THE FLUCTUATING FIELD FERROMAGNET AT LOW TEMPERATURES

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Summary

Néel's concept of fluctuating intermolecular field may be ascribed to localized but migratory elementary magnets in ferromagnetics with non-integral Bohr magneton numbers. This concept allows a low temperature ordering of elementary magnets and a variation with temperature of the effective number of nearest neighbours between which exchange interactions occur. This model alone cannot explain the approach to absolute saturation at 0 °K of a ferromagnetic, but it modifies the constant of the $T^{3/2}$ law of approach. In the case of ordering by the mutual attraction of parallel elementary magnets, each consisting of a coupled pair of spins ($s=1$) the theoretical and experimental values of this constant for nickel are reconciled.

I. INTRODUCTION

The statistical nature of the alignment of elementary magnets in a ferromagnetic domain cannot be properly accounted for in any existing theory. Néel (1932, 1934, 1940) directed attention to this deficiency of the theory of ferromagnetism by considering statistical fluctuations of intermolecular field near to the Curie temperature. He obtained a convincing correlation between specific heat, the difference between paramagnetic, θ_p, and ferromagnetic, θ_f, Curie temperatures, and the departure from linearity of the $(1/\chi - T)$ curve above θ_f. The fluctuations are considered to arise by thermal migration of the elementary magnets from one lattice site to another, being discretely located on particular sites at any instant.

In an earlier paper (Stacey 1955) this model was examined for a face-centred cubic lattice to determine the conditions under which ordering of elementary magnets on the lattice sites could explain the observed variation of intermolecular field in nickel. An analytical form for the approach to absolute saturation at 0 °K did not appear to be obtainable for this lattice, so that an important deficiency of the model was missed. The body-centred cubic lattice contains only two (instead of four) sublattices and is therefore algebraically easier to handle. It gives an exponential approach to absolute saturation, clearly in disagreement with experimental results for nickel. (A qualitative similarity between the behaviour of face-centred and body-centred lattices must be expected.)

The success of Bloch's (1932) law, $1-\sigma/\sigma_0 = CT^{3/2} + \ldots$, for the departure of spontaneous magnetization σ/σ_0 from saturation at low temperatures, T, is explained by Dyson's (1956*b*) paper in which the next term is shown to be proportional to $T^{5/2}$ and not a lower power as had been reported earlier. This

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allows the $T^{3/2}$ law quite a wide range of validity as observed experimentally, but the theoretical and experimental values of C do not agree. C depends directly upon the number, η, of nearest neighbouring lattice sites between which exchange interactions occur, and the assumption is made that η has the same value at 0 °K and the Curie point. An estimate is therefore readily made of the correction to C indicated by the fluctuating field concept.

II. Lattice Ordering by Mutual Repulsion of Elementary Magnets

In this section consideration is given to the behaviour at low temperatures of a body-centred cubic lattice, incompletely occupied by elementary magnets, between which there is an ionic repulsion exceeding their exchange interaction.

The lattice can be divided into two completely equivalent sublattices, which, in any unit cell, are represented by the cube corners and the body centre. Consider two sublattices with different populations w and x of elementary magnets, disposed on a total of N lattice sites, where

$$w+x=n, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

n being the total number of magnets, and for convenience

$$w-x=n\delta. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The w and x magnets will have different spontaneous magnetizations $(\sigma/\sigma_0)_w$ and $(\sigma/\sigma_0)_x$, and we may put

$$W=w(\sigma/\sigma_0)_w, \qquad X=x(\sigma/\sigma_0)_x,$$

so that

$$W+X=n\sigma/\sigma_0, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$
$$W-X=n(\sigma/\sigma_0)\Delta. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Each x site has eight nearest neighbours, all on the w sublattice, and similarly each w site has eight nearest neighbouring x sites. Therefore, if next nearest neighbour interactions are neglected, the intermolecular field acting on each sublattice is due to the occupation and spontaneous magnetization of the other sublattice. Equations representing the interdependence of the spontaneous magnetizations are derived in the same way as for the simple quantum-corrected Weiss theory. Equations are numbered (**5A**), (**6A**), etc. for the case of elementary magnets being single spins ($s=\frac{1}{2}$) and (**5B**), (**6B**), etc. for coupled spins ($s=1$).

$$\frac{W}{w}=\tanh\left(\frac{16J}{NkT}X\right), \quad \ldots\ldots\ldots \quad (5A)$$

$$\frac{X}{x}=\tanh\left(\frac{16J}{NkT}W\right), \quad \ldots\ldots\ldots \quad (6A)$$

$$\frac{2-\sqrt{\{4-3(W/w)^2\}}}{W/w}=\tanh\left(\frac{8J}{NkT}X\right), \quad \ldots\ldots\ldots \quad (5B)$$

$$\frac{2-\sqrt{\{4-3(X/x)^2\}}}{X/x}=\tanh\left(\frac{8J}{NkT}W\right), \quad \ldots\ldots\ldots \quad (6B)$$

where J represents the exchange energy between occupied neighbouring sites, T is temperature, and k Boltzmann's constant. Equations (**5**) and (**6**) refer to spontaneous magnetization in zero external field.

Both lattices have the same Curie temperature, θ, since both W and X are positive and by (**5**) and (**6**) they must approach zero together. Simplification of these equations for W, $X \to 0$ gives

$$\theta = \frac{8J}{k}\,\frac{n}{N}, \qquad \text{.....(7A)}$$

$$\theta = \frac{2}{3}\cdot\frac{8J}{k}\,\frac{n}{N}. \qquad \text{.....(7B)}$$

For approximation to equations (**5**) and (**6**) at low temperatures, the expansion

$$\tanh A = 1 - 2e^{-2A} + \ldots$$

is used. Substituting equations (**1**)–(**4**) and (**7**) in (**5**) and (**6**) we obtain at low temperatures:

$$1 - \frac{\sigma}{\sigma_0} = (1+\delta)\exp\left\{-2\frac{\theta}{T}\,\frac{\sigma}{\sigma_0}(1-\Delta)\right\} + (1-\delta)\exp\left\{-2\frac{\theta}{T}\,\frac{\sigma}{\sigma_0}(1+\Delta)\right\}, \qquad \text{.....(8A)}$$

$$1 - \frac{\sigma}{\sigma_0} = \tfrac{1}{2}\left(1+\delta-\frac{\sigma}{\sigma_0}\cdot\frac{1+\Delta}{2}\right)\exp\left\{-\frac{3}{2}\,\frac{\theta}{T}\,\frac{\sigma}{\sigma_0}(1-\Delta)\right\} + \tfrac{1}{2}\left(1-\delta-\frac{\sigma}{\sigma_0}\cdot\frac{1-\Delta}{2}\right)\exp\left\{-\frac{3}{2}\,\frac{\theta}{T}\,\frac{\sigma}{\sigma_0}(1+\Delta)\right\}, \qquad \text{.....(8B)}$$

provided that δ and Δ do not approach unity, i.e. n/N must be greater than $\frac{1}{2}$.

The behaviour of δ and Δ as $T/\theta \to 0$ is readily determined by considering the free energy, F, of the system.

$$F = U - kT \ln A,$$

where U is internal energy and A is the number of complexions of the system. When the spontaneous magnetizations of both sublattices approximate to unity, U and A are given by

$$U = \frac{16wx}{N}(E-J), \qquad \text{.....(9)}$$

$$A = \frac{(\frac{1}{2}N)!}{(\frac{1}{2}N-w)!\,w!}\cdot\frac{(\frac{1}{2}N)!}{(\frac{1}{2}N-x)!\,x!},$$

so that

$$\frac{1}{kT}\,\frac{\partial F}{\partial x} = \frac{16(E-J)}{NkT}(w-x) + \ln\left(\frac{x(\frac{1}{2}N-w)}{w(\frac{1}{2}N-x)}\right),$$

which is equated to zero for the required minimum of free energy.

This causes w and x to approach limiting values $\frac{1}{2}N$ and $(n-\frac{1}{2}N)$ in an exponential manner as $T\to 0$ °K, so that at low temperatures we may write $\delta=\Delta=(N/n-1)$, whence

$$1-\frac{\sigma}{\sigma_0}=\frac{N}{n}\exp\left\{-2\left(2-\frac{N}{n}\right)\frac{\theta}{T}\right\}+\left(2-\frac{N}{n}\right)\exp\left\{-2\frac{N}{n}\frac{\theta}{T}\right\}, \quad \text{..... (10A)}$$

$$1-\frac{\sigma}{\sigma_0}=\frac{1}{4}\frac{N}{n}\exp\left\{-\frac{3}{2}\left(2-\frac{N}{n}\right)\frac{\theta}{T}\right\}+\frac{1}{4}\left(2-\frac{N}{n}\right)\exp\left\{-\frac{3}{2}\frac{N}{n}\frac{\theta}{T}\right\}. \quad \text{..... (10B)}$$

In equations (**10**) the first terms predominate. Subsequent terms in the expansions involve squares of the exponentials which are not significant below $T/\theta=0\cdot 2$. Over this temperature range the $T^{3/2}$ law of Bloch (1932) gives a much better fit to experimental values than any combination of exponentials in the form of equation (**9**), which shows the unsuitability of this approach at low temperatures, and suggests an examination of the $T^{3/2}$ law.

III. The $T^{3/2}$ Law

Dyson (1956*a*, 1956*b*) gave a complete analysis of the spin-wave method of calculating the spontaneous magnetization, σ/σ_0, of a ferromagnetic at low temperatures. The important conclusion from these calculations is that the next term in the expansion of σ/σ_0 in powers of temperature, T, is proportional to $T^{5/2}$. Thus there is a useful range of temperatures over which the $T^{3/2}$ term expresses σ/σ_0 versus T as accurately as experiment can check it. Available experimental data do not allow a very close check of the $T^{3/2}$ law but Arrott (1955) has provisionally reported that more accurate measurements are being made.

Combining equations (**135**) and (**143**) in the paper by Dyson (1956*b*) we have at low temperatures

$$1-\frac{\sigma}{\sigma_0}=\frac{0\cdot 1659}{s}\left(\frac{T}{T_c}\right)^{3/2}+\ldots, \quad \text{..... (11)}$$

where $2s$ is the number of spins per elementary magnet, and T_c is a constant approximately equal to the Curie temperature θ. To give reasonable agreement with experiment we require $s=3/2$ in nickel, which is generally regarded as improbable. An alternative explanation for the value of the constant in equation (**11**) is found in the fluctuating field theory.

The quantity T_c in equation (**11**) is proportional to γ_0, the number of nearest neighbours per atom in Dyson's theory, but what appears to be significant is the average number, η, of occupied nearest neighbours to each of the lattice sites occupied by an elementary magnet. If there are fewer elementary magnets than lattice sites, η may be temperature dependent, which γ_0 is not.

The range of variation of η with temperature was calculated for nickel with $s=\frac{1}{2}$ and $s=1$ by Stacey (1955), assuming repulsive ordering of elementary magnets on a face-centred cubic lattice. It must be noted that the values for

the ordered and disordered states were accidentally inverted and that η is smaller in the low temperature ordered state. Without numerical calculation it can be seen immediately that this process would increase the disagreement between the theoretical and experimental constants of equation (**11**). We have

$$T_c = f\frac{\eta_0}{\eta_\theta}\theta, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

where η_0 and η_θ are the values of η at $T=0$ and $T=\theta$, and f is a numerical factor approximately equal to unity.

For equation (**11**) to agree with the experimental equation

$$1-\sigma/\sigma_0 = 0\cdot 11(T/\theta)^{3/2}, \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

we require $\eta_0/\eta_\theta > 1$, which can only result from what is here termed " attractive ordering ".

IV. Lattice Ordering by Mutual Attraction of Elementary Magnets

The type of order which follows from the tendency of elementary magnets to choose as neighbours magnets parallel to themselves is here examined for a face-centred cubic lattice, and η_0/η_θ is calculated for $s=\frac{1}{2}$ and $s=1$ in nickel. Attractive ordering instead of repulsive ordering is to be expected if $(E-J)$ (equation (**9**)) is negative.

Consider a face-centred cubic lattice of N sites, arranged in a cube of side $(\frac{1}{4}N)^{1/3}.a$, where a is the side of a unit cell and N is large. There are n elementary magnets disposed on the N sites. Since each site has 12 nearest neighbours, in a disordered arrangement of n magnets the average number of nearest neighbours is

$$\eta_\theta = 12n/N. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

This arrangement is approximately valid at the Curie point, θ.

At low temperatures the magnets will tend to become ordered into co-planar groups, the planes being parallel to the faces of the unit cell. This arrangement increases the number of nearest neighbour interactions, with the minimum of local concentration of magnets. In the ordered limit the elementary magnets will occupy p complete planes in each of the three mutually perpendicular directions. The whole lattice has $2(\frac{1}{4}N)^{1/3}$ planes in each direction, each plane having $2(\frac{1}{4}N)^{2/3}$ sites. For $n/N<0\cdot 25$ the planes would be expected to be incomplete and the following calculation would be invalid, but the interesting values are $n/N=0\cdot 604$, $0\cdot 302$, corresponding to $s=\frac{1}{2}$, 1 in nickel.

The intersection of three planes may occur either at a lattice site or between sites, depending upon the planes selected, but the first alternative is favoured for occupation as it gives a larger value of η and hence lower energy for any particular value of n/N.

With p planes in each direction there are $3p^2$ lines of intersection of two planes and p^3 intersections of three planes. Each line of intersection has $(\frac{1}{4}N)^{1/3}$ sites common to both planes which must be subtracted from the total count of

occupied sites to avoid counting twice. This would subtract twice the points of triple intersection, so that

$$n=3p\,.\,2(\tfrac{1}{4}N)^{2/3}-3p^2(\tfrac{1}{4}N)^{1/3}+p^3,$$

which gives

$$\frac{n}{N}=\frac{3}{2}\left[\frac{P}{(\frac{1}{4}N)^{1/3}}\right]-\frac{3}{4}\left[\frac{P}{(\frac{1}{4}N)^{1/3}}\right]^2+\frac{1}{4}\left[\frac{P}{(\frac{1}{4}N)^{1/3}}\right]^3. \quad \ldots\ldots \quad (15)$$

It may be noticed that $n/N=1$ when half the planes are occupied, i.e. $p=(\frac{1}{4}N)^{1/3}$, alternate planes having been selected for occupation by the triple intersection condition.

Along a line of intersection between two occupied planes there are $4(\frac{1}{4}N)^{1/3}$ interactions between sites in different planes in addition to the two interactions per site within the planes. This gives a total number of interactions between nearest neighbours:

$$\tfrac{1}{2}n\eta_0=2\,.\,3p\,.\,2(\tfrac{1}{4}N)^{2/3}+3p^2\,.\,4(\tfrac{1}{4}N)^{1/3},$$

$$\eta_0=6\frac{N}{n}\,\frac{P}{(\frac{1}{4}N)^{1/3}}\left(1+\frac{P}{(\frac{1}{4}N)^{1/3}}\right). \quad \ldots\ldots\ldots\ldots \quad (16)$$

Equations (**15**) and (**16**) can be used to find η_0 at any value of n/N. Values are given below for the cases of elementary magnets in nickel being single or coupled spins:

	$\frac{n}{N}=0\cdot604$ $(s=\frac{1}{2})$	$\frac{n}{N}=0\cdot302$ $(s=1)$
η_0 (ordered)	7·67	5·45
η_θ (disordered)	7·25	3·62

The values of η_θ are given by equation (**14**).

For $s=\frac{1}{2}$ the ratio η_0/η_θ is so near to unity that it cannot significantly affect the $T^{3/2}$ law, in which the constant is three times too large. For $s=1$, however, it gives an interesting agreement with the experimental law.

Combining equations (**11**) and (**12**) and using the above values of η_0 and η_θ for $s=1$ in nickel, we obtain

$$1-\frac{\sigma}{\sigma_0}=\frac{0\cdot08979}{f^{3/2}}\left(\frac{T}{\theta}\right)^{3/2}. \quad \ldots\ldots\ldots\ldots \quad (17)$$

Since substitution of a theoretical value of f would be somewhat arbitrary, the value required for agreement between theory and experiment is obtained by comparison of equations (**13**) and (**17**):

$$f=0\cdot87.$$

Dyson (1956*b*) suggests $f\sim0\cdot9$ as a conclusion of the calculation by Rushbrooke and Wood (1955) who give $f=0\cdot8$ to $0\cdot9$, so that the above value is as close as the uncertainty will permit.

V. Conclusion

The consideration of ionic ordering in a body-centred cubic lattice clearly indicates that the observed temperature dependence of spontaneous magnetization of a ferromagnetic near to complete saturation is not explicable in terms of variation of intermolecular field caused by the ordering. This conclusion may reasonably be applied to nickel, although the appropriate calculation would not so easily be carried out for a face-centred cubic lattice.

Dyson's (1956*a*, 1956*b*) removal of the theoretical doubt about the validity of the $T^{3/2}$ law, allows a comparison of the theoretical and experimental values of the constant C, in the equation

$$1-\sigma/\sigma_0=C(T/\theta)^{3/2}.$$

In nickel the agreement is not good unless one allows the elementary magnets to be spins coupled in threes. This appears improbable, although there is substantial evidence (particularly paramagnetic susceptibility) that the spins are coupled in pairs.

To explain the discrepancy on the basis of different arrangements on the lattice sites of the elementary magnets, it is necessary that a low temperature, ordered state be produced by a mutual attraction of parallel magnets. This attraction must overcome the ionic repulsion, which results from the localization of charge on atoms with vacancies in the $3d$ shells, and is contrary to an earlier calculation based on the assumption of ordering due principally to repulsion. Solid local accumulations of magnets may still be prevented by the repulsion, leading to a tendency for occupied lattice sites to form intersecting planes. This leads to an increase in the exchange energy of the lattice, and modifies the constant C. For $s=\frac{1}{2}$ the modification is not significant, but for $s=1$ it completely reconciles the theoretical and experimental values of C.

It is not necessary to the theory that the elementary magnets should be as individual as has been implied here. The consideration of an average value for the whole lattice of the effective number, η, of nearest neighbours is a concession to their quantum-mechanical indistinguishability (as well as being a necessary mathematical simplification). The difference between the described ordered and disordered states may be regarded as due respectively to unequal and equal probabilities for the occupation of lattice sites. However, it is necessary to the fluctuating field model that the $3d$ electrons (or vacancies) responsible for ferromagnetism are too tightly bound to be considered as an electron band shared by the lattice as a whole.

Fluctuations of intermolecular field are inherent in the model described. They have not been given specific consideration because they become important only in the region of the Curie temperature. In a ferromagnetic in which attractive ordering occurs at low temperatures in the manner described in Section IV, the temporary formation of small coplanar groups of elementary magnets will occur even above the Curie point. This can be described either as fluctuations or as the preservation of some local order. However, when spontaneous magnetization is small, the ordering by ionic repulsion, rejected at low temperatures, may still be significant.

VI. References

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