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Magnetism and the local molecular field

Nobel Lecture, December 11, 1970

1. The Weiss molecular field

It has long been known that ferromagnetism originates from interactions between the atomic magnetic moments which tend to align them parallel to one another in spite of thermal motion. In order to obtain a quantitative explanation of the experimental facts, Pierre Weiss[1] assumed that a ferromagnetic behaved as a pure paramagnetic, *i.e.* a paramagnetic with carriers of independent moments and magnetization given by

$$J = f(H/T) \tag{1}$$

and that the field of the interactions was equivalent to that of an imaginary magnetic field h_m, called the *molecular field,* which was proportional to the magnetization:

$$h_m = n J \tag{2}$$

and which added to the applied field *H.* One thus obtains, if *H* is sufficiently the weak, so-called Curie-Weiss law of magnetization:

$$J = \frac{CH}{T-\theta} \text{ with } \theta = nC \tag{3}$$

If θ is positive, the susceptibility J/H becomes infinite when the temperature falls below the Curie point θ. From this temperature θ to absolute zero the substance assumes under the effect of its molecular field alone $h_m = nJ$ a certain *spontaneous magnetization,* J_s.

In this conception, the molecular field is considered to be a *uniform field* inside the ferromagnetic specimen. Furthermore, to give his theory a more complete nature, P. Weiss distinguished the *energy molecular field,* defined starting from the internal energy *U* by the relationship:

$$H_m = -(\partial U/\partial J) \tag{4}$$

from the *corrective molecular field of the equation of state* h_m defined, as stated

above, by:

$$J = f\left(\frac{H + h_m}{T}\right) \tag{5}$$

A thermodynamic argument shows that the following relationship exists between these two fields:

$$H_m = h_m - T \frac{\mathrm{d}h_m}{\mathrm{d}T} \tag{6}$$

This manner of explanation, theoretically very satisfactory, enables the energy properties of ferromagnetic substances to be treated and explained elegantly and simply, but it has the disadvantage of leading one to admit as a dogma the uniformity of the molecular field and all that follows therefrom, in particular the linear variation of the reciprocal susceptibility with temperature above the Curie point. This certainly retarded progress in the theory.

2. The local molecular field

On the other hand, P. Weiss was unable to give a satisfactory solution to the problem of the origin of the molecular field. It was only in 1928 that Heisenberg found an interaction mechanism giving a satisfactory order of magnitude. From the point of view of interest to us, it is essential only to point out that this involved very short-range interactions, preponderant between first-neighbour atoms and negligible beyond the second or third neighbours.

If, then, we consider an alloy composed of two kinds of randomly distributed atoms A and B, the surroundings of the atoms may be very different and the approximation of a unique molecular field representing for all sites the action of the surroundings must be very poor. The theoretical problem of the rigorous treatment of such interactions is still far from being solved but, while retaining the simplicity of the theories based on the molecular field, we can improve them considerably by introducing what I have called local molecular fields.

Weiss' hypothesis amounts to writing that the energy E_c of the system of A and B atoms is expressed in the form:

$$E_c = -\tfrac{1}{2}n(J_A + J_B)^2 \tag{7}$$

where J_A and J_B denote the magnetizations of the A and B atoms respectively. Actually, since their energy is the sum of the contributions made by pairs of

close-neighbour atoms, A-A, A-B, and B-B, we should rather write:

$$E_c = -\tfrac{1}{2}(n_{AA} J_A^2 + 2\, n_{AB} J_A J_B + n_{BB} J_B^2) \qquad (8)$$

This amounts to abandoning the notion of a general molecular field and to introducing *local molecular fields,* $h_A = n_{AA} J_A + n_{AB} J_B$, and $h_B = n_{AB} J_A + n_{BB} J_B$, acting on the A and B atoms respectively.

I developed this way of looking at the problem for the first time[2] in 1932, and showed that the susceptibility χ of an alloy containing proportions P and Q of A and B atoms, with Curie constants C_A and C_B, was expressed by:

$$\chi = \frac{T(PC_A+QC_B) - PQC_A C_B(n_{AA} + n_{BB} - 2\,n_{AB})}{T^2 - T(P\,n_{AA}\,C_A + Q\,n_{BB}\,C_B) + PQC_A C_B(n_{AA}\,n_{BB} - n_{AB}^2)} \qquad (9)$$

Instead of being represented by a straight line, the temperature dependence of the reciprocal susceptibility $1/\chi$ was now represented by a *hyperbola.*

I applied this theory to the interpretation of the properties of platinum-cobalt alloys and, a little later[3], to iron-cobalt, iron-nickel, and cobalt-nickel alloys.

At the time, this interpretation was not received with much favour. The existence of the straight Curie–Weiss lines in the $(1/\chi, T)$ representation was so well-established that when an experiment gave a curve it was rather preferred to break it down into a series of straight lines, each corresponding to a different magnetic state obeying the Curie–Weiss law.

3. The fluctuations of the Weiss molecular field

In Weiss' original theory the molecular field coefficient n and the Curie point θ both have positive values, and it is perfectly well understood that the molecular field, having a finite and positive value when the atomic moments are all parallel and in the same direction, can cause this ordered state. Weiss and his associates soon established that the paramagnetic properties of a number of salts were conveniently interpreted by a formula of type (3), but with a negative constant θ, *i.e.* with a negative molecular field. It could not be imagined how such a field could create an order at low temperatures.

On the other hand, Weiss' theory was incapable of explaining the properties of paramagnetic metals like manganese and chromium, which have a susceptibility almost independent of the temperature and too great to be attributable to a Pauli paramagnetism, *i.e.* due to electrons in an energy band.

Such was virtually the state of the problem in 1930, at which time I was

interested in the difference between the two Curie points, *i.e.* in the fact that the Curie point θ_p deduced from the Curie–Weiss law, or paramagnetic Curie point, differed from the ferromagnetic Curie point θ_f, the temperature at which the spontaneous magnetization disappeared, whilst Weiss' theory implies the equality $\theta_f = \theta_p$. To explain this difference I invoked the thermal fluctuations of the molecular field, the existence of which seemed certain, since this field arises from the action of the neighbour atoms. These thermal fluctuations are *time-varying fluctuations*, but in this way I also came very naturally to interest myself *in spatially varying fluctuations* and to analyse more closely the consequences of the elementary law of magnetic interaction, namely the existence of a coupling energy between two close-neighbour atoms, equal to $w \cos \alpha$, where α denotes the angle between their magnetic moments.

4. Constant paramagnetism

The constant w may be either negative or positive: negative in the case of ferromagnetism and positive in the case of a negative molecular field. In the latter case recourse to the molecular field, permissible at high temperatures when the locations of all atoms are on an average identical, is no longer so at low temperature, since the atomic magnets must then tend to group themselves by pairs of atoms with antiparallel moments.

In this way I noted (ref. 5, p. 64) that in a *bcc* lattice, composed of two interlaced simple cubic sub-lattices, stable equilibrium at low temperature corresponded to an orientation of the atomic moments in one of the sub-lattices in a certain direction and an orientation in the other direction of the atomic moments in the other sub-lattice, as shown in Fig.1 for the case of a plane lattice. This assembly deforms (Fig.2) under the action of a magnetic field, and assumes an average induced magnetization, given for one atom by

$$\bar{\mu} = \frac{\mu^2 H}{6pw} \tag{10}$$

where μ denotes the atomic magnetic moment and $2p$ is the number of neighbours. In this way a *constant paramagnetism* is obtained, *i.e.* a susceptibility independent of the field and of the temperature.

However, at high temperatures, we should observe a Curie–Weiss law of type (3).
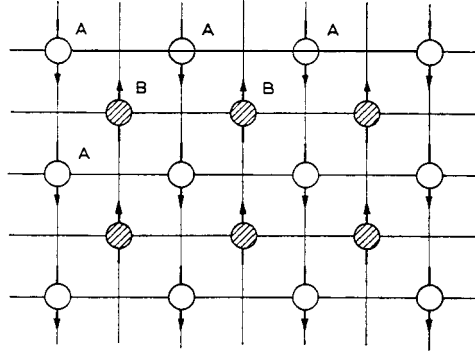
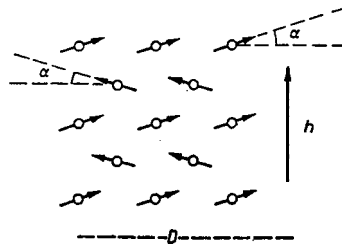Fig. 1. Resolution of a plane lattice into two sub-lattices magnetized in antiparallel.

Fig. 2. Deformation of the antiparallel arrangement of atomic magnetic moments under the action of a field h.

In order to study the transition from constant paramagnetism to Curie–Weiss paramagnetism, I assumed for the sake of simplicity that the atoms could be grouped by pairs independent of one another, the internal energy of a pair being taken as $w \cos \alpha$. This led to the variation

$$\bar{\mu} = \frac{\mu^2 H}{3w} \left[1 - \frac{2w}{kT} \frac{1}{e^{2w/kT} - 1} \right] \qquad (11)$$

The temperature dependence of the reciprocal susceptibility is shown by the curve in Fig. 3. As T is raised from o to θ, the susceptibility varies by only 1.4%.

In another paper, which appeared almost at the same time[4], I proposed interpreting the constant paramagnetism of manganese and chromium by the previous mechanism, with values of θ respectively equal to 1720°K and 4150 °K. To support this interpretation, I showed that on diluting manganese and chromium by copper, silver or gold, a progressive change from a constant paramagnetism to a Curie–Weiss paramagnetism was observed, as
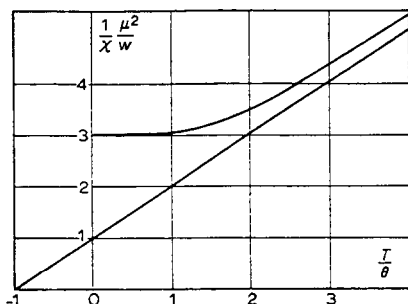
Fig. 3. Temperature dependence of the reciprocal susceptibility of an assembly of ran-
domly-oriented pairs of atoms with anti-parallel moments.

might have been expected from the previous theory when the interactions,
i.e. θ, are decreased.

In 1936, I again took up the theory of negative interactions[5], in the low-
temperature region, allowing for the *coupling of the atomic moments with the
crystal lattice.* The coupling energy was taken as $w''\cos 2\theta$, where θ denotes the
angle between the atomic magnetic moment and a privileged direction D of
the lattice. It was then shown that the magnetic susceptibility is a complex
function of the magnetic field H and the angle β that H makes with D, shown
in Fig. 4 for various values of β at 10-degree intervals.

In particular, if the field is parallel to the privileged direction, the suscep-
tibility, initially zero in weak fields, suffers a discontinuity for

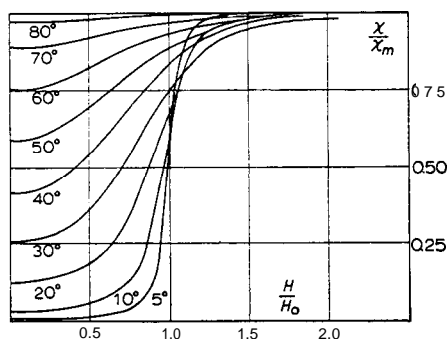$$H = H_0 = \left(8 p w w'' / \mu^2\right)^{\frac{1}{2}}$$

Fig. 4. Variation of the susceptibility of an assembly of atoms with antiparallel moments
with the magnetic field and the direction of alignment of the magnetic moments with
respect to the crystal lattice.

and takes a value $\chi_m = (\mu^2/4pw)$ independent of H: when H reaches the value H_0, the moments which were originally parallel to D and to H orient themselves abruptly in a perpendicular direction. Fifteen years later, in 1951, C. J. Gorter and his associates[5] observed this phenomenon for the first time in copper chloride, $CuCl_2 \cdot 2H_2O$, at 4.1 °K.

It was also deduced from this theory that in a polycrystalline sample, in which the directions D are randomly distributed, the susceptibility is weaker in weak fields than in strong fields, and varies schematically with temperature as shown in Fig. 5. It will be noted that there is no transition temperature: the change from constant paramagnetism to Curie–Weiss paramagnetism takes place perfectly smoothly.
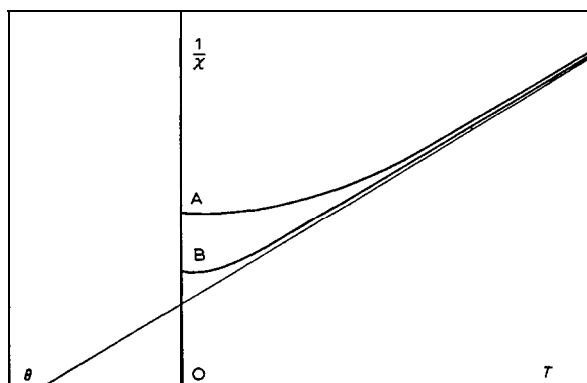

Fig. 5. Influence of the magnitude of the magnetic field on the susceptibility of an assembly of atoms with anti-parallel moments.

5. Discovery of the antiferromagnetic transition point

Still in 1936, I had the idea[5] of applying the theory of the local molecular field to the two sub-lattices A and B with magnetizations J_A and J_B used in the previous papers, and of representing the interactions by imaginary fields H_A and H_B with, at low temperature and for $H = 0$, the fundamental relationship $J_B = -J_A$.

The result was that the two sub-lattices had to acquire spontaneous magnetizations in opposite directions, disappearing at a certain transition temperature θ_N, known nowadays as the Néel temperature, following a proposal made by C. J. Gorter. We were hence faced with a new kind of magnetic material,

composed of the sum of two interlaced identical ferromagnetics spontane-
ously magnetized in opposite directions. Effects depending on the square of
the spontaneous magnetization, such as the specific heat anomaly, should thus
show the same variation as in ferromagnetic substances.

In the absence of coupling with the crystal lattice, the susceptibility remains
constant in the interval $o < T < \theta_N$ and then obeys a Curie–Weiss law for
$T > \theta_N$, without suffering a discontinuity at the Curie point.

Two years later, Squire, Bizette and Tsaï[8] discovered that MnO possessed
the predicted properties, in particular a transition temperature at $\theta_N = 116$ °K.
Much later, in 1949, C. G. Shull and S. J. Smart[9] using a neutron diffraction,
confirmed that the atomic moments effectively possessed the antiparallel
orientations predicted by the sub-lattice theory.

F. Bitter then completed the theory[10] by calculating as far as the transition
point θ_N on the susceptibility in a magnetic field parallel to the direction Δ of
alignment of the antiparallel moments, and gave the name of antiferromagnet-
ics to this new category of magnetic substances; in 1941 J. H. van Vleck[11] col-
lected and reviewed the results obtained.

Finally, the situation may be summed up as follows, according to the orienta-
tion of the magnetic field H with respect to the antiferromagnetism direction
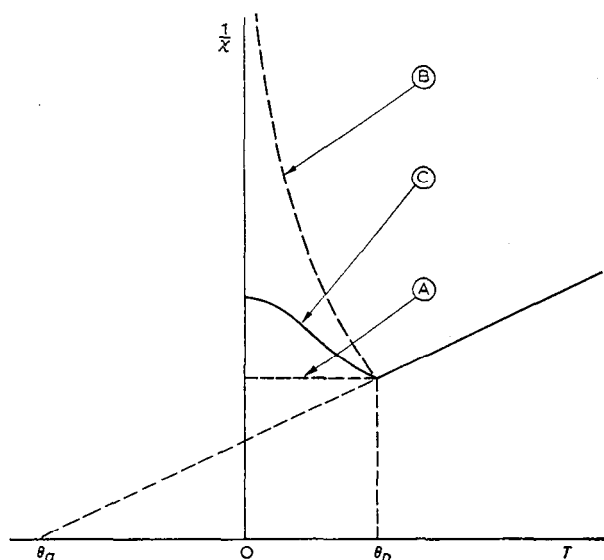Δ, i.e. the privileged direction of the crystal lattice to which the atomic mag-

Fig. 6. Temperature dependence of the reciprocal susceptibility of an antiferromagnetic
material.

netic moments are parallel, in one direction or the other, in the absence of an external applied field. When H is perpendicular to Δ, one obtains[7] curve A in Fig. 6. When H is parallel to Δ, curve B is obtained[10]. Finally, for a polycrystalline substance, the intermediate curve C is obtained, demonstrating at the Néel point θ_p the existence of a sharp maximum in the susceptibility, marked also by a sharp maximum in the specific heat. At temperatures below this maximum an antiferromagnetic order exists, which may be detected by neutron diffraction.

A large number of antiferromagnetic materials is now known: these are generally compounds of the transition metals containing oxygen or sulphur. They are extremely interesting from the theoretical viewpoint, but do not seem to have any applications.

6. Other investigations in the field of magnetism

It should be pointed out that the theoretical studies which I had developed from 1930 to 1938 had been carried out with the aim of determining the elementary interaction energies w between two close-neighbour magnetic atoms, whether similar or not. I expected to find a universal law giving w as a function of the distance between the interacting atoms alone, but this was obviously a rather oversimplified view and my expectations came to nothing. Nevertheless, positive results had been obtained and had made it possible to find interesting correlations between the anomalies of expansion, the effect of pressure, and the variation of the molecular field with temperature. Even now these questions are still on the agenda.

At all events, in 1938 I abandoned the problem of interactions and the local molecular field for about eight years to devote myself to other subjects such as the Rayleigh laws, fine particles, and the role of internal dispersion fields, to quote only those which led to the most important results.

The protection of ships against magnetic mines by a method I proposed, consisting of giving them a permanent magnetization equal and opposite to the magnetization induced by the terrestrial magnetic field, drew my attention to the laws of magnetization of ferromagnetics in weak fields, known as the Rayleigh laws. I was able to give an interpretation of these[12] based on the propagation of the Bloch walls in a randomly perturbed medium.

I also systematically studied the part played by the internal demagnetizing or dispersion fields, up to that time almost neglected. It was then possible to

deduce a more correct theory of the laws of approach of technical magnetiza-
tion to saturation taking into account the random orientation of crystallites[13]
and the presence of cavities or non-magnetic inclusions[14], and to give a more
general theory of the coercive force taking into account the irregularities of
internal mechanical tensile stresses as well as the presence of cavities or non-
magnetic inclusions[15]. On the same general lines, I developed a theory of
magnetization for ferromagnetic single crystals[16] along successive modes,
each specified by the number of *phases, i.e.* by the number of different cate-
gories of elementary domains with parallel spontaneous magnetizations.
This theory, in complete agreement with the experimental facts, put the final
full-stop to a subject which up to then had been very poorly understood.

   Finally, I showed as far back as 1942 that sufficiently small ferromagnetic
particles must enclose only a single elementary domain and, depending in
their dimensions, must behave either as a superparamagnetic substance or as a
set of small permanent magnets and show macroscopically a hysteresis loop
with a high coercive force. In this way good permanent magnets can be made
from particles of soft iron having only a shape anisotropy. These properties
and their applications were developed by L. Weil. The publication of all these
results was delayed until 1947[17] because of the German occupation and for
reasons of patent rights.

7. *Magnetic properties of the spinel ferrites*

It was in 1947, after reading a paper by Verwey and Heilmann[18] on the struc-
ture of ferrites, that I returned to the study of these substances. These ferrites
Fe_2O_3MO, with a spinel structure, where M is a divalent metal, are divided
into two categories according to their magnetic properties : *paramagnetic fer-
rites,* in which M represents zinc or cadmium, and *ferromagnetic ferrites* in which
M represents manganese, cobalt, nickel, etc. The latter have a considerable
technical interest, for these ferromagnetics are electrical insulators, but their
theoretical interest is also high in view of their curious properties, very differ-
ent from those of the classical ferromagnetics: their saturation molecular
moment of 1 to 5 μ_B (μ_B is the Bohr magneton), is much weaker than the
total magnetic moment of the ions contained in the molecule, which varies
from 1 0 to 15 μ_B. In addition, above the Curie point, the temperature de-
pendence of the reciprocal susceptibility has a quite extraordinary hyperbolic
shape, concave downwards, towards the temperature axis, and with a high

temperature asymptote extrapolating back towards a negative absolute temperature.

Mlle Serres, to whom we owe some fine experimental work on ferrites, interpreted [19] the shape of the $(1/\chi, T)$ curve by the superposition of a temperature-independent paramagnetism due to the ferric ions, equal to that of α-Fe_2O_3. But as this paramagnetism is not an atomic property, we cannot see why the ferric ions should retain in the ferrites the same constant paramagnetism as in α-Fe_2O_3.

With regard to the crystalline structure, the metal ions occupy, in the interstices of a close-packed cubic lattice of oxygen ions, sites A surrounded by four O^{2-} ions and sites B surrounded by six O^{2-} ions. There are two categories of ferrites: *normal ferrites*, in which the two Fe^{3+} ions of the molecule occupy the two sites B and the M^{2+} ion site A, and *inverse ferrites,* where one of the Fe^{3+} ions occupies site A and the other one of the two sites B. From an X-ray examination, Verwey and Heilmann concluded that the ferromagnetic ferrites are inverse and paramagnetic ferrites are normal.

8. Foundation of the theory of ferrimagnetism

To interpret the magnetic properties, I assumed [20] that the predominant magnetic interactions were exerted between the ions placed at sites A and ions placed at sites B, and that they were *essentially negative.* At absolute zero, these strong negative interactions make the magnetic moments of the A ions align themselves parallel to one another to give a resultant moment M_{as} pointing in the opposite direction to the resultant M_{bs} of the magnetic moments of the B ions, these also being all parallel. The observable spontaneous magnetization is equal to the difference $|M_{as} - M_{bs}|$.

To study the consequences of these hypotheses, I applied to the two sub-lattices A and B the concept of the local molecular field developed earlier[2]. Letting λ and μ stand for the proportions of magnetic ions, all assumed to be identical $(\lambda + \mu = 1)$, located in the A and B sub-lattices respectively, and designating by $- n$, $n\alpha$ and $n\beta$ the molecular field coefficients corresponding to the interactions AB, AA, and BB respectively, the discussion showed that the variation of the spontaneous magnetization with temperature would have to assume the rather extraordinary forms shown diagrammatically in Fig. 7, in which the capital letters correspond to the regions of the (α, β) plane shown in Fig. 8: region G at the bottom left corresponds to paramagnetism. All
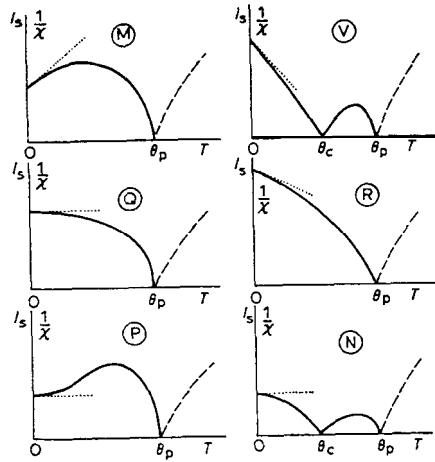
Fig. 7. Temperature dependence of the spontaneous magnetization and the reciprocal susceptibility for a ferrimagnetic material: the various types possible.
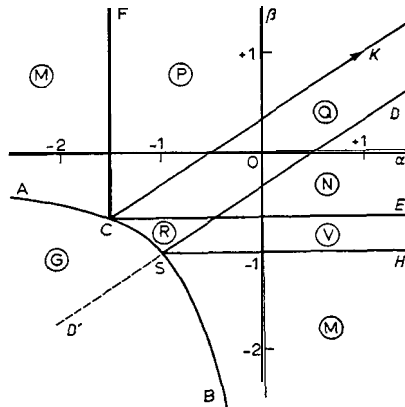

Fig. 8. Possible curve types in Fig. 7, according to the values of α and β

the curve types illustrated in Fig. 7 were subsequently found experimentally.

Above the Curie point θ_p the ferrite becomes paramagnetic, with a susceptibility χ such that:

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T-\theta} \qquad (12)$$

with the notations :

$$\frac{1}{\chi_0} = n\left(2\,\lambda\mu - \lambda^2\alpha - \mu^2\beta\right)$$

$$\sigma = n\,C^2\,\lambda\,\mu\left[\lambda(1+\alpha) - \mu(1+\beta)\right]^2$$

$$\theta = n\,C\,\lambda\,\mu(2+\alpha+\beta)$$

We are hence confronted by substances whose ferromagnetism is due to *negative interactions,* which is quite a remarkable fact, and whose properties, appreciably different from those of classical ferromagnetics, justify a special name: I proposed calling them *ferrimagnetics.*

9. Comparison *of the* theoretical *and* experimental results

This theory immediately makes it possible to interpret[20] the properties of magnesium, lead, and calcium ferrites, those of magnetite Fe_3O_4 and of manganese antimonide Mn_2Sb. As examples, Figs. 9-12 show a comparison of the experimental and the calculated values in the case of Fe_3O_4 and of Mn_2Sb for the temperature dependence of the spontaneous magnetization and of the reciprocal susceptibility. Naturally, the same set of coefficients n, α and β is used in both cases. The result was encouraging, so a considerable experimental effort was launched immediately to test the theory, since the existing experimental material was fairly meagre.
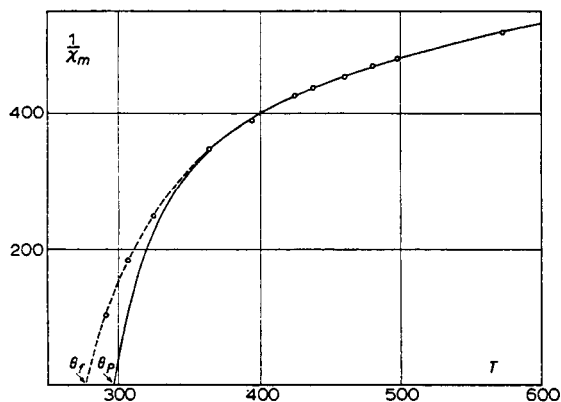

Fig. 9. Temperature dependence of the reciprocal susceptibility of magnetite (fitted curve and experimental points). Note the difference between the ferromagnetic and paramagnetic Curie points.
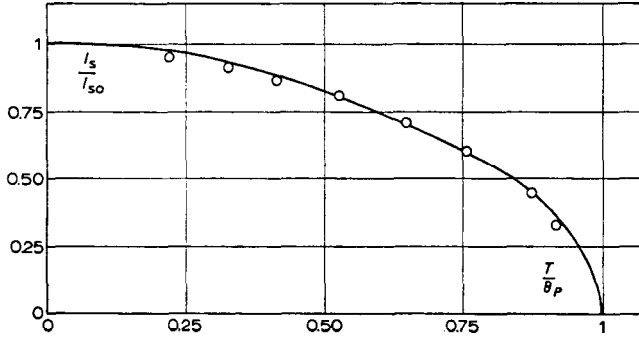
Fig. 10. Temperature dependence of the spontaneous magnetization of magnetite (experimental points and curve calculated with the molecular-field coefficients deduced from the study of susceptibility).
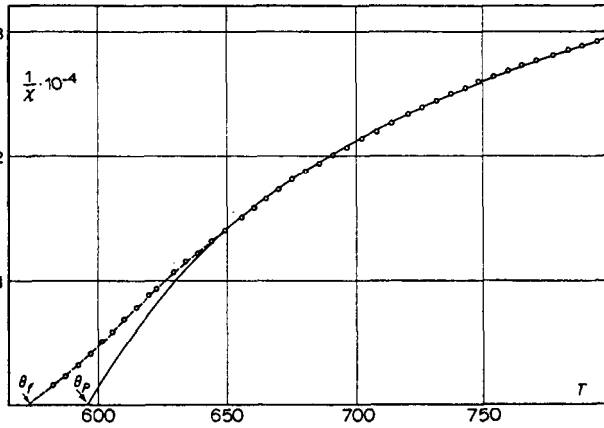

Fig. 11. Temperature dependence of the susceptibility of manganese antimonide (experimental points and fitted curve).
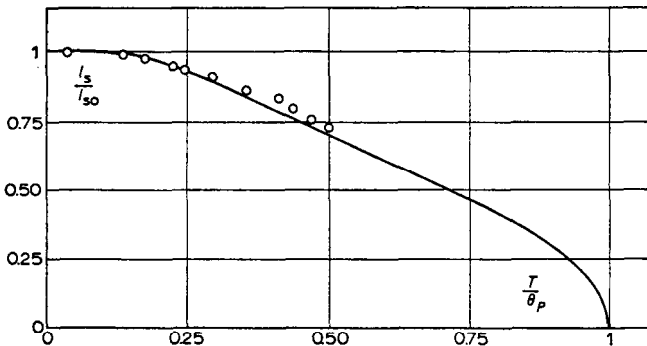

Fig. 12. Temperature dependence of the spontaneous magnetization of manganese antimonide Mn_2Sb (experimental points and curve calculated with the molecular field coefficients deduced from the study of susceptibility).
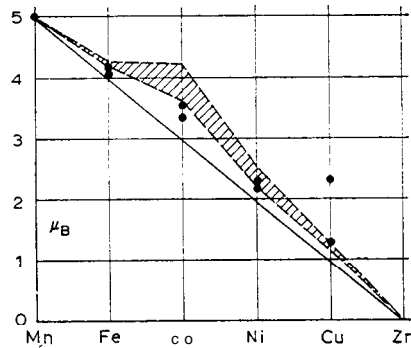
Fig. 13. Saturation magnetization of certain ferrites at absolute zero, for various M ions.

In *pure inverse ferrites* Fe_2O_3MO, with M=Mn, Fe, Co, Ni, the saturation magnetic moment at absolute zero must simply be that of the M ion, since the magnetic moments of the two Fe^{3+} ions exactly cancel each other, located as they are on different kinds of sites. Fig. 13 enables the theory to be compared with experiment. The points correspond to the experimental results[21]. The straight line corresponds to the theoretical predictions with the « spin only » values of the magnetic moments, and the shaded region to the theoretical predictions corrected by taking into account the incompletely quenched orbital angular moment, deduced from the determination of the effective moment of the corresponding paramagnetic salts. The agreement is very satisfactory. With regard to the copper ferrite, experiment shows that the saturation magnetic moment depends on its heat treatment. Cooled slowly, this ferrite assumes the inverse structure whilst at high temperatures the Fe^{3+} ions are distributed at random over the sites A and B, for the difference in energy between the normal structure and the inverse structure is slight, of the order of magnitude of kT. A detailed analysis of the phenomenon shows that this interpretation is correct and hence lends support to the theory of ferrimagnetism[22].

For the same ferrites, it has also been possible to interpret appropriately the experimental results on the temperature dependence of the spontaneous magnetization[23] and of the susceptibility above the Curie point[24]. Figs. 14 and 15, relating to the three ferrites of iron, cobalt, and nickel, show the agreement between the theory and experiment.

Over and above this, on studying magnetite by neutron diffraction, Shull *et al.*[25] confirmed that the magnetic moments of the atoms placed at sites A were effectively pointed in the direction opposite to the moments of the atoms at sites B.
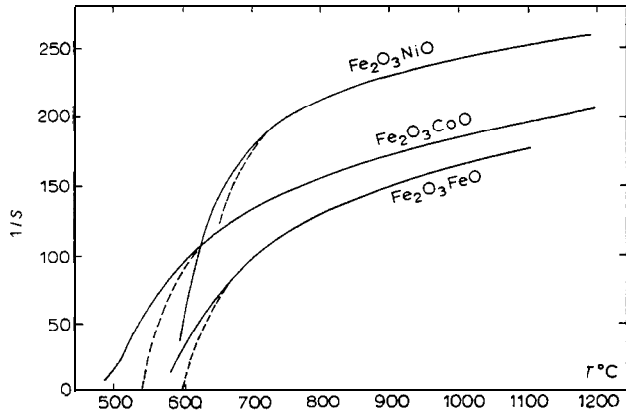
Fig. 14. Temperature dependence of the inverse susceptibility of different ferrites (experimental curves shown in full lines, calculated curves dotted).
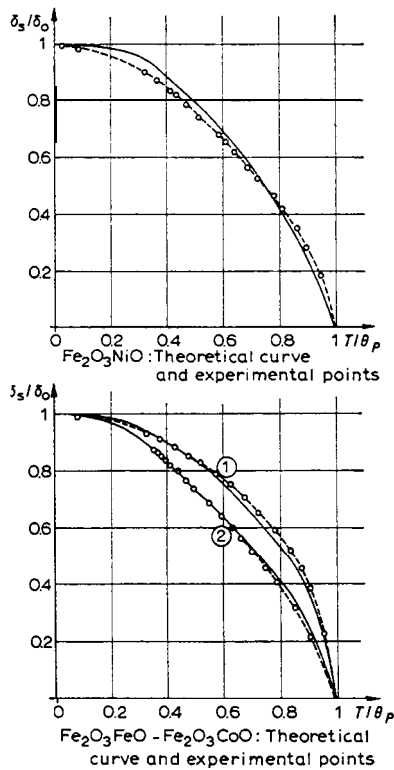

Fig. 15. Temperature dependence of the spontaneous magnetization of various ferrites (experimental points and curves calculated with the molecular-field coefficients deduced from the study of the susceptibility).
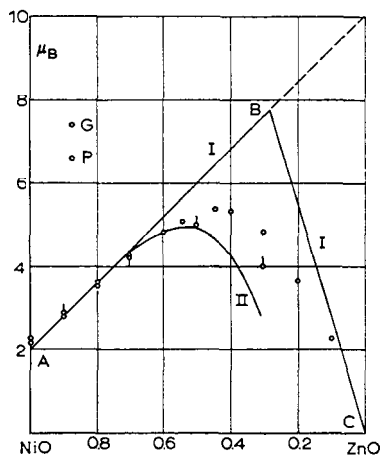
Fig. 16. Variations of the saturation magnetization of composite nickel and zinc ferrites with the zinc content (experimental points and calculated curves).

The theory of ferrimagnetism also makes it possible to explain the behaviour of composite ferrites, like the nickel-zinc ferrites with the formula $Fe_2N_{1-x}Zn_xO_4$. An atom of zinc which replaces an atom of nickel will locate itself on an A site, since that is the place preferred by zinc, simultaneously, the Fe^{3+} ion located on this A site will occupy at B the place left vacant by the departure of the Ni ion at the same time as its magnetic moment of $5 \mu_B$ reverses direction. The net variation of the saturation magnetic moment is therefore equal to $8 \mu_B$, the difference between $10\mu_B$ resulting from the reversal and $2 \mu_B$ resulting from the departure of the Ni^{2+} ion. The slope of the initial tangent to the curve giving the saturation magnetization as a function of x is therefore equal to $8 \mu_B$. The experimental results confirm this prediction[26] (Fig. 16).

10. The case of pyrrhotite

Shortly afterwards, the same theory made it possible to solve the riddle posed by pyrrhotite, Fe_7S_8, a ferromagnetic compound studied a long time ago by P. Weiss[27], which has a small saturation magnetic moment, of the order of 3 μ_B, whilst from its formula a value of about $30\mu_B$ might be expected. Pyrrhotite has the same crystal structure, Ewald's type B8, as the sulphide FeS, which is a typical antiferromagnetic: in the latter the successive planes of iron atoms, perpendicular to the ternary axis, are magnetized in a certain direction in one

sense and the other in alternation. F. Bertaut has shown[28] that actually pyrrho-
tite is a compound containing vacancies whose formula should rather be
written Fe_7S_8T, where T denotes vacancy, *i.e.* a site that would be occupied
by an Fe^{2+} ion in the compound FeS, but that is vacant in Fe_7S_8. At low tem-
perature the vacancies assume an ordered distribution and group themselves,
as shown in Fig. 17, on the even-order iron planes: in short, the vacancies tend
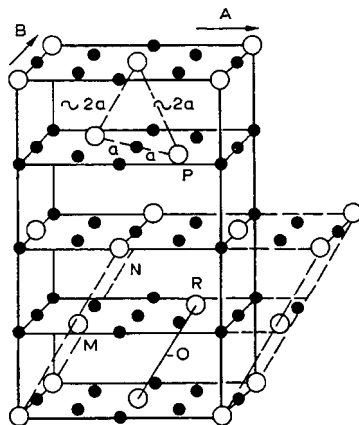

Fig. 17. Crystal structure of pyrrhotite at low temperature. The black circles represent
the iron atoms and the white circles the vacancies. The odd-order iron planes and the
oxygen atoms are not shown.

to space themselves as far as possible from one another. On the odd-order
iron planes all the sites are occupied. The two sub-lattices equivalent in the
case of FeS become different, and we are then dealing in the case of Fe_7S_8 with
true ferrimagnetism. When the temperature rises above 900 °K, the ordering
of the vacancies disappears and the two sub-lattices become statistically equiv-
alent: correlatively, the paramagnetic susceptibility of pyrrhotite assumes
values close to those of FeS.

11. Discovery of the garnet ferrites

There is no doubt that the garnet ferrites offer the finest illustration of ferri-
magnetism. These substances, with the general formula $Fe_5M_3O_{12}$, where M
is a trivalent rare-earth metal ion, form an important class of magnetic com-
pound whose properties are explained simply and accurately by ferrimagne-

tism with three sub-lattices. Besides, since the metal ions entering into their composition can be replaced by a very wide variety of other ions, these compounds are of great interest in the theoretical study of interactions. From the point of view of applications, they are excellent insulators, can be prepared in large crystals, and have very sharp resonance lines; they can be used at very high frequencies in a large number of devices.

The history of their discovery begins in Strasbourg in 1950, where Forestier and Guiot-Guillain[29] heated an equimolecular mixture of Fe_2O_3 and M_2O_3 (M = rare earth metal) and obtained strongly ferromagnetic products whose Curie points ranged from 520 to 740 °K and to which they attributed a perovskite-type structure[30]. They then demonstrated the curious fact[31] that with M = Yb, Tm, Y, Gd, or Sm, these products had two Curie points spaced about a hundred degrees apart and varying regularly as a function of the atomic radius of M.

These results attracted the attention of research workers at Grenoble: Pauthenet and Blum[32] prepared a gadolinium ferrite and showed that besides the two Curie points, $\theta_1 = 570$ °K and $\theta_2 = 678$ °K, this compound had a third transition temperature $\theta_3 = 306$ °K, identifiable as a *compensation temperature* in the sense of the ferrimagnetism theory, *i.e.* as a temperature corresponding to a change of sign of the spontaneous magnetization (types V and N in Fig. 7).

To explain these facts, I suggested[33] that the Fe^{3+} ions had to form a ferrimagnetic arrangement A, with a structure independent of M, whose resultant spontaneous magnetization magnetized the B sub-lattice of the M^{3+} ions in the opposite direction. The molecular field h_A representing the action of A on B had to be sufficiently weak for the magnetization of B to be effectively equal to $C_B h_A/T$, at least above 100 °K, the temperature θ_3 being one at which the magnetization of B is equal and opposite to that of A. In particular, it followed from this that the temperature θ_3 had to be the lower the smaller is the Curie constant C_B of the M^{3+} ions. In agreement with these predictions, it was shown a few days later[34] that the ferrites of dysprosium and erbium also had compensation temperatures, located at 246 and 70 °K respectively. Despite these successes, this assumed structure was incompatible with that of a perovskite with formula $FeMO_3$.

Starting from the assumption of another compound mixed with the perovskite, Bertaut and Forrat[35] showed in January 1956 that it was a question of a cubic compound, $Fe_5M_3O_{12}$, of space group O_h^{10} Ia3d, with 8 molecules in the unit cell, of structure identical to that of the semi-precious stones known as *garnets* (Fig. 18). The primary ferrimagnetic arrangement comprises 24 Fe^{3+}
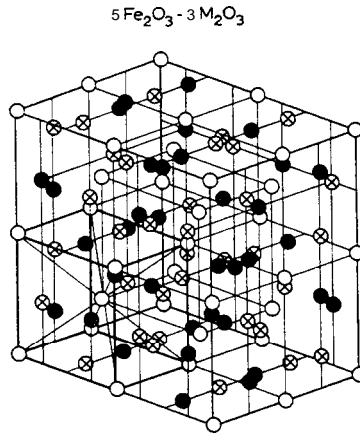
$5\,Fe_2O_3 \cdot 3\,M_2O_3$

Fig. 18. Crystal structure of the garnet ferrites. o, Fe ion on site a; ⊗, Fe ion on site d;
●, M ion on site c. (after Strukturbericht and F.Forrat)

ions on sites d surrounded by 4 O^{2-} ions, and 16 Fe^{3+} ions on sites a, sur-
rounded by 6 O^{2-} ions. This arrangement bound by strong interactions, has
magnetic properties effectively independent of the nature of the ions M, to
which it is coupled antiferromagnetically be weak interactions. It can be
studied magnetically in the isolated state by taking a non-magnetic ion such
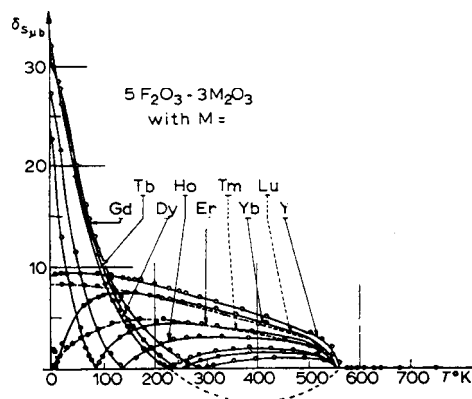as Y or Lu for M.

Fig. 19. Temperature dependence of the spontaneous magnetization of a series of garnet
ferrites. In particular, it will be noted how the compensation point varies with the atomic
number of the rare earth.

12. Interpretation by ferrimagnetism with three sub-lattices

The generalization of the theory of ferrimagnetism to 3 sub-lattices and the representation of the interactions by means of 9 local molecular fields, 6 of them independent, raises no problem. The agreement of the calculated curves with the experimental results is very satisfactory, as shown in Fig. 19 , taken from Pauthenet's fundamental paper[36] on the temperature dependence of the spontaneous magnetization of various garnets. The near identity of their Curie points well illustrates the fact that the nature of the M ions does not modify the ferrimagnetic arrangement of the Fe^{3+} ions. Above the Curie point, in the paramagnetic region, the agreement of the calculated curves with the experimental curves is also satisfactory (Fig. 20).
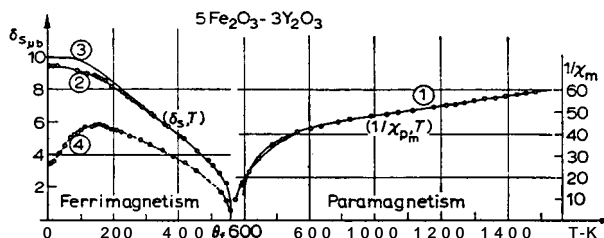

Fig. 20. Yttrium garnet. Temperature dependence of the spontaneous magnetization and of the inverse susceptibility; experimental points and curves calculated using the same molecular field coefficients. Curve (4) refers to an yttrium garnet containing a small amount of gadolinium.

13. Superexchange

Both in respect of antiferro- and ferrimagnetism, the theory makes it possible to deduce from the experimental curves the elementary interaction energy *w* between two close-neighbour magnetic atoms. This calculation undertaken for spinel ferrites and a few antiferromagnetics such as MnO or NiO brings out some new facts[20,37]. In these substances the interactions between neighbouring iron ions are negative, at exactly the mutual distances for which they are positive in the pure metal or in alloys. It is further observed that there are considerable interactions between magnetic atoms separated by oxygen atoms, which ought to act as screens. The answer is even more revolutionary: it is actually a case of *superexchange interactions,* in which the oxygen atom separating two iron atoms plays an essential part. A considerable time ago

Kramers had already predicted[38] the possibility of such interactions, but this was the first time that their objective existence had been clearly demonstrated.

Thus, in oxides and ferrites exchange interactions of the classical type M-M coexist with superexchange interactions of the type M-O-M; this, then, is first-class material for testing the theories of the various interactions.

14. Conclusions

Despite its rather naive simplicity, the local molecular-field method has had some undeniable successes in linking up, in an intellectually very satisfying way, a large number of already known facts and in leading to the discovery of new facts.

It should be noted that all the structures discussed in this paper are *collinear:* all the atomic magnets are on average (in time) parallel, in one sense or other, to the same direction. However, the method of the local molecular field may be extended also to non-collinear structures, such as that of *helimagnetism,* which Yoshimori and Villain discovered independently and absolutely un-expectedly: in this way the phenomena can be interpreted remarkably simply and specifically.

In spite of everything, it hardly seems recommendable to extend the method to more complex structures, such as the umbrella structure, requiring the main crystal lattice to be broken down into a large number of sub-lattices. Indeed, under these conditions, an atom belonging to a given sub-lattice has only a very small number of neighbours in each of the other sub-lattices, often it has only one or two. The molecular field method, which consists of re-placing the instantaneous action of an atom by that of an *average atom,* has many more chances of leading to a correct result as it deals with a greater num-ber of atoms. It is probably the more correct, the higher the atomic spin num-ber. Independently of this problem, the method applied to a large number of sub-lattices loses its main advantage of simplicity.

The method also has more insidious traps. If the parameters are suitably chosen, it can lead to the calculation of curves showing the temperature de-pendence of the spontaneous magnetization, or of the paramagnetic suscep-tibility, which coincide remarkably with the experimental results, say to within a few parts in a thousand. Under these conditions it could be expected that the elementary interaction energies deduced from these parameters would correspond to the true values with the same accuracy. Nothing is farther from

the truth: errors of 10-20% and even more are made. Some prudence is therefore indicated.

On the other hand, recourse to the local molecular field seems essential, for the most rigorous methods lead to inextricable complications. It should be remembered that we still do not have the rigorous solution to even the simplest case, this being the case of a single cubic lattice with identical atoms of spin 1/2 and interactions reduced to those exerted between close-neighbour atoms. What, then, are we to think of the case of garnets with 160 atoms in the unit cell, spins of up to 5/2, and at least six different coupling constants? The imperfections in molecular field methods must be treated with indulgence when we consider the simplicity with which the successes discussed in the first lines of these conclusions were obtained.

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