

Some New Results on Antiferromagnetism and Ferromagnetism

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1. The study of the thermomagnetic properties of a natural single crystal of rhombohedral iron sesquioxide, Fe_2O_3 , by Pauthenet, confirms the hypothesis of the superposition of a fundamental antiferromagnetism and a parasitic ferromagnetism. Below 260°K the direction of antiferromagnetism coincides with the ternary axis; above 260°K this direction is situated in the plane perpendicular to the ternary axis, with complete freedom of orientation in this plane. The parasitic ferromagnetism seems to be formed of two parts, one isotropic, the other anisotropic. The latter, tightly coupled with the direction of antiferromagnetism, can be observed only above 260°K and in a direction perpendicular to the ternary axis. The corresponding spontaneous magnetization may arise from the local imperfections in the compensation of the two constituent sublattices of the antiferromagnetism, and it is the freedom of orientation of the antiferromagnetism in the basic plane which permits observation of this spontaneous magnetization.

2. Pyrrhotite corresponds closely to the molecular formula Fe_7S_8 . The crystal structure contains holes: one of the eight sites which could be occupied by iron ions is vacant. Bertaut showed that at room temperature these holes form an ordered lattice such that the crystal unit of Fe_7S_8 does not have the NiAs unit but one much more complicated, pseudo-hexagonal and slightly monoclinic, containing 8 Fe_7S_8 . This unit is such that the successive planes of iron perpendicular to the pseudo-hexagonal axis are not identical: only the odd-numbered planes contain holes. Because the two sublattices are crystallographically different, we have imperfect antiferromagnetism or ferrimagnetism, analogous to that of ferrites. A magnetic study by Benoit, at temperatures above the Curie point, seems to show that the ordered distribution of the holes disappears at 560°K . Finally, a thermomagnetic study by Pauthenet shows that the pseudo-hexagonal axis, which at ordinary temperature is a direction of very difficult magnetization, becomes progressively, at lower temperatures, a direction of easy magnetization.

I. RHOMBOHEDRAL Fe_2O_3

AS it was foreseen in the early theory,¹ we know that in antiferromagnetic substances there exists a coupling between the direction of antiferromagnetism and the directions of the axes of the crystal, analogous to the magnetocrystalline coupling which, in ferromagnetics, ties the direction of spontaneous magnetization to the axes of the crystal. Unfortunately, the properties connected with the orientation of the direction of antiferromagnetism are much more difficult to demonstrate than those which are connected with the orientation of spontaneous magnetization. In particular, while several thousands of oersteds are usually sufficient to align the spontaneous magnetization of a ferromagnetic body in the direction of an applied magnetic field, several hundreds of thousands of oersteds are probably necessary in most cases to orient the direction of antiferromagnetism in the plane perpendicular to the preferred direction (see reference 2, p. 161). To study these couplings, which are of great theoretical interest, it is almost indispensable to prepare single crystals and to study them magnetically in different directions. Up to now two examples are known: Bizette and Tsai on the one hand, Stout and Griffel on the other, have studied ferrous fluoride FeF_2 , which is an antiferromagnetic of the classic type, while C. J. Gorter and his colleagues have studied copper chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which becomes antiferromagnetic at the temperature of liquid helium.

Thus it is particularly interesting to study from this point of view rhombohedral iron sesquioxide, $\alpha \text{Fe}_2\text{O}_3$,

which is found in nature in the form of large, almost pure crystals (hematite). Unfortunately, as is shown in the works of Townsend Smith² and especially of Chevallier,³ the magnetic properties of this substance are extremely complex. However, as we noted several years ago,⁴ it seems that these properties are the result of the presence of a fundamental antiferromagnetism superimposed on a weak parasitic ferromagnetism, one hundred to a thousand times smaller than that of ordinary ferromagnetics. This ferromagnetism could arise from a defect of stoichiometry or of defects of crystallization, and we will discuss this later.

As to the fundamental antiferromagnetism, it is probably caused by strong negative interactions of superexchange of the type Fe-O-Fe, produced by the intermediary of oxygen ions. Iron atoms are arranged in almost-plane layers, perpendicular to the ternary axis. Each layer is spontaneously magnetized to saturation in a definite direction, and the successive layers are magnetized alternately in opposite directions. This structure, deduced from the study of magnetic properties^{4,5} was subsequently confirmed by Shull and his colleagues⁶ by means of neutron diffraction.

At my request, Mr. Pauthenet has studied⁷ a natural single crystal of $\alpha \text{Fe}_2\text{O}_3$ which came from the island of Elbe and appeared quite pure. The separation of the

² T. Townsend Smith, *Phys. Rev.* **8**, 721 (1916).

³ R. Chevallier and S. Mathieu, *Ann. phys.* **18**, 258 (1943); R. Chevallier, *Rapport à la Réunion Int. Ferromagnétisme et Antiferromagnétisme*, Grenoble, 1950.

⁴ L. Néel, *Ann. phys.* **4**, 249 (1949).

⁵ L. Néel, *Ann. phys.* **3**, 137 (1948).

⁶ Shull, Strauser, and Wollan, *Phys. Rev.* **83**, 333 (1951).

⁷ L. Néel and R. Pauthenet, *Compt. rend.* **234**, 2172 (1952).

¹ L. Néel, *Ann. phys.* **5**, 232 (1936).

ferro- and antiferromagnetism is obtained by determining the variation of the specific magnetization σ in a magnetic field H which is relatively high, 5000 to 20 000 oersteds. One obtains approximately for 1 g of substance

$$\sigma = \sigma_0 + \chi H,$$

where σ_0 may be considered as the spontaneous magnetization of the ferromagnetic part while χ is the antiferromagnetic susceptibility. Measurements have been made along the ternary axis and along different directions in the basic plane, perpendicular to the ternary axis. Orientation of the crystal was controlled by x-rays.

Figure 1 gives the thermal variation of the antiferromagnetic susceptibility χ , measured along the ternary axis (curve 2) and along a perpendicular direction (curve 1). These curves are rather complicated, but as a first approximation, taking into account the inevitable imperfections inherent in a natural crystal and the difficulties of separation of superimposed ferromagnetism, they can be described schematically in the following way. In the first place, in curve 2, in the neighborhood of 260°K, there is a discontinuity of susceptibility which corresponds to that which was previously observed in the polycrystalline powder by Morin⁸ and by Guillaud.⁹ Above this temperature of 260°K the susceptibility along the axis has a value independent of the temperature, in the neighborhood of $20 \cdot 10^{-6}$. Below 260°K the susceptibility is reduced to a relatively small value which seems to approach zero at absolute zero. On the contrary, in a direction in the basal plane, the susceptibility maintains a constant value, also in the neighborhood of $20 \cdot 10^{-6}$, and independent of the temperature up to 950°K, that is up to the antiferromagnetic transition point (948°K).

The properties which we have just described correspond exactly to those of an antiferromagnetic body in which the direction of antiferromagnetism is parallel to the ternary axis below 260°K and perpendicular to this axis above. This result agrees with the conclusions of a former^{4,5} study and with the experimental results of Shull, given by neutron diffraction.⁶ This thermal variation of orientation of the direction of antiferromagnetism is obviously to be compared with the analogous phenomena observed in a great number of uniaxial ferromagnetic materials. Cobalt and manganese-bismuth also possess a temperature of transition at which the direction of spontaneous magnetization changes from one orientation to another. Finally, this interesting thermal change of the orientation of the direction of antiferromagnetism shows, in agreement with theoretical considerations and contrary to the opinions of certain authors, that the direction of antiferromagnetism is not determined by the orientation of antiferromagnetic coupling of the type Fe-O-Fe.

⁸ F. J. Morin, Phys. Rev. **78**, 819 (1950).

⁹ C. Guillaud, J. phys. et radium **12**, 489 (1951).

We have also investigated whether a small anisotropy subsists in the basic plane above 260°K, but we have verified that, within one percent, the susceptibility did not depend on direction. The result is that, under the conditions of the experiment, the direction of antiferromagnetism turns freely in the basic plane and aligns itself always in a direction perpendicular to the applied field, while the susceptibility remains independent of the temperature. Thus it appears that here is an example where the original theory of antiferromagnetism¹⁰ can be applied rigorously. It appears that the fundamental antiferromagnetic properties of α Fe₂O₃ can be interpreted in a fairly simple manner.

This is not true of the parasitic ferromagnetism. Figure 2 gives the results of Pauthenet. Everything happens as though there were present an *isotropic* parasitic ferromagnetism which disappears in the classical manner at the Curie point, about 1000°K, and on which is superimposed, above 260°K, another parasitic ferromagnetism essentially *anisotropic* and dependent

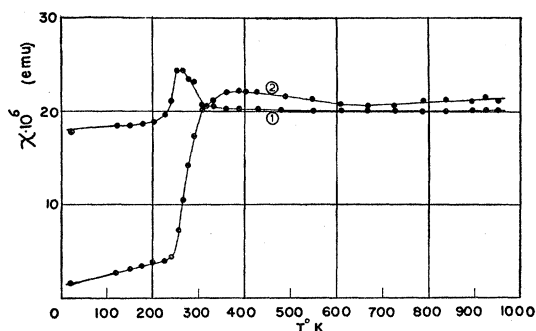


FIG. 1. Thermal variation of antiferromagnetic susceptibility of α Fe₂O₃, along a direction in the basal plane perpendicular to ternary axis (curve 1) and along the ternary axis (curve 2), (after Pauthenet).

on direction in the basic plane. This ferromagnetism disappears also around 1000°K. These results are in accord with former observations of Townsend Smith. What is new here is the disappearance of the anisotropic parasitic ferromagnetism below the transition temperature of 260°K.

This curious phenomenon can be interpreted if we suppose that the direction of the spontaneous magnetization of the anisotropic parasitic ferromagnetism is parallel to the direction of fundamental antiferromagnetism, or, more precisely, that it is parallel to the direction of spontaneous magnetization of one of the two constituent sublattices of the antiferromagnetism. Above 260°K, this parasitic ferromagnetism is easily observed in some directions in the basic plane, since the direction of antiferromagnetism can orient itself freely in this plane, which is really an exceptional fact. On the contrary, below 260°K the direction of antiferromagnetism coincides with the ternary axis; the parasitic spon-

¹⁰ L. Néel, Compt. rend. **203**, 304 (1936).

taneous magnetization is, then, also oriented along the ternary axis, but there is an equal probability that this is in one direction or in the opposite direction and there is no possibility of returning from one direction to the other since the direction of antiferromagnetism is practically fixed. The anisotropic parasitic ferromagnetism should, then, disappear, or more precisely, the magnetic fields used are much too weak to produce saturation.

One problem now remains: that of the origin of parasitic ferromagnetism and of the nature of the relation between the direction of its spontaneous magnetization and the direction of antiferromagnetism. The simplest interpretation is to suppose that the fundamental antiferromagnetism of iron sesquioxide is not perfect and that for some reason the two sublattices are not exactly identical, and that there remains a residual spontaneous magnetization due to the imperfect compensation of the two sublattices. This is a case analogous to that which we encountered in pyrrhotite and which we will take up later, but with much less dissymmetry between the two sublattices.

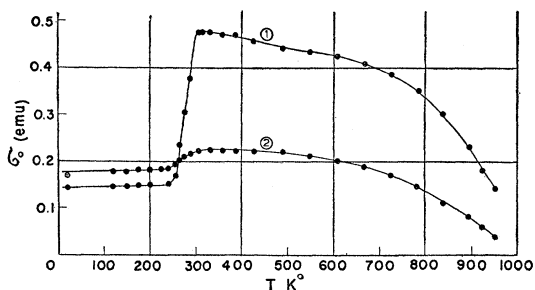


FIG. 2. Thermal variation of the parasitic ferromagnetic magnetization of α Fe_2O_3 , along a direction in the basal plane, perpendicular to ternary axis (curve 1) and along the ternary axis (curve 2).

This dissymmetry could arise, as in pyrrhotite, from a defect of stoichiometry, the exact formula of the compound studied being $\text{Fe}_{2+x}\text{O}_3$, with x small; the excess iron atoms distributing themselves on only one of the two sublattices. According to this hypothesis, one should find a relation between the magnitude of the parasitic ferromagnetism and the excess of iron or oxygen, but so far the experiments have not been conclusive. This kind of explanation, subject to the same objection, is related to the explanation that we proposed previously^{4,11} and which supposes the formation of very small magnetic particles more or less deformed, oriented by epitaxy on one of the principal faces of the crystal.

A different kind of explanation is to suppose that locally, inside of a kind of elementary domain, the two sublattices are not equivalent, either for geometrical reasons or on account of local fluctuations of composition, the average composition corresponding to Fe_3O_3 .

¹¹ L. Néel, *Compt. rend.* **228**, 64 (1949).

Each elementary domain would thus possess a resulting spontaneous magnetization parallel in one direction or the opposite to the direction of antiferromagnetism. This interpretation could also be extended to other antiferromagnetic substances than rhombohedral sesquioxide of iron, and would possibly permit explanation of the hysteresis of certain antiferromagnetic substances at low temperatures. This parasitic ferromagnetism could be checked experimentally only if the direction of antiferromagnetism, to which it is associated, had a freedom of orientation sufficient to be modified by the applied magnetic fields.

II. THE FERRIMAGNETISM OF PYRRHOTITE

Pyrrhotite is an iron sulfide in which the sulfur content is slightly greater than in FeS , which is an antiferromagnet of the classic type.^{12,13} Pyrrhotite is ferromagnetic and has been studied in detail for a long time by Weiss and his colleagues.¹⁴ The hexagonal axis is a direction of very difficult magnetization; in this direction the crystal is practically paramagnetic. In the basic plane the magnetic symmetry is less than the crystallographic symmetry; in the direction of the easiest magnetization one finds a magnetization at saturation which is remarkably small, of the order of a quarter of Bohr magneton per iron atom. The smallness of this value suggests immediately, by analogy with the ferrites, the consideration of pyrrhotite as a ferrimagnetic substance.

The study of the magnetic properties of the iron sulfides FeS_{1+x} as a function of the composition throws some light on the question. According to Haraldsen,¹² these sulfides have a crystal structure of the NiAs type, in the range $0 < x < 0.20$. However, from the point of view of magnetics they are antiferromagnetic in the interval $0 < x < 0.08$ and ferromagnetic beyond. According to Benoit,^{13,15} magnetization at saturation, at first very weak, passes through a maximum at about $x=0.14$, that is, for a formula of a type Fe_7S_8 in the neighborhood of natural pyrrhotite.

By analogy with FeO , it is likely to suppose that the successive plane layers of iron atoms, perpendicular to the hexagonal axis are, in FeS and the neighboring alloys ($x < 0.08$), magnetized alternately to saturation in opposite directions: one of the sublattices is composed of odd-numbered planes of iron atoms, the other even-numbered planes. The two sublattices are essentially and crystallographically identical, so that their spontaneous magnetizations compensate each other exactly; here we have antiferromagnetism of the classical type. On the contrary, when x is greater than 0.08 the two sublattices become different and so there is a resulting

¹² V. H. Haraldsen, *Z. anorg. u. allgem. Chem.* **231**, 78 (1937).

¹³ R. Benoit, *Compt. rend.* **234**, 2175 (1952).

¹⁴ P. Weiss, *J. phys. et radium* **8**, 542 (1899); **4**, 469 (1905); **4**, 829 (1905); P. Weiss and J. Kuntz, *J. phys. et radium* **4**, 847 (1905); P. Weiss and R. Forrer, *Ann. phys. et radium* **12**, 279 (1929).

¹⁵ R. Benoit (unpublished, private communication).

net spontaneous magnetization. The problem consists in elucidating the nature of this difference.

A first solution, proposed by several Japanese authors and in particular by Yosida, consists in noting that as a result of the bivalence of the sulfur, a composite of formula FeS_{1+x} contains necessarily $(1-2x)\text{Fe}^{++}$ ions and $(2x)\text{Fe}^{+++}$ ions. These ions possess different atomic moments, so that it is sufficient for example to suppose that the ferric ions assemble on the odd-numbered iron planes, in order to obtain the necessary dissymmetry between the two sublattices. However, serious objections may be raised against this conception. In the first place, it appears that the electrostatic forces of exchange would bring about electrical equilibrium between the successive planes of iron and consequently the two sublattices would be identical. In the second place, this conception does not take into account an important phenomenon which we are going to analyze.

The lattice of the composition FeS_{1+x} necessarily contains holes because the structure of the crystal is determined by the size of the sulfur ions, which are much larger than the iron ions. In a molecule FeS_{1+x} , there exists $1+x$ sites which may be occupied by the iron ions, and there remain x vacancies or holes. The properties of the crystal will thus depend on the actual positions of these holes. In particular the composition Fe_7S_8 may be written $\text{Fe}_7\text{S}_8\text{L}$ where L represents a hole. It seems hardly probable that at low temperature these holes will be distributed at random in the crystalline network; it is much more likely to suppose that they are ordered in a regular manner. It is tempting to wonder if the regular order of these holes would not be at the origin of the dissymmetry between the two sublattices. *A priori*, it must be relatively easy to find out with the help of x-rays if there is a regular distribution of the holes, because the reflecting power of a hole is very different from that of a ferrous or a ferric ion.

While the previous experiments have been in accord in attributing to pyrrhotite the simple NiAs structure, we asked Mr. Bertaut to take up the study again. In fact, this author in studying a natural crystal with prolonged exposures, discovered¹⁶ in the diffraction pattern several hundred spots incompatible with the NiAs structure, and he showed that pyrrhotite possessed in reality a pseudohexagonal unit, slightly monoclinic, with parameters $A=11.9A$, $B=6.865A \approx 4a$, $C=22.72A \approx 4c$, $\beta=89^\circ 33'$, where a and c are the parameters of the unit usually used. Figure 3 represents the positions of the atoms in the unit cell; this contains 64 sulfur atoms and 56 iron atoms, therefore 8 molecules of Fe_7S_8 . The black circles represent the iron atoms, the white circles the holes. In order to simplify the figure, only the iron planes containing holes are shown, that is, the odd-numbered iron planes. The even-numbered planes, which contain no holes are not represented, nor the intermediate sulfur planes.

¹⁶ F. Bertaut, *Compt. rend.* 234, 1295 (1952).

The apparently complicated structure results from the tendency of the holes to place themselves as far as possible from each other. Their minimum distance in the planes, and in neighboring planes, is always about $2a$. Let us note that the symmetry of the unit, represented by Fig. 3, is consistent with the magnetic symmetry: the two directions A and B in the basic plane are different.

Thus, as we predicted, the two sublattices of iron atoms are crystallographically different on account of the regular distribution of the holes. To finish defining the structure and to deduce from it the molecular moment, it is necessary to know also the distribution of the ferrous and ferric ions between the different available sites. This is practically impossible with x-rays. Theoretically, the problem can perhaps be solved without too much calculations. In distributing the ferric ions equally on all the planes of iron, one finds that the magnetic moment of a molecule Fe_7S_8 reduces itself

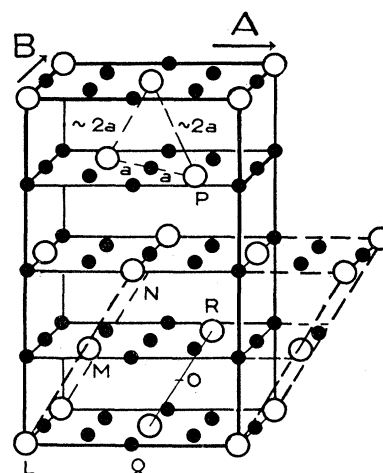


FIG. 3. Crystal lattice of pyrrhotite (after Bertaut).

to the atomic moment of the Fe^{++} ion or four Bohr magnetons, μ_B , if we neglect the orbital moment, while the experiment gives scarcely more than $2\mu_B$. Of course this value can be criticized and we can find a distribution of ions giving the correct experimental value of the saturation moment, but this has little purpose because we expect the orbital moment of the ferrous ion to play an important role. Study of the gyromagnetic ratio by Coetier yielded the extraordinary value $g=0.67$, impossible to justify *a priori*.

Thus there remains much to be done before we have a complete quantitative interpretation of the saturation moment of pyrrhotite. However, the general interpretation that we propose here nevertheless permits coordination of a certain number of experimental facts. In particular, it easily explains why ferromagnetism does not appear as soon as the composition is no longer stoichiometric, and why a minimum value of x , in the vicinity of $x=0.08$, is necessary. In fact, when x is less

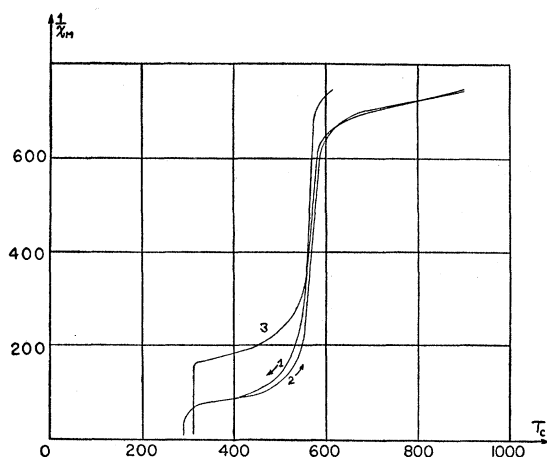


FIG. 4. Thermal variation of the reciprocal, $1/\chi_m$, of the magnetic susceptibility of a single crystal of pyrrhotite. Curves 1 and 2, artificial pyrrhotite; curve 3, natural pyrrhotite (after Benoit).

than this limiting value, the holes are too far apart for their interactions to be effective; therefore a superstructure of the holes does not form and the even and odd planes of iron remain strictly equivalent, and the compound is simply antiferromagnetic. Also, it is known that phenomena of this kind exist in alloys, the superstructures occur only in relatively narrow range around the theoretical ideal concentration.

A study of the magnetic properties of pyrrhotite above its Curie point has been made by Benoit¹³ at the laboratory in Grenoble and furnishes interesting results. Above the Curie point, about 292°C, up to 450°C, the reciprocal of the magnetic susceptibility χ_m , plotted as a function of the temperature, has the hyperbolic form characteristic of antiferromagnetism,⁵ as is shown in Fig. 4 by curve 3 relating to natural pyrrhotite and curves 1 and 2 relating to the sulfide $\text{FeS}_{1.14}$. Around 560°C a new phenomenon appears; the susceptibility undergoes a sudden discontinuity and becomes 5 or 6 times smaller. At higher temperatures, both in general behavior and in magnitude, the thermal variation of susceptibility is much like that of FeS. It is tempting to consider this temperature of 560°C as the temperature of the disappearance of the ordered structure of the holes; beyond that, the holes are distributed at random on all sites of the sublattices in such a way that the magnetic properties of the substance become like those of FeS.

In order to prove this hypothesis, Benoit tried to quench the pyrrhotite from a temperature above 560°C, in order to preserve the disordered arrangement of the holes. The ferromagnetism should then disappear and we should have antiferromagnetism of the classic type. As a matter of fact, the samples have always remained antiferromagnetic. This negative result is explained well enough if one notes that the holes should diffuse from one place to another more easily than the atoms of binary alloys; the states in unstable equilibrium should

then be more difficult to preserve than in metallic alloys. Thus it is not yet proved definitely that the ordering of the holes disappears at 560°C, but it is magnetically very probable.

Pauthenet¹⁷ has studied the thermal variation of magnetization along different crystallographic directions in a natural pyrrhotite crystal below room temperature. The measurements have confirmed the results obtained by Weiss and Forrer¹⁴ in the basic plane, which alone had been studied up to now. But, in the direction of the axis, as shown in Fig. 5 which summarizes the experiments, Pauthenet obtained unexpected results.

In the basic plane (upper part of the figure) the curves do not show any remarkable particularities, and they resemble those of any ferromagnet, except that the magnetization at saturation seems to pass through a maximum around 150°K and diminish when the temperature is lowered further. This phenomenon has already been observed by Weiss and Forrer.

Along the axis (lower part of the figure) the magnetization at room temperature is apparently proportional to the applied field, but it still remains less than one-fourth of the magnetization at saturation in the basic plane in a field of 20 000 oersteds. Thus there is a strong magnetocrystalline anisotropy which holds the spontaneous magnetization in the basic plane. When the temperature drops below 250°K, there appears a new phenomenon: a ferromagnetism superposes itself progressively on the preceding paramagnetism, the susceptibility of which varies little with the temperature. Actually, a spontaneous magnetization, parallel to the C axis (see Fig. 3), gradually increases. This spontaneous magnetization seems to pass through a maximum, around 50°K, of about one-fourth of the magnetization at saturation in the basic plane, and then to diminish slightly when the temperature is further reduced. One has the impression that the magnetizations at saturation, in the basic plane AB and along the axis C, vary in

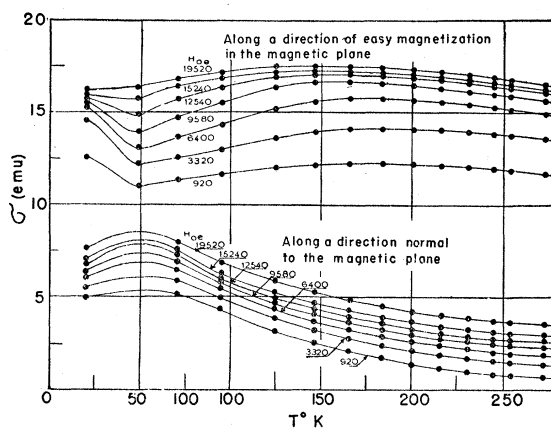


FIG. 5. Thermomagnetic study of a crystal of pyrrhotite (after Pauthenet).

¹⁷ R. Pauthenet, *Compt. rend.* **234**, 2261 (1952).

complimentary fashion: when one grows, the other shrinks, and vice versa. This all happens as if, in a portion of the substance that is larger, at lower temperatures, there is a change in the direction of easy magnetization. In itself, a change with the temperature of easy magnetization is a common phenomenon, but generally it is produced suddenly and completely at a definite temperature. Here, on the contrary, there is a progressive change as if the substance were heterogeneous. As the examples studied are of natural substances, likely to contain many impurities, it is possible that local inhomogeneities are at the origin of the observed phenomenon.

Thus it is not certain whether we are concerned with a special property of pyrrhotite, Fe_7S_8 or with a chemical effect. Experiments are in process to clarify this point. From a practical point of view, these curious phenomena complicate greatly the problem of the magnetization of pyrrhotite at saturation: is it necessary, in order to obtain the absolute value, to add the magnetization along the axis C to the spontaneous magnetization of the basic plane? It seems that one must reply in the affirmative, but the practical application of this principle is difficult. One can estimate that in the example studied the magnetization at saturation is from 21 to 22 cgs units/g.