.41)$$

where ν is the number of atoms in a volume a^3 , i.e. 1 for the simple cubic, 2 for the body-centred, and 4 for the face-centred lattice. The integral is 2.317 and we finally find for the magnetization at low temperatures

$$M = M_0 \left[1 - \frac{0.1174}{\nu} \left(\frac{kT}{\gamma} \right)^{\frac{3}{2}} \right]. \quad (8.42)$$

This $T^{\frac{3}{2}}$ law seems in good agreement with the approach to saturation of real ferromagnetic metals at low temperatures. It is clear that our model does not apply precisely to those metals, since none of them has, at $T = 0$, exactly one Bohr magneton per atom. In Fe and Co, the number is nearer 2, and a more realistic approach here would be to assume two spins per atom. These will not be free to orient themselves independently, but will be linked by the interaction within one atom, which is stronger than the interatomic forces which we have considered. The atom therefore has a resultant spin of one unit, which has three possible orientations, its component in any direction being 1, 0, or -1 . We must therefore consider 3^N states of the whole system. At temperature zero we may take all atoms in the state $m = 1$, and at low temperatures we must consider a few atoms in the state 0 and a few others in the state -1 . A detailed discussion shows, however, that the completely reversed atoms ($m = -1$) are statistically negligible at low temperatures, and that for the others (8.36) and (8.37) still apply, so that the answer (8.42) for the low-temperature law is still correct (cf. Marshall, 1954).

A further complication is that we believe the magnetic electrons to be in $3d$ states of the atom, so that their wave functions are not isotropic. Such a state would normally have an orbital angular momentum as well as that due to spin. Since it is known from the gyromagnetic effect that the orbits play no part, we must assume that, because of the effect of the neighbouring atoms, the orbital moment of each atom is locked in a certain position absolutely, or relatively to the orbits of its neighbours, so that the orbits cannot respond to an external magnetic field.

Nevertheless, the wave functions will not be isotropic, and instead of a single exchange integral γ , we should really have to introduce several different quantities. No theory has yet been developed which would allow this fact to be taken into account.

It has also not proved possible to evaluate the magnetization at temperatures near the Curie point, and therefore we do not know whether the value of the Curie temperature would come out right if we took the value of the exchange integral from the low-temperature behaviour by (8.42). We also do not know whether the nature of the singularity in the magnetization curve or in the specific heat near the Curie point would be right.

It is possible to give the limiting behaviour at high temperatures far above the Curie point. Since in our model the number of states is finite, they become all equally probable at high temperatures, and the energy content becomes equal to their mean energy, which for one spin we have found to be $\frac{1}{2}N\gamma$. The value for two spins per atom can be found equally easily. Thus the integral over the magnetic specific heat (i.e. the observed specific heat corrected for the specific heat of the lattice) should at high temperatures reach a finite, and predictable, limit. In fact, the specific heat keeps rising even above the Curie point, and the amount is far too large to represent the specific heat of the $4s$ electrons. This shows up the limitation of the spin-wave picture; the electrons must have more freedom of movement than our simple model permits.

8.4. The collective electron model

The name 'collective electron' model is not very descriptive, since any theory of ferromagnetism must of necessity take the collective effect of many electrons as the basis, but it seems to have established itself as the name for the picture in which one starts from the problem of a single electron moving in a periodic field, as we have done in Chapter IV, and then considers the interaction between the electrons as a further modification.

In this picture we therefore start from a wave function like (8.10), in which, however, now the individual particle wave functions are not atomic functions, but solutions $\psi_{\mathbf{k}}(\mathbf{r})$ for the periodic field. For simplicity we may consider only states from a given band, and thus omit the suffix l .

There are now, however, far more such functions to consider than before. For example, in the simplest case of N electrons, each in the periodic field of N atoms, we have to distribute N electrons amongst $2N$ spin and orbital states, and this gives $(2N)!/(N!)^2$ which is asymptotically 2^{2N} , instead of 2^N as in the spin-wave model. In addition, the states from which we start do not now all have the same energy. The mathematical problem arising from this model is therefore very much

harder than the previous one, and very little is as yet known about the properties of its solutions.

Some indication can, however, be obtained from the following argument, which is due to Bloch (1929): We consider only wave functions which consist of a single determinant (8.10), and we restrict ourselves to the following two cases: (a) The electrons fill the $N/2$ lowest orbital states, with two electrons in each state, which must, of course, have opposite spins. This state has total spin zero, and we shall call this determinant function Φ_0 . (b) The electrons fill the N lowest states, with one electron in each. Moreover, we assume all spins parallel. The total spin is $N/2$, and we shall call this determinant function Φ_M .

These functions are solutions of the Schrödinger equation of the system, except for the interaction between the electrons. To obtain the expectation value of the energy we must therefore add to the single-particle energy the diagonal element of the electron interaction.

In this case the single-particle functions are orthogonal, being different solutions of the same Schrödinger equation; hence the determinant function (8.10) is correctly normalized. This follows since after squaring the function, for each of the $N!$ terms in the first factor, there will only be one of the terms in the second factor that is not orthogonal to it, namely the one in which the same element is taken from each row. The square integral of each term in the determinant is evidently unity, so that the factor $1/N!$ is just right for normalization.

Now consider the diagonal element of

$$\frac{e^2}{r_{ij}}, \quad (8.43)$$

where i and j refer to two electrons and r_{ij} is their distance. Consider a particular term from the first determinant. Now two terms from the second determinant may give non-vanishing integrals: the same term as in the first factor, in which the electrons i and j appear in the wave functions with wave vectors \mathbf{k} and \mathbf{k}' , and have spins μ and μ' respectively, and that in which they have been interchanged. The first is

$$\alpha(\mathbf{k}, \mathbf{k}') = \int |\psi_{\mathbf{k}}(\mathbf{r})|^2 |\psi_{\mathbf{k}'}(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}', \quad (8.44)$$

and the second is the exchange integral

$$-\gamma(\mathbf{k}, \mathbf{k}') = \int \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}^*(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') \psi_{\mathbf{k}'}(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad (8.45)$$

if the spins μ, μ' are equal, and otherwise zero by the orthogonality of the wave functions.

Adding all terms together, and summing (8.43) over i and j , we find for the expectation value of the total energy in the case of the function Φ_0

$$2 \left\{ \sum E(\mathbf{k}) + \sum \alpha(\mathbf{k}, \mathbf{k}') - \frac{1}{2} \gamma(\mathbf{k}, \mathbf{k}') \right\}, \quad (8.46)$$

where the sum extends over values of \mathbf{k} belonging to the $\frac{1}{2}N$ lowest eigenvalues $E(\mathbf{k})$. The second term represents the electrostatic interaction of the average electron density with itself, and should be omitted, since this has already been allowed for in the definition of the single-particle potential (cf. Chapter IV), and the energy of the state Φ_0 is therefore

$$2 \left\{ \sum E(\mathbf{k}) - \frac{1}{2} \sum \gamma(\mathbf{k}, \mathbf{k}') \right\}. \quad (8.47)$$

In the same way we find for the mean energy of Φ_M

$$\left\{ \sum E(\mathbf{k}) - \frac{1}{2} \sum \gamma(\mathbf{k}, \mathbf{k}') \right\}, \quad (8.48)$$

the sums now extending over the N lowest states.

Evidently the first term in (8.48) is larger than that in (8.47), since we have moved electrons to states of higher energy. On the other hand, the other term will also be larger, since the sum now contains N^2 terms as compared to $N^2/4$ terms in (8.47), a change which should more than outweigh the factor 2 in front. Which of these two states gives lower mean energy depends therefore on the ratio of the exchange term to the single-particle energy.

For an idea of the magnitudes, one may take the case of free electrons. Then

$$\gamma(\mathbf{k}, \mathbf{k}') = \frac{4\pi^2 e^2}{V(\mathbf{k} - \mathbf{k}')^2}, \quad (8.49)$$

where V is the volume (cf. (6.65)). Hence (8.47) becomes

$$2 \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| < k_0} d^3\mathbf{k} \frac{\hbar^2}{2m} k^2 - \frac{2\pi^2 e^2 V}{(2\pi)^6} \int_{|\mathbf{k}| < k_0} \frac{d^3\mathbf{k} d^3\mathbf{k}'}{|\mathbf{k} - \mathbf{k}'|^2}, \quad (8.50)$$

where

$$k_0^3 = \left(\frac{3\pi^2 N}{V} \right). \quad (8.51)$$

After evaluating the integrals, the energy per unit volume is

$$\frac{\hbar^2}{10\pi m} k_0^5 - \frac{2e^2}{(2\pi)^3} k_0^4. \quad (8.52)$$

Similarly, for Φ_M ,

$$\frac{\hbar^2}{20\pi m} 2^{\frac{1}{2}} k_0^5 - \frac{e^2}{(2\pi)^3} 2^{\frac{1}{2}} k_0^4. \quad (8.53)$$

Of these two expressions, the second is lower if

$$k_0 < \frac{5me^2}{2\pi^2 \hbar^2} \frac{2^{\frac{1}{2}} - 2}{2^{\frac{1}{2}} - 2}. \quad (8.54)$$

It would therefore appear that the state with all electron spins parallel is the lowest state of the system if the electron density is low enough.

This result is no more than an indication of a trend, and an illustration of the fact that the exchange energy, which tends to set the spins parallel, increases more slowly with electron density than the kinetic energy of the Fermi gas, which favours opposite spins, so that ferromagnetism is favoured by a low electron density (small k_0). If one can generalize the result to electrons in a periodic field, (8.54) shows that a high effective mass favours ferromagnetism, which is in the right direction for the electrons in the narrow d -band of the actual ferromagnetic substances.

However, it is obvious that (8.52) and (8.53) must not be regarded as approximations to the correct position of the lowest energy level even for the hypothetical case of free electrons in the field of a uniform positive charge distribution. It is true that Φ_0 is the only state which has the lowest possible single-particle energy, and Φ_M is of all states of maximum spin the one with the lowest single-particle energy. But it is possible to construct very many other states of spin 0 or spin $\frac{1}{2}N$ by raising a few electrons to states just outside the edge of the Fermi sphere. This raises the single-particle energy by a very small amount, but in mixtures of such states we have freedom to make the exchange energy more negative. In fact, the matrix element (8.49) of the electron interaction is particularly large for states with very nearly the same momentum, and therefore the interaction energy is particularly sensitive to a mixture of states differing by very small changes in the electron momenta.

The importance of considering linear combinations of the determinantal function is also brought out by the fact that we must expect electrons with opposite spin, which are therefore not kept apart from each other by the Pauli principle, to be pushed from each other by the Coulomb force. This effect, which was mentioned in connexion with Wigner's work in § 5.2, represents a correlation between the electrons in coordinate space, and this can be achieved only by using linear combinations of products in momentum space. This effect reduces the electrostatic interaction, particularly in the case of low spin, and therefore tends to work against ferromagnetism.

The problem is even more difficult if we are not content to find out whether the state of lowest energy has a high spin value, but also want to find the magnetization as a function of the temperature. To do so, we must consider also the situation when not all the electrons occupying orbital states singly have their spins parallel. In that case we have, even for a given momentum distribution of the electrons, and for given total

spin, many different determinantal wave functions, as in the spin-wave model.

Because of these mathematical difficulties no convincing solution of the problem has as yet been given. Nevertheless, the collective electron picture has certain advantages over the spin-wave model. It fits in naturally with the fact that the saturation moment is in general not a whole number of Bohr magnetons per atom, and it explains the rising specific heat well above the Curie point.

In the original paper by Bloch (1929) to which I have referred, the problem is simplified by assuming for each state a definite distribution of electrons in momentum space and then replacing the energy of all states of given spin, by their average. Stoner (1948) has given an extensive discussion of the consequences of this model.

8.5. Neutron scattering

It has been pointed out by Moorhouse (1951) that experiments on the scattering of very slow neutrons by ferromagnetic crystals would be capable of giving some rather detailed insight into the mechanism of ferromagnetism. Although suitable experiments are not easy and have not yet been carried out, it is of some interest to discuss this point as an amusing illustration.

The situation is very similar to that discussed in § 3.5. In a perfect crystal with complete translational symmetry, neutrons could not be scattered if their wave vector was less than the smallest non-zero vector of the reciprocal lattice. 'Wrong' spins, however, represent a deviation from this translational symmetry, just like the lattice waves considered in § 3.5. We have therefore to consider processes in which a 'wrong' spin is produced or absorbed. The first, which means that an electron which was in the direction of predominant magnetization is turned into the 'wrong' direction, with corresponding reversal of the neutron spin, requires energy and is therefore rare for slow neutrons. The second, in which the neutron turns a 'wrong' spin in the 'right' direction, may happen for very small neutron velocity, though it depends, of course, on the presence of 'wrong' spins and will therefore not happen at zero temperature.

We shall discuss this first using the spin-wave model.

For the absorption of a spin wave we have, by an obvious extension of (3.43) and (3.44),

$$\left. \begin{aligned} \mathbf{k}' &= \mathbf{k} + \mathbf{g} + \mathbf{K} \\ \frac{\hbar^2}{2M} k'^2 &= \frac{\hbar^2}{2M} k^2 + \epsilon(\mathbf{g}) \end{aligned} \right\} \quad (8.55)$$

The spin-wave energy function $\epsilon(\mathbf{g})$, which for the nearest-neighbour approximation is given by (8.37), is qualitatively of a similar form to the phonon energy function which appears in (3.44), except that it has a continuous derivative near the minimum as well as near the maximum. A one-dimensional representation of (8.55) would therefore be almost like Fig. 6, except that the 'comb' should be replaced by a cosine curve. This fact would widen the distance between the two points of intersection near each minimum, and therefore widen the peaks due to magnetic scattering as compared to the thermal peaks. On the other hand, the amplitude of the spin-wave curve is very much larger than that for phonons, which goes in the opposite direction. Moorhouse shows that, except for the peaks of lowest order, the spin waves give sharper peaks than the phonons.

For this estimate one has to know the value of the exchange integral γ ; Moorhouse estimated this by extrapolating the low-temperature magnetization law (8.42) to the Curie point. This estimate has been improved by Marshall (1954), who pointed out that it is more consistent to fit (8.42) to the low-temperature magnetization measurements. In addition, he applied a spin-wave model with two spins per atom, which is nearer the correct value for iron. Both changes go in the direction of making the peaks still sharper.

The sharpness of successive peaks measures, in fact, the width of the spin-wave curve at different heights, and would therefore provide a detailed check on the spin-wave picture.

That these results are characteristic of the spin-wave model can be seen already from the fact that in the Weiss model the energy required to reverse a spin is assumed to depend only on the magnetization. In that case the scattered neutrons should all have the same energy, and presumably be distributed more or less uniformly in direction.

It is not easy to make a reliable prediction for the collective electron model. In the approximation in which the exchange energy is a function of the total magnetization, the spin reversal would imply moving an electron from the border region of the Fermi distribution of 'wrong electrons' to a place in the border region of the 'right electrons'. Near saturation the first Fermi distribution contains very few electrons, and we are near the origin in k space. The final point must have a momentum near k_0 . The increased kinetic energy just outweighs the gain in exchange energy, since the two Fermi functions must be in equilibrium with each other. The energy change may therefore have all values of the order of kT , and it would have no strong correlation with

the momentum transfer. This model therefore does not seem to lead to sharp peaks.

8.6. Remark on magnetization curves

The problem of spontaneous magnetization, with which this chapter has been concerned, represents only the raw material for most problems of practical interest. In subjecting a ferromagnetic material to an external field, one does not usually change the intensity of spontaneous magnetization in each small domain, but merely the orientation and the size of the different domains, unless one is fairly close to the Curie point or is dealing with extremely strong fields.

It is impossible, within the scope of this discussion, to do justice to this wide and important field, but a few remarks may help to show its connexion with the previous sections.

In the first place, it is of vital importance to take into account the fact that the spontaneous magnetization will be directed in one of a few crystallographically equivalent directions. Our previous formulae made the energy a function of the magnitude of the resultant spin, but since the spin came in only through the Pauli principle, only the relative spin direction of the electrons was important, not the absolute direction in space.

A directional dependence must therefore be due to magnetic interactions. The magnetic interaction between the electron spins cannot be responsible, at any rate in a cubic crystal, since it must be a quadratic function of the magnetization vector, and hence for cubic symmetry must be isotropic.

We do, however, find a suitable effect in the interaction of the spin (or spins) of each atom with the orbital motion. This effect is proportional to the product of the spin moment with the magnetic field due to the orbital motion. This magnetic field would vanish if it were not for the electron spin, since the evidence of the gyromagnetic effect shows that the orbital moments do not contribute appreciably to the magnetization, so that the different orientations of the orbit, which are degenerate in the atom, must be separated by the anisotropic field of adjacent atoms.

The spin will induce a moment in the atom, of which the leading term will therefore be proportional to the magnetic field of the spin, and, again by symmetry, have the same direction. To this order there is still no directional effect. However, in the strong local field due to the spin in the same atom, the susceptibility is not strictly constant. The field

dependence of the atomic susceptibility is governed by the ratio between μH (where μ is the Bohr magneton) and the energy differences ΔE between the states corresponding to different orientations of the orbital wave function. These energy differences vanish for the free atom, and are expected to be reasonably small in the crystal. The H^2 terms in the atomic susceptibility (odd powers of H must go out by symmetry) are therefore not negligible.

In a single crystal it should therefore be easy to arrange all the domains in one of the directions of easy magnetization. To magnetize the crystal fully in a different direction requires, however, an external field strong enough to compete with the anisotropic part of the induced atomic field. Experimentally the magnetic fields necessary for this are of the order of a few hundred gauss, and this is quite compatible with the higher-order terms to which I have referred.

On the basis of the factors so far included, an infinitesimal field would be sufficient to magnetize a crystal up to its intrinsic magnetization in the direction of easy magnetization, and in any other direction up to the magnetization obtainable by turning all domains into that direction of easy magnetization which forms the smallest angle with the external field.

Hence we would expect an infinitely large initial susceptibility, and it is, in fact, correct that the initial susceptibility is extremely high for pure and well-grown crystals. To understand the actual susceptibility, and the hysteresis phenomena, one must consider the mechanism by which the domains are oriented. It is easy to see that this cannot take place by rotating the direction of magnetization gradually, since this involves passing through unfavourable directions which, in the absence of a strong external field, are not possible directions for the magnetization. What will happen instead is that domains with the correct orientation will grow at the expense of others, and this process depends on the nature of the boundaries between domains.

In an absolutely perfect crystal the boundaries would be able to move freely throughout the crystal, but, for example, a region of strain or impurities may reduce the exchange forces, so that at this point the spins have a smaller tendency to be parallel to each other, and a boundary passing through such a region contains less energy than if it passes through undisturbed material. The boundaries will therefore in practice be found in such positions of relative stability, and a magnetic field of finite strength is needed to move each boundary over the obstacles formed by less favourable positions. If the movement of boundaries is severely impeded, as in a quenched material with high internal stresses, one finds

high coercive forces, i.e. strong fields are required before an appreciable number of boundaries start moving.

Another fascinating problem is the speed of motion of the boundaries in an undisturbed region of the crystal.

8.7. Anti-ferromagnetism

Another important field which I shall not be able to cover adequately is the phenomenon of anti-ferromagnetism, which has been explored and described by Néel (1932, 1936).

Certain substances, including metals, alloys, and non-metallic crystals, show an anomaly in the specific heat at a temperature below which the magnetic susceptibility is smaller than above. Néel explained this as a tendency of adjacent atoms to have their spins opposite rather than parallel. In that case one would expect that, at sufficiently low temperature, the lattice could be subdivided into two sub-lattices, so that all or most of the spins of one sub-lattice were mutually parallel, but opposite to those of the other.

A large number of the properties can be described in terms of a Weiss model like that used in § 8.1, except that one has to assume that the force on each spin contains a term proportional to the total moment of the sub-lattice to which the spin belongs, and a term in the total moment of the other; since the tendency is towards opposing spins, the constant of proportionality in the second term must now be negative.

At first sight it might be expected that just such a behaviour would result if, in the spin-wave model of § 8.2, we assume the exchange integral γ to be negative. One might therefore expect that all substances for which the Heitler–London approximation of a fixed number of electrons in each atom is reasonably applicable should be either ferromagnetic or anti-ferromagnetic (unless γ happens to be zero). However, this is not borne out by a closer discussion of the model.

If in the formulae of § 8.2 we assume γ negative, then the state of lowest energy corresponds to the largest value of ϵ/γ . Now, whereas the smallest value of this ratio is easily found to be zero, and belongs to stationary states of a very simple kind, the highest value of ϵ/γ is not known. We have shown that it cannot exceed $2N$, but it is easy to see that it cannot, in fact, reach this value.

We have, in § 8.2, constructed a simple stationary state belonging to $\epsilon = 0$, and it corresponds very closely with the intuitive picture of a ferromagnetic state in which all spins are parallel. But the corresponding intuitive picture of adjacent spins being opposite, as in a chess board

pattern, is not similarly a stationary state. One verifies fairly easily from (8.23), particularly in the form (8.33), that it is not a correct solution of this equation to assume $A = 1$ for the spin arrangement which has all adjacent spins opposite, and $A = 0$ for all others. The reason is quite clear: the exchange phenomenon does not allow spins to stay in their places, but they will change places with each other. This makes no difference (and is, in fact, unobservable) when they are all parallel but is important when they are not.

Because of these difficulties, no precise solution describing the highest values of ϵ/γ is available, and we do not know whether this model with negative γ would show the features of anti-ferromagnetism.

There is, however, little doubt that qualitatively the anti-ferromagnetism is due to an exchange interaction opposite in sign to the ferromagnetic case. It was at first regarded as a difficulty that the phenomenon was observed in oxides and other compounds in which the distance between the magnetic ions is so large that one could hardly expect the exchange interaction, which depends on the overlap of the atomic wave functions, to be at all appreciable. This was resolved by a suggestion due to Kramers (1934) of an indirect exchange involving several electrons, in which an intermediate non-magnetic atom takes part.

Terms representing such a multiple exchange are, in principle, contained in (8.12). They were neglected in deriving (8.21) since they contain higher powers of the 'overlap factor' (8.14), and in the ferromagnetic case they would have altered the results only in quantitative detail. However, as one knows from the binding energies of molecules, the overlap integral is not really small for realistic distances, and its square is certainly very much larger than the overlap between two magnetic ions which are two inter-atomic distances apart.

We may, for example, imagine that two magnetic ions each containing one electron are separated by a non-magnetic ion containing, in a closed shell, several electrons. Let u, w be wave functions in the two magnetic ions, and v_1, v_2 two different orbital states in the atom in the middle. We take all these with parallel spin, and number the electrons 1 to 4. Then the numerator of (8.12) contains a term of the kind

$$-u^*(x_1)v_1^*(x_2)v_2^*(x_4)w^*(x_3)\{V_{12}+V_{14}+V_{23}+V_{34}\}u(x_2)v_1(x_3)v_2(x_1)w(x_4) \quad (8.56)$$

integrated over all coordinates. The corresponding term is absent when the electrons in states u and w have opposite spin.

In current work on this subject it is usual to consider a slightly different mechanism of indirect exchange, which depends on the possibility of a virtual state in which the non-magnetic ion in the centre had lost or gained an electron from one of its neighbours. In the framework of the approximation outlined in § 8.2 such terms belong to an approximation of higher order (as does (8.56) because it contains four overlap factors) but in a realistic picture they need not, in fact, be small.

A summary of the current theory of anti-ferromagnetism can be found in a review by van Vleck (1951).

Notes added in Proof: It is worth pointing out that in the cases of one or two dimensions the spin-wave model gives, in place of (8.41), an integral in which $x^2 dx$ is replaced by dx or $x dx$ respectively. The integral then diverges at $x = 0$, showing that the approximations are not justified and that the proportion of 'wrong' spins is not small. Only the three-dimensional case, therefore, shows ferromagnetic behaviour.

The effect of the β^2 terms in (8.21) has been discussed in several papers. Carr (1953) comes to the conclusion that they may be neglected if one alters the meaning of the parameters α and γ to a slight extent.

Note added January 1956

W. Marshall (*Proc. Roy. Soc. A*, **232**, 48, 1955) gives a variation method to show that the simple model of this chapter, with interactions between adjacent magnetic atoms only, will not give an ordered state as a ground state for anti-ferromagnetism. It is conceivable that a more exact calculation would reverse this result, but in either case the energy difference between the lowest ordered and the lowest disordered state would be very small, so that the actual occurrence of anti-ferromagnetism is likely to depend on other small effects, such as the interactions between more distant atoms. This view seems quite compatible with the empirical evidence.