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NUCLEAR FERROMAGNETISM

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ABSTRACT. It is shown that at sufficiently low temperatures metals become ferromagnetic owing to an orientation of the nuclear spins. The domain structure of such ferromagnetics is analogous to that of ordinary ferromagnetics.

§ 1

At the low temperatures which have been reached up to the present time the nuclear spins of solids are still oriented completely at random. The solid accordingly has a considerable entropy. This led Gorter (1934) and Kurti and Simon (1935) to suggest that a magnetic-cooling method depending on the magnetism of atomic nuclei would allow still lower temperatures to be reached. F. Simon (1939) has discussed this possibility in some detail and concluded that it should be possible to realize it experimentally. A theoretical discussion of some of the properties of solids at these very low temperatures should, therefore, be of interest.

By analogy with other order-disorder transitions we expect to find a temperature, T_0, at which a second-order transition occurs. Below this temperature the nuclear spins should show long range order. Two possible types of order can be distinguished. Either the nuclear spins are oriented in such a way that the resultant moment of the solid vanishes (antiparallel spins), or the nuclear spins have a resultant magnetic moment (parallel spins). In the latter case the solid becomes ferromagnetic.

§ 2

The transition temperature T_0 is determined by that part of the total energy of the solid which depends on the orientation of the nuclei. The state which is realized at the absolute zero of temperature is the state of lowest energy and may correspond to either parallel or antiparallel nuclear spins. It has previously been shown (Fröhlich and Nabarro, 1940), quoted as "I") that in the case of monovalent metals the magnetic interaction between the conduction electrons and the nuclei leads to an indirect coupling between the magnetic moments of the nuclei which is usually much larger than their direct magnetic interaction.

The magnetic interaction between electronic spin and nuclear moment is well known from investigations on the hyperfine structure of spectral lines. This interaction is particularly large for s-electrons where, in the case of free atoms, it leads to a splitting of the s-energy level into two levels corresponding to opposite electron spins. In metals a conduction electron has an equal probability of being near any one nucleus. The total splitting of its energy level is thus composed of the contributions of all nuclei. The contributions of nuclei with antiparallel spins cancel, and the total splitting is proportional to the total angular momentum $\hbar M$ of all N nuclei of the metal. Its value $\Delta E(M/N)$ is very nearly equal to the hyperfine splitting ϵ in free atoms, if all nuclear spins are parallel. Thus approximately (cf. Fröhlich and Nabarro, 1940; equation (4))

$$\Delta E(M/N) \simeq \frac{\epsilon}{i+\frac{1}{2}} \frac{M}{N}, \qquad \ldots\ldots(1)$$

where $\hbar i$ is the spin of a single nucleus.

The splitting of the energy levels is linear in ϵM. However, the splitting alone does not lead to a change in the total energy of the metal, for the contributions of electrons with opposite spins just cancel. Only by turning the spins of some of the electrons will a net energy decrease be obtained, and this decrease is proportional to $(\epsilon M)^2$. This may be seen by considering the magnetic interaction to be replaced by an external field $H(M)$ which leads to the same splitting, i.e. $\Delta E(M/N) = 2\mu H(M)$, where μ is the Bohr magneton. From (1),

$$H(M) = \frac{\epsilon}{2\mu(i+\frac{1}{2})} \frac{M}{N}. \qquad \ldots\ldots(2)$$

The energy in this case is well known to be

$$U(M) = -\tfrac{1}{2}\chi_{\mathrm{P}} H^2(M) V, \qquad \ldots\ldots(3)$$

i.e. of the second order in $H(M)$. Here V is the volume and χ_{P} is the paramagnetic susceptibility. According to the theory of metals, χ_{P} is given by

$$\chi_{\mathrm{P}} \simeq \frac{3}{2} \frac{\mu^2 N}{\zeta V}, \qquad \ldots\ldots(4)$$

where

$$\zeta \simeq \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3} \qquad \ldots\ldots(5)$$

is the range of energies occupied by the conduction electrons. Substituting from (4) into (3),

$$U(M) \simeq -\frac{3}{16} \frac{\epsilon^2 N}{(i+\frac{1}{2})^2 \zeta} \frac{M^2}{N^2}. \qquad \ldots\ldots(6)$$

An energy of this type (i.e. one which is proportional to $-M^2$) is assumed in the Weiss theory of ferromagnetism. It was therefore concluded in 1940 that below the Curie temperature T_0 monovalent metals should show nuclear ferromagnetism. The Curie temperature was given (cf. equation (18) of our 1940 paper) by

$$KT_0 \simeq \epsilon^2/8\zeta. \qquad \ldots\ldots(7)$$

It is of the order of 10^{-6}° abs. The highest values are those for Cu, 133 Cs, and 87 Rb with Curie temperatures of 3, 2 and 1×10^{-6}° respectively.

§ 3

We have carried the analogy between nuclear and ordinary ferromagnetism one step further by considering the question of domain structure. In the absence of an external magnetic field, ordinary ferromagnetic substances are usually composed of domains each polarized to saturation. The directions of polarization of these domains differ, and there is no resulting magnetic moment. In attempting to consider the domain structure of nuclear ferromagnetism we found that our arguments of 1940 are not entirely conclusive, but we shall show below that these results can be derived in a more rigorous way. Consider, for instance, a macroscopic specimen consisting of two domains of equal size but with opposite polarization M. In this case, according to equation (1), there is no splitting of the energy levels, and from equation (6) one would conclude that there is no change in the total energy. This latter conclusion is certainly wrong because the two parts of the specimen, if considered separately, would both show an equal energy decrease $U(M)$, and the total energy of the whole specimen should differ from the sum of the energies of the two parts by relatively small surface corrections. This discrepancy is caused by our having started from a consideration of the splitting of energy levels, which is an effect of the first order in ϵM, whereas the final total energy change (6) is of the second order in ϵM. Thus we should, from the beginning, have considered effects which are of the second order in ϵM.

Let us treat the electrons as effectively free, and describe the interaction between electronic and nuclear spins by a change in the potential energy of the electron. Figure 1 represents the potential energy in a crystal having all the nuclear spins parallel. The full line is the potential in the absence of spin-spin interaction; the dashed and dotted lines are the potentials of electrons with spins upward and downward respectively. The nuclear spins in the left half of figure 2 are parallel to those in figure 1, the nuclear spins in the right half are in the opposite direction. In figure 1 the effect of the spin-spin interation is to cause electrons to move from states with upward spin to states with downward spin throughout the crystal. In figure 2 the same change takes place in the left half of the crystal and the reverse change in the right half. In figure 1 the energy levels of electrons are shifted by $\frac{1}{2}\Delta E(M/N)$, but the total energy change is proportional to $(\Delta E)^2$. In figure 2 there is no first-order shift in the individual energy levels and the total energy change is again proportional to $(\Delta E)^2$. There is, however, a first-order change in the wave-function, as a result of which electrons

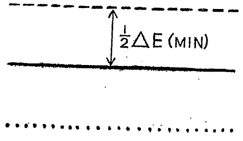

Figure 1. Electron potentials in a crystal consisting of a single domain : —— neglecting spin-spin interaction; - - - - electron spin upward; . . . . . . electron spin downward.

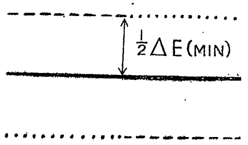

Figure 2. Electron potentials in a crystal consisting of two domains with opposite polarization.

with upward spin are found more often in the right half of the crystal than in the left. There is an opposite change in the concentration of electrons with downward spin, and thus no resultant shift of electric charge. The partial confinement of electrons of one spin to one half of the crystal raises their kinetic energy and so leads to a positive boundary energy between the two domains.

The calculations are simple to carry out if the domain structure is laminar and the projection of the nuclear spin on the electron spin varies sinusoidally along the x-coordinate. By analogy with equation (1) the potential energy of an electron with given spin direction is then

$$W=\frac{1}{2}\frac{\epsilon i}{i+\frac{1}{2}}\sin\frac{2\pi x}{l}, \qquad \ldots\ldots(8)$$

where $l/2$ is the width of a domain, and the whole crystal contains an even number of domains. It is shown in the appendix that the total energy perturbation U of all electrons is given by

$$U=U_0 f(l), \qquad \ldots\ldots(9)$$

where

$$U_0=-\frac{3}{32}\frac{\epsilon^2 N}{\zeta}\frac{i^2}{(i+\frac{1}{2})^2} \qquad \ldots\ldots(10)$$

and

$$f(l)=\frac{1}{2}+\frac{1}{4}\left(\frac{l}{a}-\frac{a}{l}\right)\log\frac{1+a/l}{|1-a/l|}. \qquad \ldots\ldots(11)$$

Here a is of the order of the distance between neighbouring nuclei, and is given by

$$a=\left(\frac{\pi}{3}\frac{V}{N}\right)^{1/3}. \qquad \ldots\ldots(12)$$

For large domains, $l \gg a$, and $f(l)$ tends to l. The energy given by (9) and (10) then differs from (6) only in replacing the factor M^2/N^2 by $i^2/2$, that is, in replacing the square of the mean polarization by the mean square of the polarization. In the next approximation in a/l, equations (9)–(11) become

$$U=U_0\left(1-\frac{1}{3}\frac{a^2}{l^2}\right). \qquad \ldots\ldots(13)$$

As expected, the energy increases with decreasing size of the domains. It follows from (11) that the energy is a steadily decreasing function of l. This shows that the state of lowest energy is actually that in which the domains are very large. The solid is therefore ferromagnetic.

In an ordinary ferromagnetic specimen the size of the domains is determined by a balance between the energy of the Bloch walls between domains and the energy of the demagnetizing field. The former depends on absolute value of the exchange energy and on its anisotropy. The surface energy which has been calculated above is the analogue of the exchange energy. We expect to find a dependence of the spin-spin interaction energy on the direction of polarization referred to the crystal axes, but we have not yet considered its magnitude. We believe it is due to the deviations of the electron wave-functions from s wave-functions, combined with spin-orbit coupling.

§ 4

From the above considerations it can be concluded that the nuclear ferromagnetism of metals has the same characteristics as ordinary ferromagnetism,

Thus in the absence of an external field one should expect a specimen to be divided into domains which are polarized to saturation but with different directions of polarization so that the total magnetic moment vanishes. The saturation polarization is about a thousand times smaller than in ordinary ferromagnetic substances because the nuclear magnetic moment is of the order of 1/1000 Bohr magneton. It should nevertheless be easy to measure.

APPENDIX

Consider a cubic specimen of side L. The wave function of an electron with momentum $\hbar k$ is given by

$$\psi_k=e^{ik\cdot r}/L^{3/2}, \qquad \ldots\ldots(\text{A }1)$$

Let L/l be an integer. Then the first-order perturbation due to the interaction $W(8)$ vanishes unless $k_x=\pm\pi/l$. In this case one half of the energy levels move to higher energies and the other half to lower energies, so that the average energy change vanishes again.

In second order the perturbation energy is given by

$$\overline{W}=-\sum_{k'}\frac{|W_{kk'}|^2}{E_{k'}-E_k}, \qquad \ldots\ldots(\text{A }2)$$

where $W_{kk'}=\int\psi_{k'}^* W\psi_k d\tau$ is the matrix element of W and

$$E_k=\frac{\hbar^2 k^2}{2m} \qquad \ldots\ldots(\text{A }3)$$

is the energy of the electron in zero order.

From (A 1) it follows that

$$|W_{kk'}|^2=\left\{\begin{array}{lll}\dfrac{1}{4}\dfrac{\epsilon^2 i^2}{(i+\frac{1}{2})^2} & \text{if} & k'_x=k_x\pm\dfrac{2\pi}{l},\ k'_y=k_y,\ k'_z=k_z \\ 0 & & \text{otherwise.}\end{array}\right\} \qquad \ldots\ldots(\text{A }4)$$

According to (A 3) and (A 4)

$$E_{k'}-E_k=\frac{\hbar^2}{2m}\frac{4\pi}{l}\left(\frac{\pi}{l}\pm k_x\right), \qquad \ldots\ldots(\text{A }6)$$

and the total energy perturbation U of all electrons is given by

$$U=-\frac{1}{4}\frac{\epsilon^2 i^2}{(i+\frac{1}{2})^2}\frac{2m}{\hbar^2}\frac{l}{4\pi}\Sigma\left(\frac{1}{\pi/l+k_x}+\frac{1}{\pi/l-k_x}\right), \qquad \ldots\ldots(\text{A }6)$$

where the sum extends over all occupied energy levels. It can be transformed into an integral over the volume

$$k_x^2+k_y^2+k_z^2\leqslant k_0^2 \qquad \ldots\ldots(\text{A }7)$$

where k_0 is the wave number of the highest occupied state. After carrying out the integration over k_y and k_z the sum becomes

$$N\int_0^{k_0}\left(\frac{1}{\pi/l+k_x}+\frac{1}{\pi/l-k_x}\right)(k_0^2-k_x^2)\,dk_x\Big/\int_0^{k_0}(k_0^2-k_x^2)\,dk_x$$
$$=\frac{3N}{2k_0^3}\int_0^{k_0}\left(\frac{1}{\pi/l+k_x}+\frac{1}{\pi/l-k_x}\right)(k_0^2-k_x^2)dk_x. \qquad \ldots\ldots(\text{A }8)$$

The integrand $1/(\pi/l-k_x)$ has a singularity at $k_x=\pi/l$, where the first-order perturbation does not vanish. As a consequence the integration should be carried out from 0 to $\pi/l-\delta$, and from $\pi/l+\delta$ to k_0, where δ measures the first-order energy splitting. Assuming δ to be small, this is equivalent to taking the principal value of the integral $\int dk_x/(\pi/l-k_x)$. This finally leads to equations (9)–(11).

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