



HAL
open science

Antiferromagnetism and Ferrimagnetism

Louis Néel

► **To cite this version:**

| Louis Néel. Antiferromagnetism and Ferrimagnetism. Proceedings of the Physical Society. Section A, 1952, 65 (11), pp.869–885. 10.1088/0370-1298/65/11/301 . hal-02888376

HAL Id: hal-02888376

<https://hal.science/hal-02888376v1>

Submitted on 29 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Antiferromagnetism and Ferrimagnetism

To cite this article: Louis Néel 1952 *Proc. Phys. Soc. A* **65** 869

View the [article online](#) for updates and enhancements.

Related content

- [Antiferromagnetism](#)
A B Lidiard
- [Ferrites](#)
A Fairweather, F F Roberts and A J E Welch
- [Ferrimagnetism](#)
W P Wolf

Recent citations

- [Magnetic Structure and Metamagnetic Transitions in the van der Waals Antiferromagnet CrPS₄](#)
Yuxuan Peng *et al*
- [Synthesis of CoFe₂O₄ Nanoparticles: The Effect of Ionic Strength, Concentration, and Precursor Type on Morphology and Magnetic Properties](#)
Izabela Malinowska *et al*
- [Impact of dehydration and mechanical amorphization on the magnetic properties of Ni\(ii\)-MOF-74](#)
Senada Muratovi *et al*

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

Section A

VOL. 65, PART 11

1 November 1952

No. 395A

Antiferromagnetism and Ferrimagnetism*

By LOUIS NÉEL

Laboratoire d'Électrostatique et de Physique du Métal, Université de Grenoble

7th Holweck Lecture, delivered 27th May 1952; MS. received 27th May 1952

ABSTRACT. The present position of our knowledge of antiferromagnetism, including ferrimagnetism, is reviewed, and some very interesting phenomena concerning the magnetic behaviour of certain ferrites and of pyrrhotite are described and explained.

I—ANTIFERROMAGNETISM

§ 1. THE NEGATIVE MOLECULAR FIELD AND ANTIPARALLEL SYSTEMS

WE know that in his celebrated theory of ferromagnetism (Weiss 1907) represented the interactions between the magnetic moments of neighbouring atoms by means of a molecular field

$$H_m = nJ \quad \dots (1)$$

proportional to the magnetization J , n being a constant. The magnetic susceptibility s of the substance is therefore given by the Curie-Weiss equation

$$s = C/(T - nC). \quad \dots (2)$$

The reciprocal of the susceptibility $1/s$ decreases linearly with absolute temperature and, when n is positive, becomes zero at a temperature $\theta = nC$, called the Curie temperature, or better the Weiss temperature, below which the substance is spontaneously magnetized under the action of its own molecular field: in this way one can account for the principal properties of ferromagnetic substances like iron, nickel, etc. When n is negative s takes a finite value at absolute zero equal to $-1/n$.

About 1932 I suggested (Néel 1932 a) that eqn. (2), which is based on the hypothesis of a random orientation of the atomic magnetic moments in the absence of an applied field, ought to break down at low temperatures because antiparallel arrangements of atomic moments should be formed under these conditions. In fact, the original crystalline lattice ought to break down into two sub-lattices A and B, with the moments of the atoms in A directed in one sense and those in B directed in the opposite sense, as shown in fig. 1. Energy considerations

* Delivered in French; translated into English by Professor L. F. Bates.

show that these two sub-lattices should be such that an atom in the sub-lattice A should have the maximum possible number of neighbours in sub-lattice B and vice versa: in fig. 1 all the neighbours of an atom A are of type B. Under the action of a field h this antiparallel arrangement is deformed (fig. 2).

An elementary calculation on classical lines, applied to elementary moments which are capable of being freely rotated, shows that when the temperature is

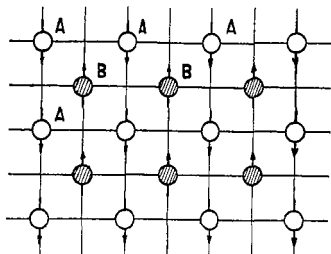


Fig. 1. Resolution of a plane lattice into two sub-lattices.

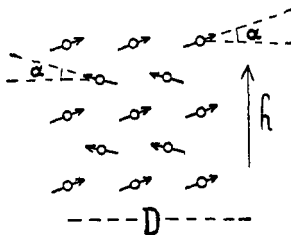


Fig. 2. Action of a field h on an antiparallel arrangement, the direction of antiferromagnetism is given by D.

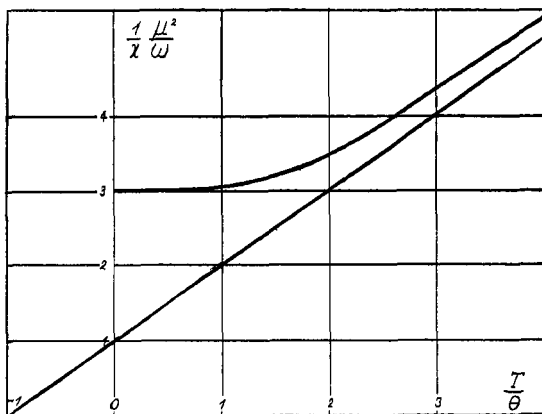


Fig. 3. Variation with temperature of the susceptibility of an antiparallel arrangement of moments; the asymptote corresponds to the Curie-Weiss law.*

markedly below $-nC$ the magnetic susceptibility of the system is constant, independent of the temperature, and given by

$$s = -k/n, \quad \dots\dots(3)$$

where k is a numerical coefficient equal, for example, to $\frac{1}{3}$ for a body-centred-cubic lattice or for the two-dimensional case represented in fig. 1. At high temperatures with respect to $-nC$ the antiparallel arrangement is destroyed and eqn. (2) is again obeyed. In conjunction with the properties of a diatomic arrangement one deduces that $1/s$ varies with T in the manner indicated by the curve of fig. 3: the asymptote of this curve corresponds to the Curie-Weiss law given by eqn. (2).

* In diagrams for which blocks were already available χ and S are sometimes used to indicate susceptibility.

§ 2. THE INTERPRETATION OF THE MAGNETIC PROPERTIES OF MANGANESE AND CHROMIUM

The mechanism which has just been described gives at low temperatures something which may be conveniently termed *constant paramagnetism*. I proposed at the time (Néel 1932b) to explain on these lines the magnetic properties of manganese and chromium which, in effect, exhibit a constant paramagnetism too large to be explained by the Pauli theory of paramagnetism arising from free or partially free electrons. According to the point of view proposed here, one therefore attributes to the atoms of manganese or of chromium a definite magnetic

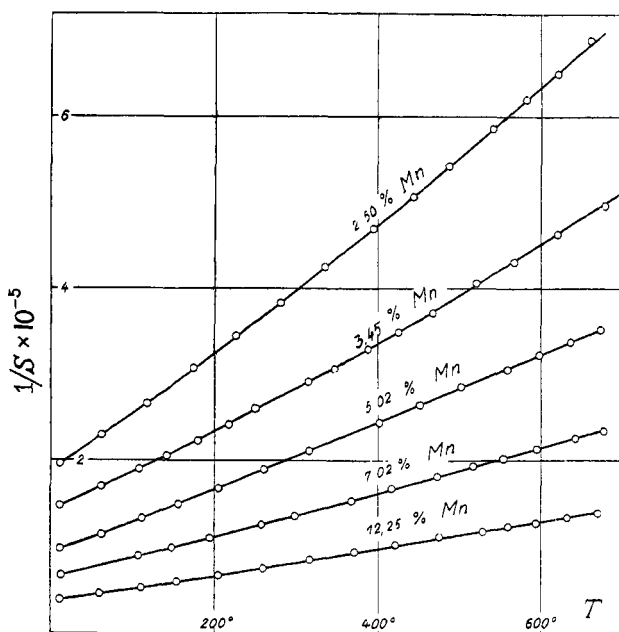


Fig. 4. Variation with temperature of the reciprocal of the susceptibility of solid solutions of manganese in silver.

moment. I estimated the value of nC to be 1720°K for manganese and 4150°K for chromium, so that the region of temperature at which measurements can be made is limited to that where the susceptibility is practically independent of temperature. Yet, on decreasing the interactions between the magnetic atoms, it should be possible to reach the region of the curve in fig. 3 which is close to the asymptote and to obtain direct evidence of the magnetic moments of the substances under consideration. By dissolving manganese or chromium in a non-magnetic metal like gold, silver or copper, I showed that one obtains solid solutions obeying the Curie-Weiss law: fig. 4 shows, for example, the experimental results for manganese dissolved in silver. With the aid of the Curie constant C thus obtained one finds for manganese or chromium an atomic moment a little less than 4 Bohr magnetons.

§ 3. THE EFFECT OF MAGNETO-CRYSTALLINE COUPLING

A little later, in 1936, I examined (Néel 1936 a) the effect of magneto-crystalline coupling between the lattice and the atomic moments. Let us call D the common direction along which the atomic moments of the two sub-lattices are aligned at absolute zero, in one sense or the other; this may also be called the direction of antiferromagnetism. When the moments are not coupled with the lattice, that is to say where there exist only exchange forces of an isotropic kind, the direction D is orientated perpendicular to the applied field. When coupling exists D occupies a privileged direction and is fixed with respect to the lattice in the absence of an applied field, and remains orientated in this direction when the applied field is weak. If the applied field is already normal to the privileged direction the results are the same as those obtained when coupling is absent; but if the field is applied parallel to the privileged direction and if the temperature is close to absolute zero the susceptibility is at first zero in weak fields, then for a certain critical field H_0 decoupling takes place and the direction D turns suddenly to set perpendicular to the field: at the same time the susceptibility suffers a discontinuous change and takes a finite value, identical with that of the preceding case. Figure 5 gives the

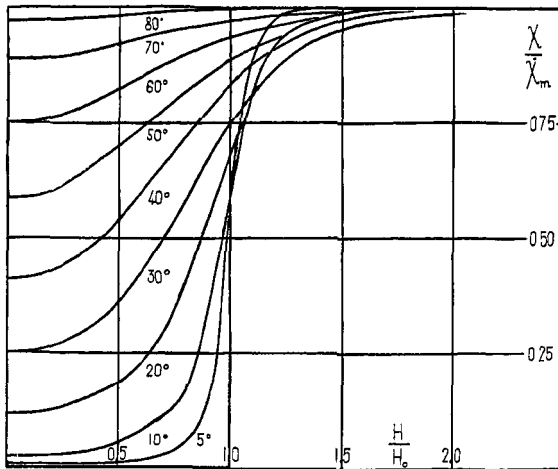


Fig. 5. Susceptibility as a function of field for different orientations of the field with respect to the direction of antiferromagnetism.

values of the susceptibilities for different directions of the field H with respect to the orientation of the privileged direction as a function of the reduced field H/H_0 .

This phenomenon and its discontinuity have recently been observed by C. J. Gorter and his collaborators (Poullis *et al.* 1951, Poullis 1952) in the course of a study of the magnetic properties of a crystal of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) at liquid helium temperatures.

When the directions D are randomly distributed, as is probably the case in a polycrystalline substance, one recognizes that the susceptibility must vary with the field: curve A of fig. 6 gives an example of the thermal variation of the susceptibility in weak fields and curve B that in strong fields. The theory of the phenomena of D coupling has recently been taken up in Japan by Nagamiya (1951) and his collaborators (Yosida 1952). It is possible that the hitherto unexplained

variations of the magnetic susceptibility of platinum as a function of field and temperature, studied in detail by Collet and Foëx (1931) and Foëx (1939), have their origin in a similar mechanism.

§ 4. THE MOLECULAR FIELD APPLIED TO ANTIFERROMAGNETISM

The method proposed above only gives results applicable to the two extreme cases of very low or very high temperatures. In order to obtain a more precise idea of the phenomena in the intermediate region I proposed in 1936 (Néel 1936 b) to treat negative interactions by the method of the molecular field, considering the two sub-lattices A and B to be spontaneously magnetized, each in an inverse sense, under the action of two molecular fields $n_{aa}J_a$ or $n_{bb}J_b$, proportional to the magnetization J_a or J_b , of its own sub-lattice and the other $n_{ab}J_b$ or $n_{ba}J_a$, proportional to the magnetization of the other sub-lattice. The molecular field acting on sub-lattice A will be, for example,

$$H_a = n_{aa}J_a + n_{ab}J_b. \quad \dots\dots(4)$$

Here, on account of symmetry, $n_{aa} = n_{bb}$ and $n_{ab} = n_{ba}$, but the two coefficients n_{aa} and n_{ab} are not equal because they represent short-distance interactions which

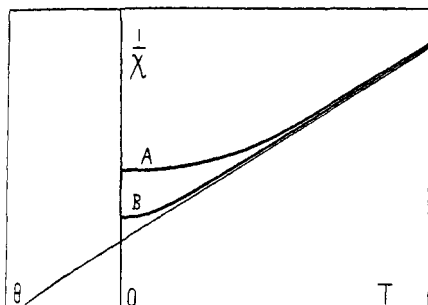


Fig. 6. Action of the field on the susceptibility of an antiferromagnetic arrangement. A, weak fields, B, strong fields.

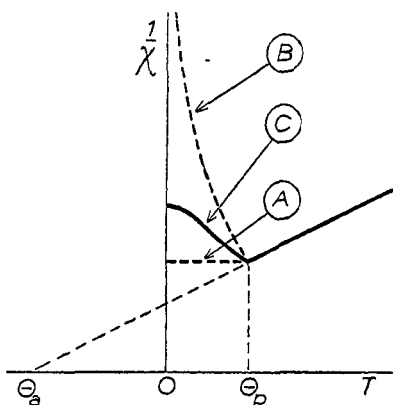


Fig. 7. Variation of the reciprocal of the susceptibility of an antiferromagnetic with temperature. A, the direction of antiferromagnetism is perpendicular to the applied field; B, parallel to the applied field; C, in any direction.

are different. In addition, the coefficient n_{ab} is essentially negative, otherwise one would have ordinary ferromagnetism.

The analysis of the problem thus shows that the two sub-lattices acquire spontaneous magnetizations which are equal and opposite in sign and decrease with temperature to become zero at a definite temperature of transition T_a . In fact, at temperatures below T_a the magnetic moments are ranged in a regular manner, while above this temperature complete statistical disorder obtains in the substance. From an energy point of view this ordered phase behaves like an ordinary ferromagnetic, and is characterized by a specific heat anomaly of which the order of magnitude and type of thermal variation are the same as for a ferromagnetic substance.

As far as the magnetic properties are concerned, since the resultant spontaneous magnetization of the ordered phase is zero because the spontaneous magnetizations of the sub-lattices exactly compensate one another, the substance always remains paramagnetic whatever the temperature. The application of an external field perturbs the system and gives rise to a magnetic susceptibility which, in the absence of magnetocrystalline coupling with the lattice, remains *constant* up to the transition temperature T_a . Above this temperature the susceptibility obeys the Curie-Weiss law represented by eqn. (2) with a negative Curie point $\theta = nC$. On the whole the thermal variation of the susceptibility is represented by Curve A of fig. 7. One notes that the transition point (θ_p in the figure) is marked by a sharp change, that is to say by a discontinuity of the rate of change of susceptibility with respect to temperature. Such are the essential features of what it is now convenient to call *antiferromagnetism*.

When coupling exists between the atomic moments and the crystalline lattice the susceptibility always follows curve A when the applied field H is perpendicular to the direction of antiferromagnetism D , but, when the field H is parallel to this direction, Bitter has shown (1938) that one obtains a curve like B (fig. 7) with a susceptibility which disappears at absolute zero. Finally, with the directions D randomly distributed, one ought to observe a mean curve C, as Van Vleck (1941) has pointed out: the susceptibility at absolute zero is thus equal to two-thirds of its value at the transition point.

At the outset even manganese hardly seemed to satisfy the predictions of the theory: its specific heat anomaly was rather controversial, but Bizette, Squire and Tsai were soon able to prove (1938) that the oxide MnO possessed the properties characteristic of an antiferromagnetic body, with a sharp break in the susceptibility curve at 122°K accompanied by a specific heat anomaly and an anomaly in its thermal expansion. A little later Foëx and Graaf (1939) discovered that Cr_2O_3 showed analogous properties. The list of antiferromagnetic substances then grew rapidly, mainly due to Bizette and Tsai (1951), with the addition of MnS, MnTe, FeO, FeS, CoO, NiO, etc. The properties of these substances agree quite well with the curve C given by Van Vleck (fig. 7). In addition, one observes an increase of susceptibility with field, below the transition temperature, which represents a progressive decoupling for the direction D , predicted by the original theory.

Yet the most satisfactory confirmation of the fundamental ideas was really given by Shull. The theory of antiferromagnetism is based in effect on the breakdown of the crystalline lattice into two sub-lattices magnetized in opposite senses. If atoms possessing magnetic moments directed in opposite senses may be considered different from one another, then we have to deal with a kind of superlattice; such a superlattice cannot be revealed by means of x-rays whose diffraction is not affected by the orientation of the moments, but one can show it to exist by using a beam of neutrons, when extra diffraction lines are obtained which are characteristic of the antiferromagnetic state and which disappear when the temperature of the substance is raised above the transition temperature. Shull *et al.* (1951 b) should be given the credit for the experiments which permit us to fill in details of the antiferromagnetic structure. Figure 8, due to these authors, allows us to compare the diffraction diagrams of MnO above and below the transition point. One observes from the (111) plane the extra diffraction lines due to the magnetic superlattice. These experiments have shown that the atoms of

manganese are arranged in successive planes perpendicular to a ternary axis and that these planes are magnetized alternately in opposite senses: now this is exactly the structure which I was led to propose some time ago (Néel 1948) from purely magnetic considerations. Neutron diffraction experiments also permit us to fix D the direction of antiferromagnetism. This is parallel to a quaternary axis for the cases of MnO, MnS, MnTe, CoO and NiO, while it is parallel to a ternary axis in FeO.

§ 5. PROPERTIES OF SOME ANTIFERROMAGNETIC CRYSTALS

In the case of a single crystal the relations between the axis of symmetry of the crystalline lattice and the direction D can be studied by purely magnetic methods. Let us take for example manganese difluoride MnF_2 , which is a tetragonal uniaxial

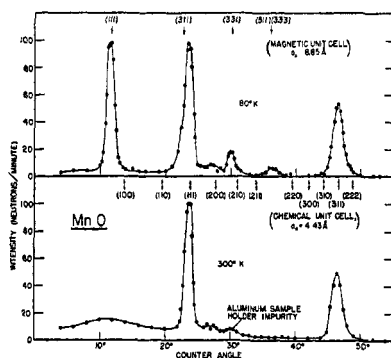


Fig. 8. Diffraction of neutrons by MnO (C. G. Shull). One notes the extra peak due to the antiferromagnetic resolution into two sub-lattices.

crystal of the rutile type. From the measurements of Bizette and Tsai (1939) on powdered specimens, and of Stout and Griffel (1949) on the single crystal, it is seen that in the antiferromagnetic region the susceptibility remains practically independent of temperature when it is measured in a direction perpendicular to the quaternary axis, which corresponds to curve A of fig. 7, whilst it tends to become zero at $0^\circ K$ after the manner of curve C along the direction of the axis: these are the properties which one would expect when the antiferromagnetic direction coincides with the quaternary axis. The rhombic sesquioxide of iron $\alpha\text{Fe}_2\text{O}_3$ is equally interesting: it exhibits a fundamental antiferromagnetism superimposed upon a very weak ferromagnetism whose origin is not very clear (Néel 1949) but which we may neglect here. The study of its magnetic properties suggested to me (Néel 1948, 1949) that at ordinary temperatures the successive layers of iron atoms, perpendicular to the ternary axis, were magnetized consecutively in opposite directions, with a direction of antiferromagnetism perpendicular to the ternary axis. These two predictions were confirmed by Shull *et al.* (1951 b) by means of neutron diffraction.

As has been shown by Morin (1950) and by Guillaud (1951) by magnetic studies, the sesquioxide of iron exhibits an anomaly at a temperature of $-78^\circ C$. M. Pauthenet has undertaken the study of this question in my laboratory using a single crystal of haematite. The results (Néel and Pauthenet 1952) were roughly as follows: in a direction perpendicular to the ternary axis the susceptibility remains practically constant from liquid air temperatures up to the transition

temperature 675° c. On the other hand, in the direction of the axis the susceptibility is at first very weak at low temperatures, taking a value in the region of -78° c almost equal to the value along the perpendicular direction and maintaining that value up to the transition point. These facts may be explained very easily if one supposes that the direction of antiferromagnetism coincides with the ternary axis below -78° c and moves into the perpendicular plane, *with freedom of orientation*, at higher temperatures. This change in orientation may be likened to those undergone by the directions of easy magnetization in uniaxial ferromagnetic bodies like cobalt or MnBi. It is to be noted that in the case of the latter substance Guillaud (1943) has shown that there exists a plane of easy magnetization perpendicular to the hexagonal axis below 84° k, whilst the hexagonal axis becomes an axis of easy magnetization above that temperature.

§ 6. THE APPROXIMATE NATURE OF THE THEORY

As we have just seen, the theory of antiferromagnetism, based on the reduction to two sub-lattices and extension thereto of the hypothesis of the molecular field, has permitted us to predict and to coordinate a large number of experimental facts: one could hardly expect more. On one hand, its classical nature does not allow it to be rigorously applied except to atoms possessing a relatively large magnetic moment; on the other hand, the representation of interactions by a molecular field is the better the larger the number of neighbours which act magnetically upon a given atom. It is, therefore, a theory of limited application very badly adapted, for example, to the case of a linear chain of atoms, of spin $s = \frac{1}{2}$, as Kramers (1952) has noted. One might also raise the same objections to the molecular field theory of ferromagnetism, whose utility one nevertheless appreciates: it is only necessary to bear in mind the limited and approximate nature of the theory which one uses.

II—FERRIMAGNETISM

§ 1. IMPERFECT ANTIFERROMAGNETISM

In an antiferromagnetic substance the two sub-lattices are physically and essentially identical, so that their spontaneous magnetizations compensate one another exactly, and the resultant spontaneous magnetization is consequently exactly zero. But one could very well imagine, for some reason or other, that the two sub-lattices are not exactly equivalent; the spontaneous magnetization of one of the sub-lattices will then be greater than that of the other, and the resultant spontaneous magnetization will be different from zero, as in a ferromagnetic substance. This is the reason why the iron sulphide FeS is a normal antiferromagnetic, where the number of atoms of sulphur is equal to the number of atoms of iron, for the two sub-lattices are then exactly the same. But when there is a net excess of sulphur, as in the case of pyrrhotite FeS_{1.17}, the two sub-lattices are different and ferromagnetism is exhibited: we will return to this example later. It is probable that the small superimposed ferromagnetism of α -Fe₂O₃ arises in an analogous manner.

However, the outstanding example of these phenomena is that of the ferrites Fe₂O₃.MO, where M is a bivalent metal, such as copper, nickel, cobalt, iron, manganese, etc. The crystalline lattice is then of the spinel type Al₂O₃.MgO. The metallic ions may occupy two different categories of sites from the crystallographic point of view: A sites surrounded by four atoms of oxygen and B sites

surrounded by six atoms of oxygen. For each molecule there are one A site and two B sites. Verwey (Verwey and Heilmann 1947, Verwey and de Boer 1936) showed by x-ray studies that the ferromagnetic ferrites which are of interest to us possess a structure which is called *inverse*, in which the A site is occupied by a Fe^{3+} ion and the two B sites by the M^{2+} ion and the other Fe^{3+} ion. Experiment shows that magnetically these substances are characterized by a feeble saturation magnetization with respect to the total magnetic moment of the ions which are present, and above the Curie point by a thermal variation of the susceptibility which is distinctly different from that of ordinary ferromagnetics; by representing the reciprocal of the susceptibility $1/\chi$ as a function of the temperature T one obtains a hyperbola instead of a straight line, as is evident in the early measurements of Mile Serres (1932) and the more recent results of Fallot and Maroni (1951) (cf. fig. 12). This was an irritating puzzle for the theoreticians.

In order to interpret these properties I supposed (Néel 1948) that in these substances the principal magnetic interactions were those of the ions situated in A sites with the ions situated in B sites, and that the interactions AB were *negative*.

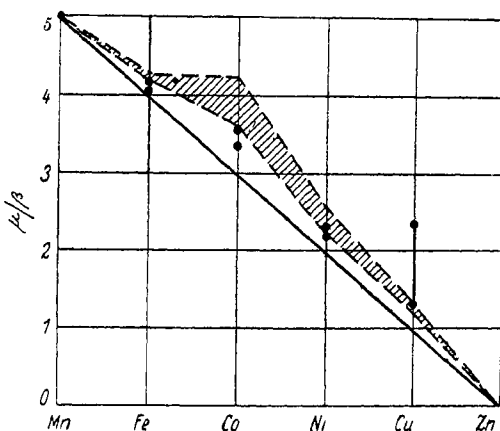


Fig. 9. Comparison of molecular moments predicted by theory and experimental values for certain ferrites.

One may easily show that if the interactions AB are sufficiently large with respect to the interactions AA between atoms situated in A sites and the interactions BB between atoms situated in B sites, two magnetic sub-lattices are formed, composed of the ions situated in sites A and of the ions situated in sites B respectively: these two sub-lattices are both magnetized to saturation at absolute zero, but in *opposite senses*. As these two sub-lattices are essentially different, there exists a resultant spontaneous magnetization which is not zero and a ferromagnetism which arises, paradoxically enough, from negative interactions. In view of this fact and of the rather special properties which follow from it, I thought it appropriate to give the name *ferrimagnetism* to this mechanism.

§ 2. PROOFS OF FERRIMAGNETISM

It follows from the above hypothesis that at low temperatures the magnetic moments of the two ferric ions in the molecule compensate one another because they belong to different sub-lattices: the molecular moment is therefore merely equal to that of the ion M^{2+} . Figure 9 gives in Bohr magnetons the saturation

molecular moments of a number of ferrites (black circles) from determinations made in different laboratories. The hatched region corresponds to the predicted theoretical moments, taking account of probable orbital moments; the continuous line refers to moments due to spin only. The agreement is very satisfactory except in the case of copper: we shall see later a reason for this apparent exception.

Neutron diffraction has brought an even more direct confirmation of the ferrimagnetic structure: Shull *et al.* (1951 a) has shown that in the case of magnetite the ions situated in A sites possess magnetic moments oppositely directed to the resultant total magnetization.

Another striking confirmation of the theory is given by the variation with concentration of the molecular moment of the theory and experimental values of certain mixed ferrites in which a

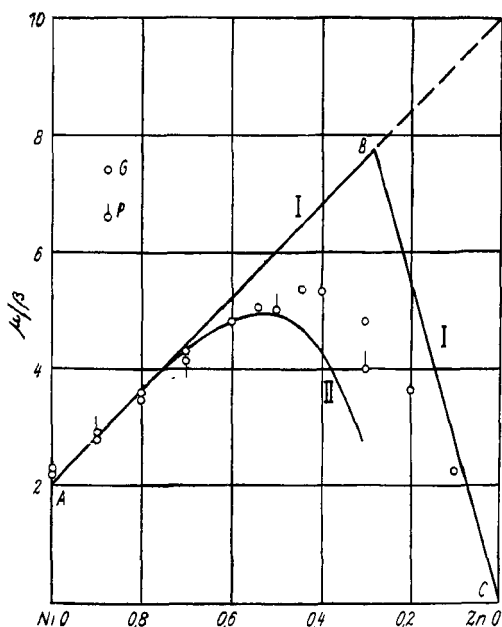


Fig. 10. Comparison of molecular moments predicted by theory and the experimental values for the series of mixed ferrites of nickel and zinc: G, Guillaud's values, P, Gorter's values.

portion of the ions M is replaced by non-magnetic Zn^{2+} ions. For zinc ferrite is a *normal* ferrite, i.e. a ferrite in which the two Fe^{3+} ions are in the two B sites, whilst the Zn^{2+} ion occupies the A site, for which it has a special affinity. When in an inverse ferrite one replaces an M ion in a B site by a Zn ion, that Zn ion goes into an A site causing the movement of an Fe^{3+} ion from a B to an A site. This results in the reversal of the magnetic moment of this Fe^{3+} ion, which is equal to five Bohr magnetons. The net effect is that the replacement of an M ion by a Zn ion produces an increase of moment equal to $10 - m$ Bohr magnetons, m denoting the moment of the M ion. These predictions were verified in a remarkable manner by the experiments of E. W. Gorter (1950) at Eindhoven and by Guillaud (1949) at Bellevue. Figure 10 shows as an example the results obtained with mixed ferrites of nickel and zinc: on the NiO side the experimental moments fall remarkably well upon the theoretical line AB.

The case of copper ferrite, to which we have just referred, is particularly interesting: here we have an inverse ferrite in which the affinity of the M ion, namely the Cu^{2+} ion, for the B sites is particularly weak. It therefore happens that at high temperatures these ions are randomly distributed over the A and B sites: on the average one-third are on the A sites and two-thirds on the B sites. When the temperature is lowered they all progressively reoccupy the B sites. Quenching permits us to keep in unstable equilibrium the different intermediate

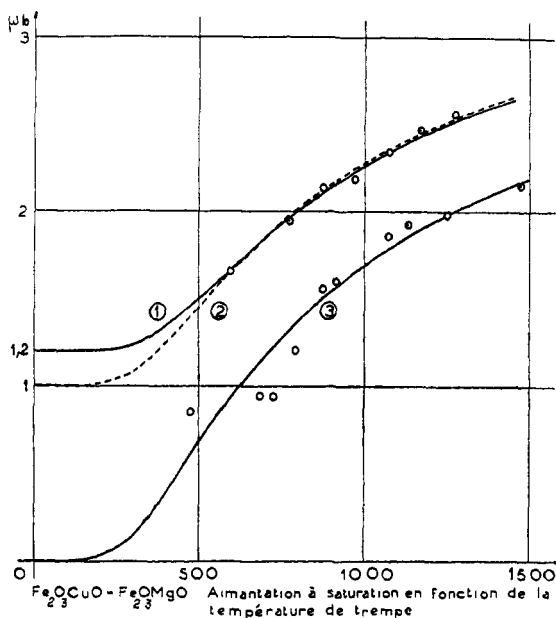


Fig. 11. Saturation magnetization of copper and magnesium ferrites as a function of quenching temperature; theoretical curves shown by full lines. Upper curve $\text{Fe}_2\text{O}_3\text{CuO}$; lower curve $\text{Fe}_2\text{O}_3\text{MgO}$.

states and, therefore, makes manifest the variations of molecular moment as a function of the quenching temperature. Pauthenet and Bochirol (1951) have studied this phenomenon in my laboratory and have shown that the observed moments agree well with the moments predicted by the statistical theory. In fig. 11 the observed values are compared with the theoretical curves (full lines) in the case of copper ferrite and the closely analogous magnesium ferrite. These atomic migrations within the crystalline lattice, thus demonstrated by magnetic methods, have been confirmed by x-ray analysis by one of my collaborators, M. Bertaut (1951).

In conclusion, we see that it is possible to predict the molecular moment of ferrimagnetic bodies with much greater exactness than that of the ordinary ferromagnetics, iron, nickel or cobalt. This was *a priori* very unexpected.

§ 3. APPLICATION OF THE MOLECULAR FIELD THEORY TO FERRIMAGNETISM

We have thus been able to extend the theory of ferrimagnetism by generalizing the hypothesis of the molecular field and by representing the different interactions present, AA, AB and BB, by three molecular field coefficients. We thus show that

the susceptibility s above the Curie point is represented by a hyperbolic type of expression of the form

$$1/s = T/C + 1/\chi_0 - \sigma/(T - \theta), \quad \dots\dots(5)$$

where C is the Curie constant corresponding to the given ions in the absence of interactions, and χ_0 , σ and θ are functions of the three molecular field coefficients n_{AA} , n_{AB} and n_{BB} . Fallot and Maroni have shown that the susceptibility of ferrites can be effectively represented by an expression of the form (5). We merely note, as is obvious from fig. 12, that in the region of the Curie point there occur some rather marked discrepancies between experiment and theory whose origin is analogous to that of the discrepancies observed in the case of ordinary ferromagnetics between the paramagnetic Curie point and the ferromagnetic Curie point: they are simply due to the effect of the *fluctuations of the molecular field* which I studied previously (Néel 1932 a). In fact, when one represents magnetic interactions by a molecular field it is necessary to suppose that this field fluctuates about the mean value in space and time with an amplitude which is the greater

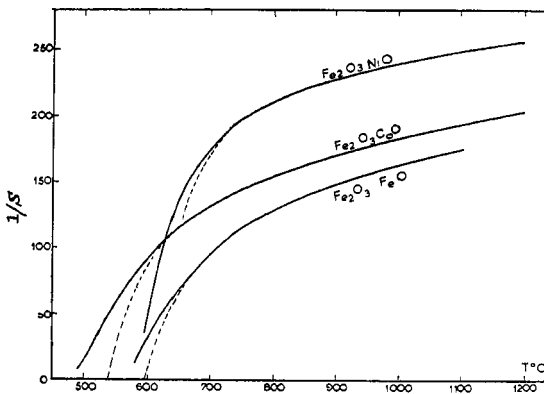


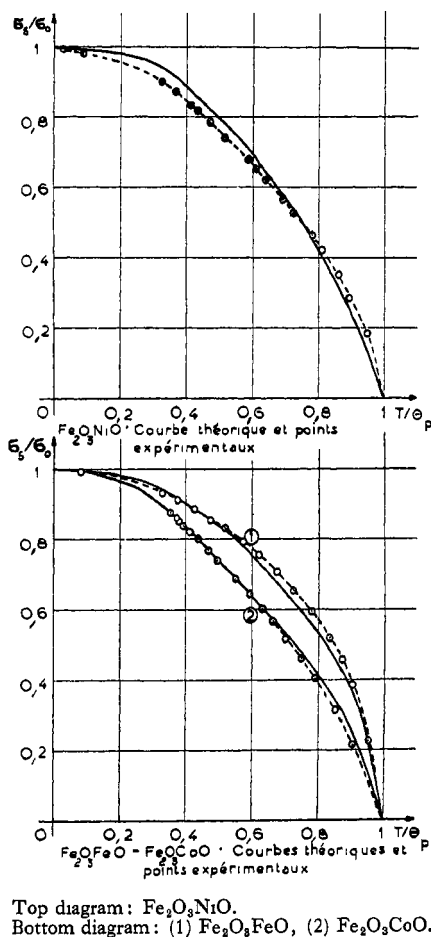
Fig. 12. Experimental values (full lines) of the reciprocal of the susceptibility of the ferrites of nickel, cobalt and iron as functions of temperature. The theoretical hyperbolae are shown by the broken lines

the smaller the number of neighbouring atoms reacting with one another. Consequently, the disappearance of the ordered state takes place at a temperature a little lower (20° to 50° c) than the theoretical temperature corresponding to a molecular field which does not fluctuate.

The study of paramagnetic properties above the Curie point thus provides values of the three coefficients of the molecular field which, with the values of the moments of the ions, are sufficient to specify completely, to a first approximation, a ferromagnetic ferrite; one can thus calculate the curve of the thermal variation of the spontaneous magnetization without recourse to any other data. The comparison of these curves with the experimental curves provides a proof of the value of the method of the molecular field applied to ferrimagnetism. Figure 13, taken from a work by Pauthenet and Bochirol (1951), allows us to compare the experimental values of the spontaneous magnetization with the theoretical curves for the three ferrites of iron, cobalt and nickel. The agreement is very satisfactory. We notice that these curves appear very different from the corresponding curves for ferromagnetics, being in general more flattened than these.

§ 4. FEATURES OF FERRIMAGNETISM

One must emphasize that ferrimagnetism is essentially associated with a paramagnetic law of the hyperbolic form (eqn. (5)); the hyperbola may, of course, degenerate into its asymptotes. In order to conclude from the examination of the experimental data that ferrimagnetism rather than ferromagnetism exists, it is therefore necessary that the variation of the susceptibility with temperature above



Top diagram: Fe_2O_3NiO .
 Bottom diagram: (1) Fe_2O_3FeO , (2) Fe_2O_3CoO .

Fig. 13. Spontaneous magnetization of the ferrites of nickel, cobalt and iron as a function of the reduced temperature; experimental points and theoretical curves calculated from paramagnetic data.

the Curie point should be of the form (5). But quite recently Zener (1952) proposed a breakdown of the iron lattice into two simple cubic sub-lattices, one composed of Fe^{3+} ions of five Bohr magnetons, the other of Fe^{-} ions of one Bohr magneton, the latter being orientated in the opposite sense to the former: the iron would then be a ferrimagnetic. Independently of the objections based on energy considerations which such a conception would raise, if it were true one should find

above the Curie point a hyperbolic variation of the reciprocal of the susceptibility, $1/s$. In practice one actually finds the ordinary Curie-Weiss law. It therefore does not seem possible to accept Zener's point of view.

§ 5. OTHER FERRIMAGNETIC SUBSTANCES

Many other ferrimagnetic substances are recognized today in addition to the ferrites, for example, the antimonide of manganese, Mn_2Sb , studied at low temperatures by Guillaud (1943). In the crystalline lattice of this substance there are in effect two kinds of atoms of manganese possessing different electron structures: some are in a $3d^7$ state with three Bohr magnetons, the others are in a $3d^5$ state with five Bohr magnetons pointing in the opposite sense to the former: the theoretical molecular moment would thus be equal to two Bohr magnetons, whilst experiment gives 1.87. The form of the thermal variation of $1/s$ confirms this interpretation, as shown in fig. 14, which reproduces the experimental points of Mille Serres

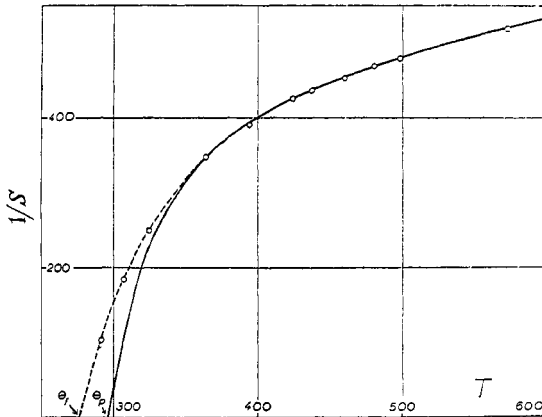


Fig. 14. Variation of the reciprocal of the susceptibility of Mn_2Sb with temperature (experimental points with fitted theoretical curve).

(1947), while the theoretical hyperbola is given by the full curve. One notices the difference between the theoretical Curie point obtained by extrapolation from the hyperbola and the true Curie point: again this is a result of the effect of fluctuations of the molecular field already mentioned. The curves of the thermal variation of the spontaneous magnetization are likewise different from those of ordinary ferromagnetics: but the experimental values on the contrary approximate very well to the values calculated from the theory of ferrimagnetism if we use the values of the coefficients deduced from the study of paramagnetism (Néel 1948).

Another good example, of more interest, is that of the sulphides of iron. The sulphide of iron FeS in stoichiometric proportions is an antiferromagnetic substance with a transition point at $325^\circ C$. It belongs to the Ewald type B8, like $NiAs$. Let us number consecutively the planes of iron atoms perpendicular to the ternary axis; we may then imagine that one of the sub-lattices is formed by the planes of even order and that the other is formed by the planes of odd order.

For the non-stoichiometric sulphides the magnetic properties change gradually as the proportion of sulphur increases, and for the compound $FeS_{1.09}$ approx

ferromagnetic properties appear. In particular, the saturation magnetization seems to pass through a maximum in the region of the composition $\text{FeS}_{1.14}$, which is approximately Fe_7S_8 : one is reminded of pyrrhotite. The saturation magnetization of pyrrhotite is small, and of the order of 0.36 Bohr magnetons per atom of iron: it is reasonable to suppose that we have here a case of ferrimagnetism due to lack of equality between the two sub-lattices, which were originally the same in FeS . This inequality should probably be associated with the unequal proportion of atoms of iron and sulphur in pyrrhotite. Moreover, as sulphur must always remain bivalent, the composition FeS_{1+x} must necessarily contain $1-2x$ of Fe^{2+} ions and $2x$ of Fe^{3+} ions. Also, one may suppose, on one hand with Hirone and Tsuya (1951) and on the other hand with Yosida (1951), that the ferric ions

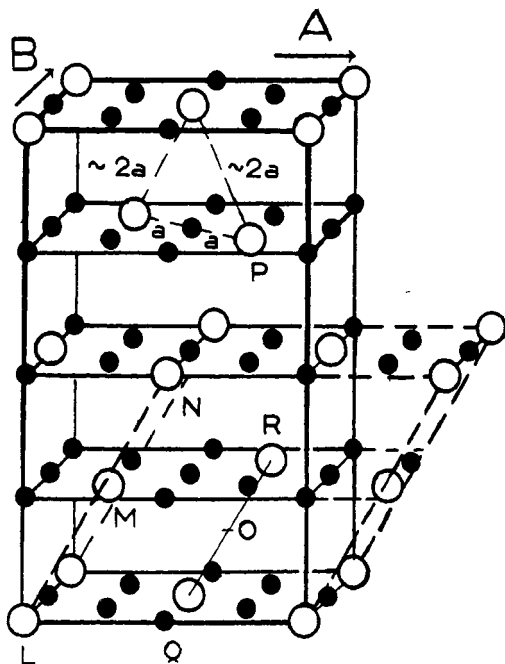


Fig. 15. Lattice structure of pyrrhotite.

collect on the iron planes of even order perpendicular to the ternary axis, and that the planes of odd order contain only ferrous ions. In this way one obtains the necessary lack of symmetry and the correct order of magnitude for the saturation moment.

Unfortunately, this explanation is not very satisfactory, for it neglects one essential fact: the crystalline lattice of FeS_{1+x} must be an incomplete lattice with x unoccupied places which are normally occupied by Fe^{2+} ions in FeS . I therefore think that these vacancies, or holes, must arrange themselves regularly on iron planes of even order and give rise to the required lack of symmetry. If this idea is correct, this lack of symmetry must correspond to a kind of superstructure discernible by x-rays, because the scattering powers of the holes and of the iron ions are different. I therefore asked M. Bertaut, the x-ray specialist in my laboratory, to find if pyrrhotite actually had the structure of NiAs and if the

diffraction pattern did not contain by accident some supplementary lines. By making exposures which were sufficiently prolonged, Bertaut (1952) has actually found 240 diffraction spots which may be attributed to this superstructure and which indicate an ordered distribution of the holes: consequently it appears that this is the first known example of a structure containing holes in ordered arrangement. Figure 15 shows the structure obtained, corresponding to the formula $\text{Fe}_7\text{S}_8\text{T}$, where T is a hole. This figure shows the arrangement of the iron atoms and the holes in the planes of odd order. For the sake of clarity, planes of iron of even order, which contain no holes, have not been depicted, neither have the intermediary planes of sulphur. One of the sub-lattices is therefore probably formed by the planes of iron with holes, the other by planes without holes. One would like to study the position of the ferric ions, but this is not possible by x-ray methods. In any case, as the two sub-lattices are unsymmetrical, ferromagnetism necessarily follows.

In the paramagnetic region the susceptibility of pyrrhotite shows the characteristic hyperbolic behaviour of ferrimagnetism, but as Benoît (1952) showed at Grenoble, a new phenomenon appears at 600°C : the susceptibility undergoes a sharp discontinuity and becomes much more weak. It possesses, above this temperature, a value and a thermal variation which very much resemble those of FeS. It therefore appears most reasonable to attribute this discontinuity to the disappearance of the superstructure. Above 600°C the holes distribute themselves randomly on all the iron planes, and the two sub-lattices should become identical; the substance should then show properties very close to those of FeS, as is found by experiment.

§ 6. CONCLUSION

It follows from this account that the idea of ferrimagnetism and its treatment by the method of the molecular field are on the whole fairly fruitful in spite of their somewhat undue simplicity. Undoubtedly it would be desirable to apply more highly developed methods to these problems, but when we consider that there do not yet exist moderately rigorous and satisfactory solutions for the case of a simple cubic lattice occupied by ions with spin $s = \frac{1}{2}$, and with one single exchange integral, it seems very unlikely that we shall get an immediate solution of the problem of spinels, with two different kinds of atoms with different spins, greater than $\frac{1}{2}$, and nine exchange integrals, all different! For the time being it is not unwise to use a simple method even if it is a little rough and ready.

Finally, let us note that the studies of magnetic properties of antiferromagnetic and ferrimagnetic substances have enabled us, from the experimental data, to prove the necessary existence between magnetic atoms of indirect exchange interactions in which an intermediary, non-magnetic atom plays an essential part; there exists in this way magnetic coupling by the intermediary action of atoms of sulphur or of oxygen of the type Fe-O-Fe, Mn-O-Mn, Fe-S-Fe, etc. This is the superexchange whose possibility Kramers (1934) previously envisaged on theoretical grounds.

REFERENCES

- BENOÎT, R., 1952, *C. R. Acad. Sci., Paris* **234**, 2174.
 BERTAUT, F., 1951, *J. Phys. Radium*, **12**, 252; 1952, *C. R. Acad. Sci., Paris*, **234**, 1295.
 BITTER, F., 1938, *Phys. Rev.*, **54**, 79.
 BIZETTE, H., 1951, *J. Phys. Radium*, **12**, 161.
 BIZETTE, H., SQUIRE, C. F., and TSAI, B., 1938, *C. R. Acad. Sci., Paris*, **207**, 449.
 BIZETTE, H., and TSAI, B., 1939, *C. R. Acad. Sci., Paris*, **209**, 205.

- COLLET, P., and FOËX, G., 1931, *J. Phys. Radium*, **2**, 290.
 FALLOT, M., and MARONI, P., 1951, *J. Phys. Radium*, **12**, 256.
 FOËX, G., 1939, *Congrès de Magnétisme de Strasbourg*, **3**, 187.
 FOËX, G., and GRAAF, S., 1939, *C. R. Acad. Sci., Paris*, **209**, 106.
 GORTER, E. W., 1950, *C. R. Acad. Sci., Paris*, **230**, 192.
 GUILLAUD, C., 1943, *Thesis*, Strasbourg; 1949, *C. R. Acad. Sci., Paris*, **229**, 1133; 1951, *J. Phys. Radium*, **12**, 489.
 HIRONE, T., and TSUYA, N., 1951, *Phys. Rev.*, **83**, 1063.
 KRAMERS, H. A., 1934, *Physica*, **1**, 182; 1952, *Ibid.*, **18**, 101.
 MORIN, F. J., 1950, *Phys. Rev.*, **78**, 819.
 NAGAMIYA, T., 1951, *Prog. Theor. Phys.*, **6**, 342.
 NÉEL, L., 1932 a, *Ann. Phys., Paris*, **17**, 5; 1932 b, *J. Phys. Radium*, **3**, 160; 1936 a, *Ann. Phys., Paris*, **5**, 232; 1936 b, *C. R. Acad. Sci., Paris*, **203**, 304; 1948, *Ann. Phys., Paris*, **3**, 137; 1949, *Ibid.*, **4**, 249.
 NÉEL, L., and PAUTHENET, R., 1952, *C. R. Acad. Sci., Paris*, **234**, 1991.
 PAUTHENET, R., and BOCHIROU, L., 1951, *J. Phys. Radium*, **12**, 249.
 POULIS, N. J., 1952, *Commun. Phys. Lab. Univ. Leiden*, nos. 283 b, 287 a, 288 d.
 POULIS, N. J., VAN DEN HAENDEL, J., UBBINK, J., POULIS, J. A., and GORTER, C. J., 1951, *Phys. Rev.*, **82**, 552.
 SERRES, A., 1932, *Ann. Phys., Paris*, **17**, 53; 1947, *J. Phys. Radium*, **8**, 146.
 SHULL, C. G., WOLLAN, E. O., and STRAUSSER, W. A., 1951 a, *Phys. Rev.*, **81**, 483.
 SHULL, C. G., STRAUSSER, W. A., and WOLLAN, E. O., 1951 b, *Phys. Rev.*, **83**, 333.
 SHULL, C. G., and WILKINSON, M. K., 1952, *Bull. Amer. Phys. Soc.*, **27**, 24.
 STOUT, J. W., and GRIFFEL, M., 1949, *Phys. Rev.*, **76**, 144.
 VERWEY, E. J., and DE BOER, J. H., 1936, *Rec Trav. Chim., Pays-Bas*, **55**, 131.
 VERWEY, E. J., and HEILMANN, E. L., 1947, *J. Chem. Phys.*, **15**, 174.
 VAN VLECK, J. H., 1941, *J. Chem. Phys.*, **9**, 85.
 WEISS, P., 1907, *J. Phys.*, **6**, 661.
 YOSIDA, K., 1951, *Prog. Theor. Phys.*, **6**, 356; 1952, *Ibid.*, **7**, 25.
 ZENER, C., 1952, *Phys. Rev.*, **85**, 324.

Spin Degeneracy and the Theory of Collective Electron Ferromagnetism

By A. B. LIDIARD*

Department of Theoretical Physics, King's College, London

Communicated by C. A. Coulson; MS. received 7th April 1952

ABSTRACT. The theory of ferromagnetism is often developed on the assumption that the exchange energy responsible for the magnetization is adequately represented as a sum of exchange integrals between pairs of electrons with mutually parallel spins. This is equivalent to using for the total wave function a determinant built up of one-electron functions. For the magnetized states of interest in ferromagnetism a single determinant wave function must be regarded as inadequate on account of the so-called spin or exchange degeneracy, which requires us to use instead appropriate linear combinations of the degenerate determinants. In the present paper a model is presented for which the results of neglecting or taking account of this spin degeneracy are identical. The model can be handled exactly and leads to equations for the free energy, magnetization, etc., which are a generalization of Stoner's theory of ferromagnetism to a system with two energy bands; these could be the overlapping 3d and 4s bands in the iron transition series. The calculations are not necessarily restricted to ferromagnetic metals and would apply equally well to those that are paramagnetic.

* Now at Department of Physics, University of Illinois, Urbana, U.S.A.