3 December 1971, Volume 174, Number 4013 SCIENCE

Magnetism and Local Molecular Field

Louis Néel

It has been known for a long time that ferromagnetism is due to interactions between atomic magnetic moments tending to align them parallel to one another despite the thermal agitation. In order to obtain a quantitative explanation of the experimental facts, Pierre Weiss postulated *(1)* that a ferromagnet behaved as a pure paramagnet, that is, a paramagnet with carriers of independent moments, with a magnetization given by

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

and that the effect of these interactions was equivalent to that of an imaginary magnetic field h_m, called the molecular field, proportional to the magnetization J

$$h_m = nJ \tag{2}$$

and adding to the applied field H. If H is sufficiently low, one thus obtains the magnetization law called the Curie-Weiss law:

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

with $\theta = nC$. If θ is positive, the susceptibility J/H becomes infinite when the temperature drops below the Curie point θ. From this temperature θ down to absolute zero, the substance exposed to the action of its molecular field alone $h_m = nJ_s$ acquires a certain spontaneous magnetization J_s.

In this treatment, the molecular field is considered to be a uniform field inside the ferromagnetic sample. In addition, in order to give a more finished character to his theory, P. Weiss had been led to distinguish between the energetic molecular field defined on the basis of the internal energy U by the relation

$$H_m = -\frac{\partial U}{\partial J} \tag{4}$$

and the corrective molecular field of the equation of state h_m defined, as we have stated above, by

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

Thermodynamic reasoning shows that these two fields are related as follows:

$$H_m = h_m - T\frac{dh_m}{dT} \tag{6}$$

This particular approach, very satisfying to the mind, permits one to treat and explain the energetic properties of ferromagnetic substances in an elegant and simple manner. It has the disadvantage of forcing one to admit as dogma the uniformity of the molecular field and everything that follows from it, in particular, the linear character of the thermal variation of the reciprocal susceptibility above the Curie point. Advances of the theory have certainly been retarded by this.

Local Molecular Field

On the other hand, P. Weiss was unable to offer a satisfactory solution to the problem of the origin of the molecular field. It was not until 1928 that Heisenberg found a mechanism of interactions that gave a satisfactory order of magnitude. From the point of view of interest to us, it is important to note only that these were interactions with a very short range, predominating between nearest-neighbor atoms and negligible beyond the second or third nearest neighbors.

Hence, if one considers an alloy consisting of two species A and B of atoms distributed at random, the surroundings of the atoms may be vastly different, and the approximation of a single molecular field representing the action of the surroundings for all the sites must be very poor. The theoretical problem of treating such interactions in a rigorous manner is still far from resolved, but, while retaining the simplicity of the theories based on the molecular field, one can improve them considerably by making use of what I have termed the local molecular field.

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

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

where J_A and J_B designate the respective magnetizations of atoms A and atoms B. Actually, since this energy is the sum of the contributions of pairs of nearest neighbor atoms A—A, A—B, and B—B, one should rather write

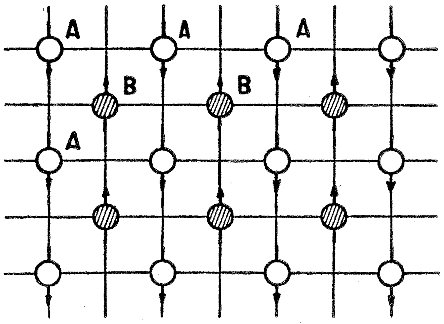
$$E_c = -\tfrac{1}{2}(n_{AA}J_A^2 + 2n_{AB}J_AJ_B + n_{BB}J_B^2) \tag{8}$$

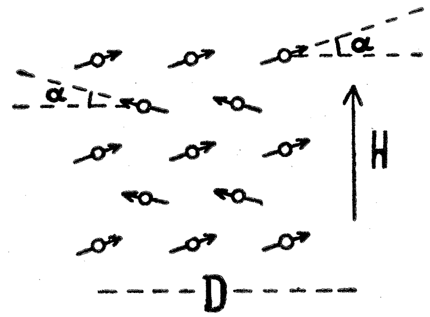
This amounts to abandoning the notion of a general molecular field and introducing local molecular fields, $h_A = n_{AA}J_A + n_{AB}J_B$ and $h_B = n_{AB}J_A + n_{BB}J_B$ acting on atoms of species A and atoms of species B, respectively.

I first developed this approach *(2)* in 1932 and showed that the susceptibility χ of an alloy containing proportions P and Q of atoms A and B, with Curie constants C_A and C_B, was written as

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

The author is professor of physics at the University of Grenoble, France. This article is the lecture he delivered in Stockholm, Sweden, in 1970, when he received the Nobel Prize in Physics, a prize which he shared with Dr. Hannes Alfvén. Minor corrections and additions have been made by the author. The article is published here with the permission of the Nobel Foundation and will also be included in the complete volume of *Les Prix Nobel en 1970* as well as in the series Nobel Lectures (in English) published by the Elsevier Publishing Company, Amsterdam and New York. Dr. Alfvén's lecture appeared in the 4 June 1971 issue of *Science*.





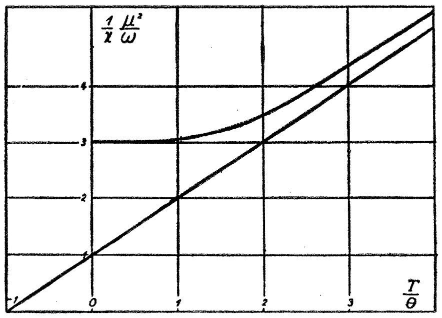


Fig. 1 (left). Decomposition of a planar lattice into two oppositely magnetized sublattices. Fig. 2 (middle). Motion of an antiparallel array of atomic moments acted upon by a field *H*. Fig. 3 (right). Thermal variation of the reciprocal susceptibility of an array of randomly oriented pairs of antiparallel moments.

Instead of being represented by a straight line, the thermal variation of the reciprocal susceptibility $1/\chi$ was henceforth 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 great approval. The existence of Curie-Weiss straight lines in the $[(1/\chi),T]$ representation was a dogma so entrenched that when the experiment would give a curve, it was preferred to resolve it into successive straight lines, each corresponding to a different magnetic state obeying the Curie-Weiss law.

Fluctuations of the Weiss Molecular Field

In the primitive theory of Weiss, the molecular field coefficient n and the Curie point θ both had positive values, and one can understand perfectly that this molecular field, which has a finite positive value when all the atomic moments are parallel and pointing in the same direction, can cause this state of ordering. Weiss and his co-workers soon noted that the paramagnetic properties of a certain number of salts were suitably interpreted by a formula of the type of Eq. 3, but with a negative constant θ, that is, with a negative molecular field. How such a field could produce ordering at low temperature cannot be visualized.

On the other hand, the Weiss theory was unable to account for the properties of paramagnetic metals such as manganese and chromium, which had a susceptibility approximately independent of temperature and too large to be attributable to Pauli paramagnetism, that is, that of electrons in an energy band.

Such was approximately the state of the question in 1930 when I became interested in the difference between the two Curie points, that is, in the fact that the Curie point θ_p deduced from the Curie-Weiss law, or the paramagnetic Curie point, differed from the ferromagnetic Curie point θ_f, the temperature of disappearance of spontaneous magnetization, whereas the Weiss theory implies the equality $\theta_f = \theta_p$. To explain this difference, I used the thermal fluctuations of the molecular field, whose existence appeared certain, since this field is due to the action of the neighboring atoms. These thermal fluctuations are fluctuations in time, but I was thus naturally led to become interested in the spatial fluctuations and to analyze more closely the consequences of the elementary law of magnetic interaction: namely, the existence of a coupling energy between two nearest-neighbor atoms, equal to $w \cdot \cos \alpha$, where α denotes the angle of their magnetic moments.

Constant Paramagnetism

The constant w may be negative or positive: negative in the case of ferromagnetism and positive in the case of the negative molecular field. In the latter case, the recourse to the molecular field, admissible at high temperature when the situations of all the atoms are identical on the average, is no longer admissible at low temperature, since the atomic magnets must then tend to become grouped in pairs of atoms with antiparallel moments.

I thus noted (*2*, p. 64) that in a

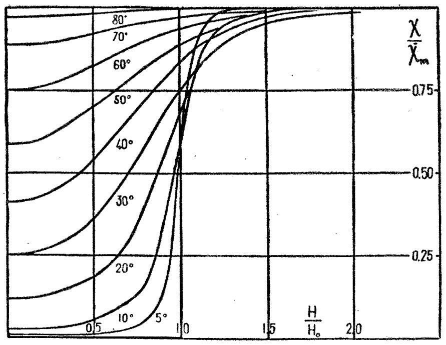


Fig. 4. Variation of the susceptibility of an array of antiparallel moments as a function of the magnetic field and of the direction of alignment of magnetic moments relative to the crystal lattice.

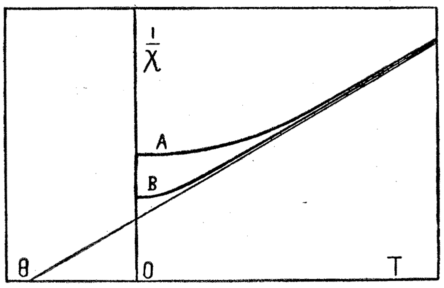


Fig. 5. Influence of the magnitude of the magnetic field on the susceptibility of an array of antiparallel moments.

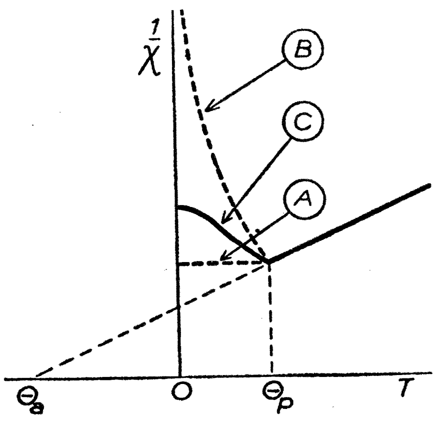
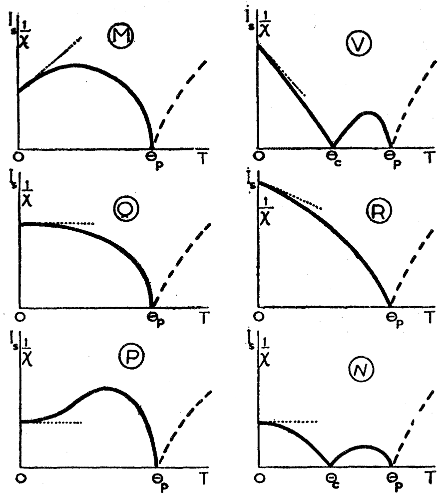


Fig. 6. Thermal variation of the reciprocal susceptibility of an antiferromagnetic substance.



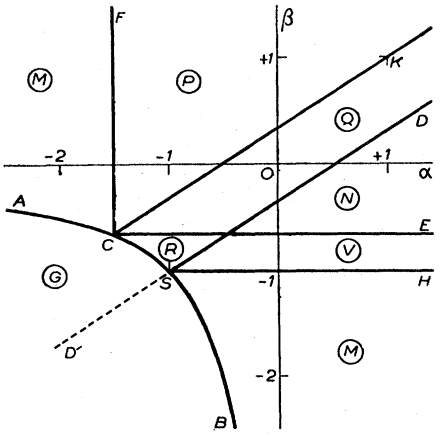


Fig. 7 (left). Thermal variation of the spontaneous magnetization and reciprocal susceptibility of a ferrimagnet: different possible types. Fig. 8 (right). Possible types of the curves of Fig. 7 according to the values of α and β.

body-centered cubic lattice composed of two simple cubic interpenetrating sublattices, the stable equilibrium at low temperature corresponded to an orientation in a certain direction of the moments of atoms in one of the sublattices and to an opposite orientation of the atomic moments of the other sublattice, as is shown in Fig. 1 in the case of a planar lattice. This array is perturbed (Fig. 2) under the action of a magnetic field and acquires an average induced magnetization per atom given by

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

where μ is the atomic moment and $2p$ the number of neighbors. One thus obtains a constant paramagnetism, that is, a susceptibility independent of the field and temperature.

However, at high temperature, a Curie-Weiss law of the type of Eq. 3 applies again.

To study the transition between the constant paramagnetism and the Curie-Weiss paramagnetism, I assumed for simplicity that the atoms could be grouped in pairs independent of one another, the internal energy of one pair being taken equal to $w \cdot \cos \alpha$. One thus obtained the variation

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

The thermal variation of the reciprocal susceptibility is represented by the curve of Fig. 3. When T changes from zero to θ, the susceptibility changes by only 1.4 percent.

In another paper published at approximately the same time (*4*), I proposed that the constant paramagnetism of manganese and chromium be interpreted by the preceding mechanism, with values of θ equal, respectively, to $-1720°$ and $-4150°$K. To support this interpretation, I showed that on diluting manganese and chromium with copper, silver, or gold, one observed a gradual transition from a constant paramagnetism to a Curie-Weiss paramagnetism, as could have been expected from the preceding theory when there is a decrease in the interactions, that is, in θ.

In 1936, I returned (*5*) to the theory of negative interactions in the range of low temperatures, taking into account the coupling of atomic moments with the crystal lattice. The coupling energy was taken equal to $w'' \cos 2\theta$ where θ is the angle of the atomic moment with a preferred direction D of the lattice. One can then show that the magnetic susceptibility is a complicated function of the magnetic field H and of the angle β between H and D, as represented in Fig. 4 for different values of β spaced 10° apart.

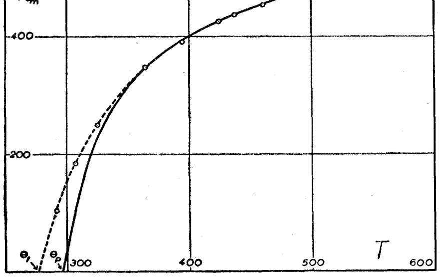
In particular, if the field is parallel to the preferred direction, the susceptibility, at first null in weak fields, undergoes a discontinuity for $H = H_0 = (8pww''/\mu^2)^{1/2}$ and takes a value $\chi_m = \mu^2/4pw$ independent of H: when H reaches the value H_0, the moments originally parallel to D and H become suddenly oriented in a perpendicular direction. Fifteen years later, in 1951, C. J. Gorter and co-workers observed (*6*) this phenomenon for the first time in the chloride $CuCl_2 \cdot 2H_2O$ at 4.1°K.

From this theory one can also deduce that in a sample with a confused crystallization, where the directions D are distributed at random, the susceptibility in weak fields is weaker than in strong fields and varies with temperature as indicated schematically in Fig. 5. We note that there is no transition temperature: the transition from constant paramagnetism to Curie-Weiss paramagnetism takes place in a perfectly continuous manner.

Discovery of the Antiferromagnetic Transition Point

Still in 1936, it occurred to me (*5*) to apply the theory of the local molecular field to the two sublattices A and B of magnetization J_A and J_B used in the previous papers, and to represent the interactions by imaginary fields H_A and H_B with, at low temperature and for $H = 0$, the fundamental relation $J_B = -J_A$.

As a result, the two sublattices had to acquire spontaneous magnetizations pointing in opposite directions and disappearing at a certain transition temperature θ_N, today called the Néel temperature according to a proposal



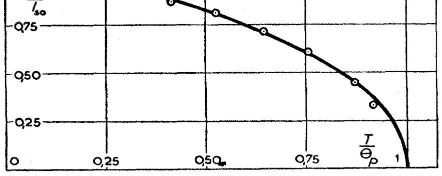


Fig. 9 (left). Thermal variation of the reciprocal magnetic susceptibility of magnetite (adjusted curve and experimental points). Note the difference between the ferromagnetic Curie point and the paramagnetic Curie point. Fig. 10 (right). Thermal variation of the spontaneous magnetization of magnetite (experimental points and curve calculated with molecular field coefficients deduced from the study of susceptibility).

put forward by C. J. Gorter. We were thus dealing with a magnetic substance of a new type, essentially composed of two identical interpenetrating ferromagnetics spontaneously magnetized in opposite directions. Effects dependent on the square of the spontaneous magnetization, such as the specific heat anomaly, should thus display the same behavior as in ferromagnetic substances.

In the absence of coupling with the crystal lattice, the susceptibility remains constant in the interval $0<T<\theta_N$, then follows a Curie-Weiss law for $T>\theta_N$ without undergoing a discontinuity at the Curie point.

Two years later, Squire, Bizette, and Tsai (*7*) discovered that MnO had the properties that had been anticipated, and in particular a transition temperature at $\theta_N = 116°K$. Much later, in 1949, using neutron diffraction, C. G. Shull and S. J. Smart (*8*) confirmed that the atomic moments did indeed possess the antiparallel orientations predicted by the theory of sublattices.

F. Bitter later completed the theory (*9*) by calculating up to the transition point θ_N the susceptibility in a magnetic field parallel to the direction Δ of alignment of antiparallel moments and gave the name antiferromagnetics to this new category of magnetic substances, and in 1941 J. H. van Vleck (*10*) made a synthesis of the results that had been obtained.

Finally, the situation can be summarized as follows depending on the orientation of the magnetic field *H* relative to the direction Δ of antiferromagnetism, that is, the preferred direction of the crystal lattice to which the atomic moments are parallel, in one or the other direction, in the absence of an applied external field. When *H* is perpendicular to Δ, the curve A of Fig. 6 is obtained (*11*). When *H* is parallel to Δ, the curve B is obtained (*9*). Finally, for a substance with confused crystallization, the average curve C is obtained, which shows at the Néel point θ_p the existence of a sharp susceptibility maximum also marked by a sharp specific heat maximum. At temperatures below this maximum, an antiferromagnetic ordering detectable by neutron diffraction exists.

Today, an extremely large number of antiferromagnetic substances are known: these are generally transition metal compounds of oxygen or sulfur. They are extremely interesting from the theoretical standpoint but do not appear to have any practical applications.

Other Research in the Field of Magnetism

It is important to note that the theoretical studies which I made from 1930 to 1938 were performed for the purpose of determining the elementary energies *w* of interaction between two nearest-neighbor magnetic atoms, like or unlike. There was hope at the time of finding a universal law giving *w* as a function only of the distance between the interacting atoms. This was obviously a somewhat simplistic view, and the hope was illusory. Nevertheless, positive results had been obtained and had made it possible to find interesting correlations between the anomalies of expansion, influence of pressure, and thermal variation of the molecular field. These questions still remain unsolved to this day.

However it may be, in 1938 I abandoned the problem of interactions and of the local molecular field for about 8 years in order to devote myself to other subjects: Rayleigh laws, fine grains, role of internal dispersion fields—to name only those that led to the most important results.

The protection of ships against magnetic mines by a method which I had proposed, consisting of imparting to them a permanent magnetization equal and opposite to the magnetization induced by the earth's magnetic field, directed my attention to the laws of magnetization of ferromagnetics in weak fields, referred to as Rayleigh laws. I was able to offer an interpretation of the latter (*12*) based on the propagation of Bloch walls in a medium perturbed in an aleatory manner.

I also studied in a systematic manner the theretofore more or less neglected role of internal demagnetizing fields or dispersion fields. It then became possible to deduce from them a more accurate theory of the laws of approach to saturation of the technical magnetization, taking into account the random orientation of the crystallites (*13*) and the presence of cavities or nonmagnetic inclusions (*14*), and to propose a more general theory of the coercive field allowing for the irregularities of internal mechanical strains as well as for the presence of cavities or nonmagnetic inclusions (*15*). Along the same general lines, I developed a theory of magnetization of ferromagnetic single crystals (*16*) according to successive modes, each characterized by the number of phases, that is, the number of different categories of elementary domains with spontaneous parallel magnetizations. This theory, which was in complete agreement with the experimental facts, concluded a subject which until then had been very poorly understood.

Finally, I showed as early as 1942 that sufficiently small ferromagnetic

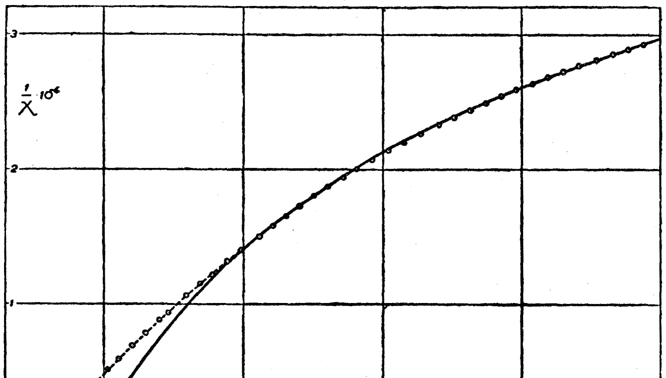


Fig. 11. Thermal variation of the reciprocal susceptibility of manganese antimonide (experimental points and adjusted curve).

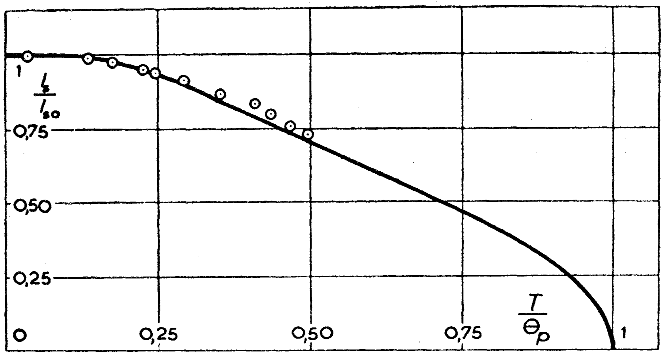


Fig. 12. Thermal variation of the spontaneous magnetization of manganese antimonide Mn_2Sb (experimental points and curve were calculated with molecular field coefficients deduced from the study of susceptibility).

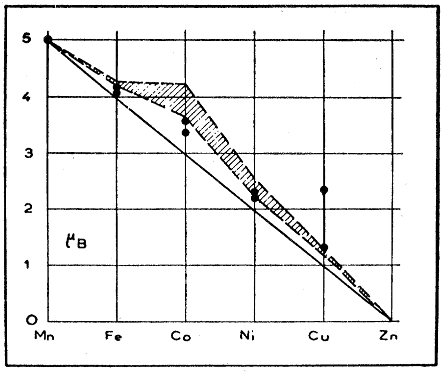


Fig. 13. Absolute saturation magnetization of certain ferrites for different ions M.

grains should contain only a single elementary domain and should behave, according to their size, either as a superparamagnetic substance or as a set of small permanent magnets, and present macroscopically a hysteresis cycle with a high coercive field. One can thus fabricate good permanent magnets from soft iron grains possessing only a form anisotropy. These properties and their applications were developed by L. Weil. The publication of all these results was delayed (*17*) until 1947 by the German occupation and for proprietary reasons.

Magnetic Properties of Ferrite Spinels

In 1947, after reading a paper by Verwey and Heilmann (*18*) on the structure of ferrites, I returned to the study of these substances. These ferrites Fe_2O_3MO which have the spinel structure, where M is a divalent metal, are classified into two categories according to their magnetic properties: paramagnetic ferrites where M stands for zinc or cadmium, and ferromagnetic ferrites where M stands for manganese, cobalt, nickel, and so on. The latter are of major technical interest since they are electrically insulating ferromagnets, but they are of no less interest theoretically in view of their curious properties, which are very different from those of classical ferromagnets: their saturation molecular moment from 1 to $5\mu_B$ (μ_B is the Bohr magneton) is much weaker than the total magnetic moment of the ions contained in the molecule, which varies from 10 to 15 μ_B. In addition, above the Curie point the thermal variation of the reciprocal susceptibility has a rather unusual hyperbolic shape with a concavity directed toward the temperature axis and, toward elevated temperatures, an asymptote that extrapolates toward a negative absolute temperature.

Miss Serres, who has made some beautiful experimental studies of ferrites, interpreted (*19*) the shape of the curve $[(1/\chi),T]$ in terms of a superposition of a paramagnetism independent of temperature, due to ferric ions, and equal to that of αFe_2O_3. But since this paramagnetism is not an atomic property, we do not see why ferric ions would retain in ferrites the same constant paramagnetism as in αFe_2O_3.

As far as the crystal structure is concerned, the metal ions occupy, in the interstices of a close-packed cubic lattice of oxygen ions, A sites surrounded by four O^{2-} ions and B sites surrounded by six O^{2-} ions. Two categories of ferrites exist: normal ferrites where the two Fe^{3+} ions of the molecule occupy the two B sites and the M^{2+} ion occupies the A site, and inverse ferrites where one of the Fe^{3+} ions occupies the A site and the other occupies one of the two B sites. From an x-ray study, Verwey and Heilmann concluded that ferromagnetic ferrites are inverse and that paramagnetic ferrites are normal.

Principles of the Theory of Ferrimagnetism

To interpret the magnetic properties, I postulated (*20*) that the predominant magnetic interactions took place between the ions located on the A sites and the ions located on the B sites and that they were essentially negative. At absolute zero, these strong negative interactions force the moments of A ions to orient themselves parallel to one another to give a resultant M_{as} whose direction is opposite to that of the resultant M_{bs} of the moments of B ions, all of which are also parallel. The observable spontaneous magnetization is equal to the difference $|M_{as} - M_{bs}|$.

To study the consequences of these hypotheses, I applied the concept of the local molecular field developed earlier (*2*) to the two sublattices A and B. Denoting by λ and μ the proportions $(\lambda + \mu = 1)$ of magnetic ions, all assumed to be identical and located on the sublattices A and B, respectively, and designating by $-n$, $n\alpha$, and $n\beta$ the molecular field coefficients corresponding to the interactions AB, AA, and BB, respectively, the theory showed that the thermal variation of the spontaneous magnetization had to assume the rather unusual shapes schematized in Fig. 7, where the capital letters correspond to areas of the plane (α, β) represented in Fig. 8; area G at the lower left corresponds to a paramagnetism. All the types of curves represented in Fig. 7 were ultimately confirmed experimentally.

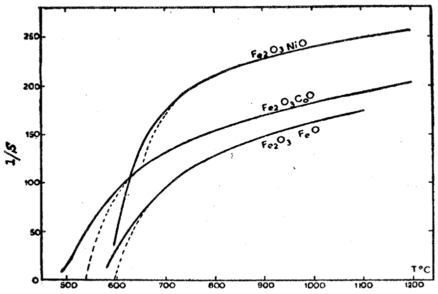


Fig. 14. Thermal variation of the reciprocal susceptibility of different ferrites (experimental curves are represented by solid lines and calculated curves by dashed lines).

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 notation

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

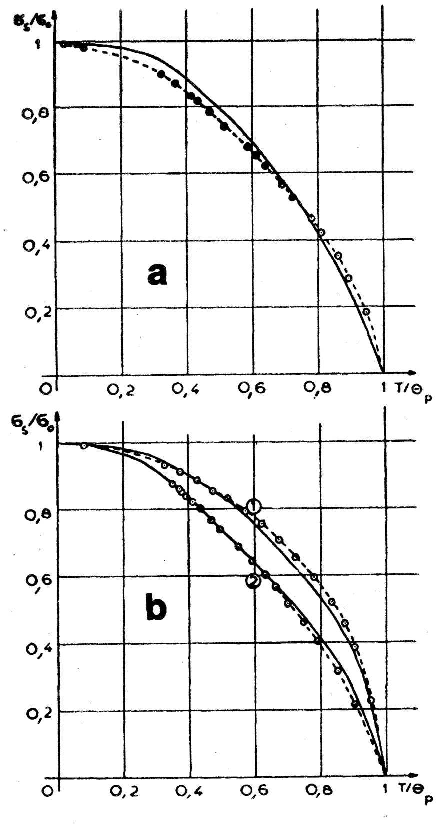
$$\sigma = nC^2\lambda\mu[\lambda(1 + \alpha) - \mu(1 + \beta)]^2$$

$$\theta = nC\lambda\mu(2 + \alpha + \beta)$$

We are therefore dealing with substances whose ferromagnetism is due, quite surprisingly, to negative interactions and whose properties, notably different from those of classical ferromagnets, deserve a special designation: I proposed to call them ferrimagnets.

Comparison of Theoretical and Experimental Results

This theory permits an immediate interpretation (*20*) of the properties of magnesium, lead, and calcium ferrites and those of magnetite Fe_3O_4 and manganese antimonide Mn_2Sb. Figures 9 through 12 show, for example, a comparison of the experimental and calculated values for Fe_3O_4 and Mn_2Sb for the thermal variations of the spontaneous magnetization and the reciprocal susceptibility, the same values of the coefficients n, α, and β being of course used in both cases. The result was encouraging, and therefore a broad experimental effort was immediately



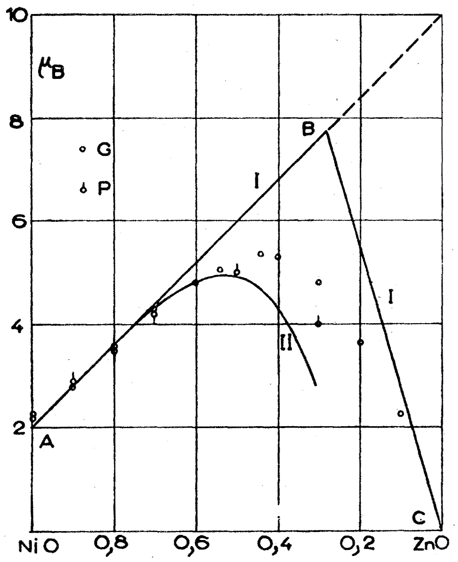


Fig. 15 (left). Thermal variation of the spontaneous magnetization of different ferrites (experimental points and curves calculated with molecular field coefficients deduced from the study of susceptibility). The results for Fe_2O_3NiO are shown in (a) and those for Fe_2O_3FeO and Fe_2O_3CoO are shown in (b) as curves 1 and 2, respectively. Fig. 16 (right). Variation with the zinc content of the saturation magnetization of mixed nickel and zinc ferrites (experimental points and calculated curves).

launched to test the theory, the existing experimental material being still rather scant.

In inverse pure ferrites Fe_2O_3MO, with M = Mn, Fe, Co, Ni, the saturation magnetic moment at absolute zero should simply be equal to that of the ion M, since the moments of the two Fe^{3+} ions compensate each other, being located on sites of different kinds. Figure 13 permits one to compare the theory with the experiment. The points correspond to the experimental results (*21*). The straight line corresponds to the theoretical predictions with the spin moment alone, and the crosshatched area to the theoretical predictions corrected by taking into account the not completely quenched orbital moment, deduced from the determination of the effective moment of the corresponding paramagnetic salts. The agreement is very satisfactory. As far as copper ferrite is concerned, the experiment shows that the saturation moment depends on the thermal treatment. When cooled slowly this ferrite assumes the inverse structure, whereas at high temperature the Fe^{3+} ions become randomly distributed on the A and B sites, since the energy difference 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 it therefore supports the theory of ferrimagnetism (*22*).

It has also been possible, for the same ferrites, to give an adequate interpretation of the experimental results pertaining to the thermal variation of the spontaneous magnetization (*23*) and of the susceptibility above the Curie point (*24*). Figures 14 and 15, pertaining to the three ferrites of iron, cobalt, and nickel, show the agreement between theory and experiment.

Moreover, in a neutron-diffraction study of magnetite, Shull and coworkers confirmed (*25*) that the magnetic moments of the atoms located on the A sites were indeed oriented in the opposite direction from the moments of the atoms located on B.

The theory of ferrimagnetism also provides an explanation of the behavior of mixed ferrites, such as those of nickel-zinc with the formula $Fe_2Ni_{(1-x)}Zn_xO_4$. A zinc atom replacing a nickel atom will occupy an A site, since that is the site preferred by zinc; simultaneously, the Fe^{3+} ion located on this A site will occupy at B the place left vacant by the departure, while at the same time its moment, equal to $5\mu_B$, is reversed. The net variation of the saturation moment is therefore equal to $8\mu_B$, which is the difference between the $10\mu_B$ due to the reversal and the $2\mu_B$ due to 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).

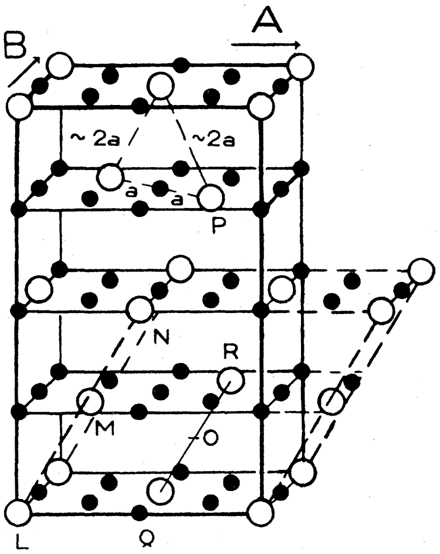


Fig. 17. Crystal structure of pyrrhotine at low temperature. The closed circles represent iron atoms and the open circles, vacancies. Even-order planes of iron and oxygen atoms are not shown.

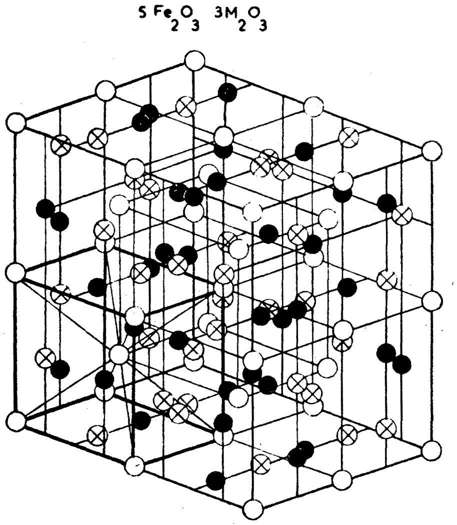


Fig. 18. Crystal structure of iron garnets. The open circles represent Fe ions on *a* sites, the crossed circles Fe ions on *d* sites, and the closed circles M ions on *c* sites. [After Strukturbericht and F. Forrat.]

The Case of Pyrrhotine

Soon thereafter, the same theory made it possible to resolve the enigma posed by pyrrhotine Fe_7S_8, a ferromagnetic compound which had long been studied (*27*) by P. Weiss and which has a weak saturation moment of the order of $3\mu_B$, whereas on the basis of its formula a value almost ten times as large had been expected. Pyrrhotine has the same crystal structure, Ewald type *B*8, as the sulfide FeS, which is a typical antiferromagnet; in the latter the successive planes of iron atoms, perpendicular to the threefold axis, are magnetized along a certain direction and point alternately in one direction and in the opposite direction. F. Bertaut showed *(28)* that pyrrhotine is actually a vacancy-type compound whose formula should rather be written as Fe_7S_8T, where T designates a vacancy, that is, a site which would be occupied by an Fe^{2+} ion in the compound FeS but which is vacant in Fe_7S_8. At low temperature, the vacancies assume an ordered distribution and cluster, as shown in Fig. 17, on the even-order planes of iron; in short, the vacancies tend to move as far as possible from one another. On the odd-order planes of iron all the sites are occupied. The two equivalent sublattices in the case of FeS become different, and in the case of Fe_7S_8 we are dealing with true ferrimagnetism. When the temperature rises above 900°K, the ordering of the vacancies disappears and the two sublattices become statistically equivalent; correlatively, the paramagnetic susceptibility of pyrrhotine takes values close to those of FeS.

Discovery of Iron Garnets

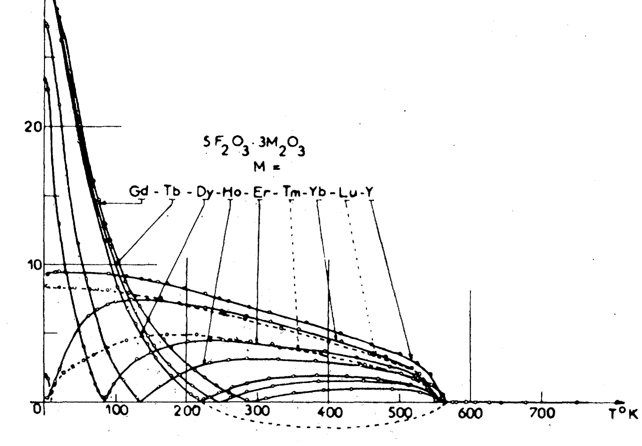
However, the best illustration of ferrimagnetism is undoubtedly provided by iron garnets. These substances, with the general formula $Fe_5M_3O_{12}$ where M is a trivalent rare earth ion, constitute an important class of magnetic compounds whose properties are explained simply and accurately by a ferrimagnetism with three sublattices. Moreover, since the metal ions entering into their constitution can be replaced by a great variety of other ions, these compounds are of great interest in the theoretical study of interactions. From the standpoint of applications, they are excellent insulators, which can be prepared in large crystals and possess very narrow resonance lines; they can be used at very high frequencies in a great variety of devices.

The history of their discovery begins in Strasbourg in 1950, where Forestier and Guiot-Guillain *(29)*, by heating an equimolar mixture of Fe_2O_3 and M_2O_3 (M is a rare earth), obtained strongly ferromagnetic products whose Curie points ranged from 520° to 740°K and to which they ascribed a perovskite-type structure *(30)*. They then revealed a curious fact *(31)*: when M was Yb, Tm, Nd, Gd, or Sm these products had two Curie points separated by about 100°K and varying regularly as a function of the atomic radius of M.

These results attracted the attention of the Grenoble researchers; 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 terms of the theory of ferrimagnetism, that is, as a temperature corresponding to a change of sign of the spontaneous magnetization (types V and N of Fig. 7).

To account for these facts, I suggested *(33)* that the Fe^{3+} ions form a ferrimagnetic aggregate A whose structure is independent of M and whose resultant spontaneous magnetization magnetized the sublattice B of M^{3+} ions in the opposite direction. The molecular field h_A representing the action of A on B should be sufficiently weak that, at least above 100°K, the magnetization of B is essentially equal to $C_B h_A/T$, the temperature θ_3 being that at which the magnetization of B is equal and opposite to that of A. This led, in particular, to the result that the temperature θ_3 had to be lower as the Curie constant C_B of the M^{3+} ions was smaller. In keeping with these predictions, it was shown *(34)* a few days later that the ferrites of dysprosium and erbium also had compensation temperatures at 246° and 70°K, respectively. Despite these successes, the fact remained that this postulated structure was incompatible with that of a perovskite $FeMO_3$.

The compound involved was probably a different one, mixed with perovskite. Starting from this idea, Bertaut and Forrat showed *(35)* in January 1956 that this was a cubic compound $Fe_5M_3O_{12}$ of space group O^{10} *Ia*3*d*, with eight molecules in the unit cell and a structure identical to that of the semiprecious stones known as garnets (Fig. 18). The primary ferrimagnetic array is made up of 24 Fe^{3+} ions on the *d* sites, surrounded by four O^{2-} ions, and 16 Fe^{3+} ions on the *a* sites, surrounded by six O^{2-} ions. This array, linked by strong interactions, possesses magnetic properties essentially independent of the nature of the M ions, to which it is coupled antiferromagnetically by weak interactions. It can be studied magnetically in the isolated state by taking for M a nonmagnetic ion such as Y or Lu.



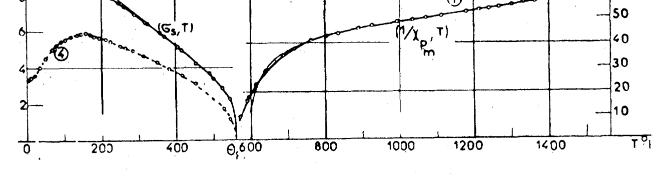


Fig. 19 (left). Thermal variation of the spontaneous magnetization of a series of iron garnets. Note in particular the variation of the compensation point with the atomic number of the rare earth. Fig. 20 (right). Yttrium garnet: thermal variation of the spontaneous magnetization and of the reciprocal susceptibility; experimental points and curves calculated by using the same molecular field coefficients. Curve 4 pertains to an yttrium garnet containing a slight amount of gadolinium. Below the Curie point is the region of ferrimagnetism and above it the region of paramagnetism.

Interpretation by a Ferrimagnetism with Three Sublattices

The generalization of the theory of ferrimagnetism to three sublattices and the representation of the interactions by means of nine local molecular fields, six of which are independent, do not present any problem. The agreement of the calculated curves with the experimental results is very satisfactory, as shown in Fig. 19, extracted from Pauthenet's fundamental paper (*36*) and showing the thermal variation of the spontaneous magnetization of different garnets. The quasi-identity of their Curie points is a good illustration of the fact that the nature of the M ions does not modify the ferrimagnetic array of Fe^{3+} ions. Above the Curie point, in the paramagnetic region, the agreement of the calculated curves with the experimental ones is equally satisfactory (see Fig. 20).

Superexchange

In the case of both antiferro- and ferrimagnetism, theory makes it possible to deduce the elementary energy of interaction *w* between two nearest-neighbor magnetic atoms from the experimental curves. This calculation, undertaken for ferrite spinels and some other antiferromagnets such as MnO or NiO, revealed some new facts (*37*). In these substances, the interactions between neighboring iron ions are negative at separations where they are positive in the pure metal or alloys. On the other hand, one observes the existence of significant interactions between magnetic atoms separated by oxygen atoms which must act as a shield. The answer is quite revolutionary: these are actually superexchange interactions, in which the oxygen atom separating two iron atoms plays an essential part. Long ago, Kramers (*37*) had anticipated the possibility of such interactions, but this was the first time that their objective existence was being clearly demonstrated.

Thus, exchange interactions M—M of the classical type and superexchange interactions of the type M—O—M coexist in oxides and ferrites; these are, therefore, choice materials for testing the theories of different interactions.

Conclusions

Despite its somewhat naive simplicity, the method of the local molecular field has had undeniable success in satisfactorily explaining a large number of previously known facts and in opening the way for the discovery of new facts.

Let us note, however, that all the structures that have been discussed above are collinear structures: on the average (in time) all the atomic magnets pointing in one or the opposite direction are parallel to a single direction. However, the local molecular field method can also be extended to noncollinear structures such as that of helimagnetism, which Yoshimori and Villain discovered independently in an absolutely unexpected manner; one can thus interpret phenomena in a remarkably simple and concrete manner.

Nevertheless, the method can hardly be recommended for more complex structures such as the umbrella structure, which requires the decomposition of the principal crystal lattice into a large number of sublattices. Indeed, under these conditions an atom belonging to a given sublattice has only a very small number of neighbors (one or two) in each of the other sublattices, and the molecular field method, which consists in replacing the instantaneous action of an atom by that of an average atom, will be more likely to yield a correct result, the larger the number of atoms to which it is applied. Its correctness probably also increases as the atomic spin becomes larger. Independently of this problem, the method applied to a large number of sublattices completely loses its chief advantage, simplicity.

The method also involves more insidious traps. If a judicious choice of parameters is made, the method can lead one to calculate curves and thermal variations of the spontaneous magnetization or paramagnetic susceptibility that coincide remarkably well with the experimental results, for example, to within a few thousandths. Under these conditions, one could expect that the elementary interaction energies deduced from these parameters would correspond to the actual values with the same accuracy. This is not so; errors of 10 to 20 percent and even greater are frequently made in this manner. A certain amount of caution thus becomes imperative.

On the other hand, recourse to the local molecular field seems indispensable since more rigorous methods lead to insurmountable complications. Consider for example that the rigorous solution is not yet known for the simplest case, that of a simple cubic lattice with identical atoms of spin 1/2, and interactions reduced to those present between nearest-neighbor atoms. How then should one treat the case of garnets with 160 atoms in the unit cell, spins up to 5/2, and at least six different coupling constants? One must therefore be lenient toward the imperfections of the molecular field methods, considering the simplicity with which the successes recalled in the first few lines of these conclusions were obtained.

References and Notes

1. P. Weiss, *C. R. H. Acad. Sci.* **143**, 1137 (1906); *J. Phys. Paris* **6**, 666 (1907).
2. L. Néel, *Am. Phys. Paris* **17**, 5 (1932).
3. ———, *C. R. H. Acad. Sci.* **198**, 1311 (1934).
4. ———, *J. Phys. Paris* **3**, 160 (1932).
5. ———, *Am. Phys. Paris* **5**, 232 (1936).
6. N. J. Poulis, J. van den Haendel, J. Ubbink, J. A. Paulis, C. J. Gorter, *Phys. Rev.* **82**, 52 (1951).
7. C. Squire, H. Bizette, B. Tsai, *C. R. H. Acad. Sci.* **207**, 449 (1938).
8. C. C. Shull and S. J. Smart, *Phys. Rev.* **76**, 1256 (1949).
9. F. Bitter, *ibid.* **54**, 79 (1938).
10. J. H. van Vleck, *J. Chem. Phys.* **9**, 85 (1941).
11. L. Néel, *C. R. H. Acad. Sci.* **203**, 304 (1936).
12. ———, *Cah. Phys.* **1942**, No. 12, 1 (1942); *ibid.* **1943**, No. 13, 18 (1943).
13. ———, *C. R. H. Acad. Sci.* **220**, 814 (1945).
14. ———, *ibid.*, p. 738.
15. ———, *Cah. Phys.* **1944**, No. 25, 21 (1944); *C. R. H. Acad. Sci.* **223**, 198 (1946); *Ann. Univ. Grenoble* **22**, 299 (1946).
16. ———, *J. Phys. Paris* **5**, 241, 265 (1944).
17. ———, *C. R. H. Acad. Sci.* **224**, 1488, 1550 (1947); *ibid.* **225**, 109 (1947).
18. E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.* **15**, 174 (1947).
19. A. Serres, *Ann. Phys. Paris* **17**, 53 (1932).
20. L. Néel, *ibid.* **3**, 137 (1948).
21. P. Weiss and R. Forrer, *ibid.* **12**, 279 (1929); E. W. Gorter, *C. R. H. Acad. Sci.* **230**, 192 (1950); C. Guillard, *ibid.* **229**, 1133 (1949).
22. L. Néel, *C. R. H. Acad. Sci.* **230**, 190 (1950).
23. R. Pauthenet and L. Bochirol, *J. Phys. Paris* **12**, 249 (1951).
24. M. Fallot and P. Maroni, *ibid.*, p. 256.
25. C. G. Shull, E. O. Wollan, W. A. Strauser, *Phys. Rev.* **81**, 483 (1951).
26. L. Néel, *C. R. H. Acad. Sci.* **230**, 375 (1950).
27. P. Weiss, *J. Phys. Paris* **8**, 542 (1899); *ibid.* **4**, 469, 829 (1905); ——— and R. Forrer, *Ann. Phys. Paris* **12**, 279 (1929).
28. F. Bertaut, *C. R. H. Acad. Sci.* **234**, 1295 (1952).
29. H. Forestier and G. Guiot-Guillain, *ibid.* **230**, 1844 (1950).
30. G. Guiot-Guillain and H. Forestier, *ibid.* **231**, 1832 (1951).
31. H. Forestier and G. Guiot-Guillain, *ibid.* **235**, 48 (1952); G. Guiot-Guillain and H. Forestier, *ibid.* **237**, 1654 (1953).
32. R. Pauthenet and P. Blum, *ibid.* **239**, 33 (1954).
33. L. Néel, *ibid.*, p. 8.
34. G. Guiot-Guillain, R. Pauthenet, H. Forestier, *ibid.*, p. 155.
35. F. Bertaut and F. Forrat, *ibid.* **242**, 382 (1956).
36. R. Pauthenet, *Ann. Phys. Paris* **3**, 424 (1958); *ibid.* **7**, 710 (1952).
37. H. A. Kramers, *Physica* **1**, 182 (1934).