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Thermodynamic Theory of "Weak" Ferromagnetism In Antiferromagnetic Substances

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A thermodynamic theory of "weak" ferromagnetism in α-Fe_2O_3, $MnCO_3$, and $CoCO_3$ is developed on the basis of Landau's theory of phase transitions of the second kind. It is shown that "weak" ferromagnetism is due to relativistic spin-lattice interaction and magnetic dipole interaction. A strong dependence of the properties of such "weak" ferromagnetics upon the magnetic symmetry of the crystal is noted. Their behavior in an external magnetic field is studied.

SOME ANTIFERROMAGNETIC crystals, for example α-Fe_2O_3 and the carbonates $MnCO_3$ and $CoCO_3$, exhibit a spontaneous magnetization. However, its magnitude is extremely small and varies from 10^{-2} to 10^{-5} of the nominal value. In α-Fe_2O_3 it amounts, according to measurements of Néel and Pauthenet,[1] to 0.02%; in the carbonates, according to measurements of A. S. Borovik-Romanov and M. P. Orlova,[2] to 0.2% for $MnCO_3$ and 2% for $CoCO_3$. The smallness of the spontaneous magnetization indicates that here we are not dealing with ordinary exchange ferromagnetism; for it, the spontaneous magnetization is equal in order of magnitude to the nominal value except in the vicinity of the Curie point.

In a recent work of Yin-Yuan Li,[3] this phenomenon is attributed to the existence of antiferromagnetic domains with magnetized boundaries. But as the author himself points out, the formation of such domains is energetically disadvantageous and would be possible only because of inhomogeneities and impurities in the crystal. Consequently the ferromagnetic properties of a crystal would depend greatly on its purity and homogeneity, would vary from specimen to specimen, and obviously would disappear completely in an ideal crystal.

Work[2] on very pure polycrystalline specimens indicates that the ferromagnetism remains even in this case; and by the same token, a connection between the "weak" ferromagnetism and any kind of nonequilibrium phenomenon appears very improbable. We shall show that many properties of such "weak" ferromagnetics are as immediate consequence of thermodynamics and can be fully explained by their magnetic symmetry, within the framework of the theory of phase transitions of the second kind developed by Landau.[4,5]

MAGNETIC SYMMETRY

Apart from the anomalous smallness of the spontaneous magnetic moment, "weak" ferromagnetism is characterized by great sensitivity to the symmetry of the crystal.

Consider, for example, the two isomorphic antiferromagnetics α-Fe_2O_3 and Cr_2O_3. They both belong to the rhombohedral system, and their arrangement of atoms has the symmetry of the space group D_{3d}^6.[6] In their unit cell are four Fe^{+3} or Cr^{+3} ions, located along a body diagonal of the rhombohedron (*cf.* Fig. 1). Neutronographic studies of Shull *et al.*[7] and of Brockhouse[8] have established that in the antiferromagnetic state, the magnetic and geometric unit cells coincide. The spins of ions 1, 2, 3, and 4 differ only in sign, and their sum over the cell is equal to zero; in α-Fe_2O_3, $s_1 = -s_2 = -s_3 = s_4$, and in Cr_2O_3, $s_1 = -s_2 = s_3 = -s_4$ (*cf.* Fig. 1 b, c). The direction of the spins with respect to the crystal axes in Cr_2O_3 has not been determined. α-Fe_2O_3 can exist in two different antiferromagnetic states, depending on the temperature: for $T < 250°K$ the spins point along the crystal axis (state I), and for $250°K < T < 950°K$ they lie in one of the vertical planes of symmetry at a small angle to the basal plane (111) (state II).

It is found that Cr_2O_3 in general possesses no ferromagnetism, and that α-Fe_2O_3 is ferromagnetic only in state II. With a lowering of the temperature, the spontaneous magnetic moment disappears when the transition occurs from state II to state I.

Suppose that we know the symmetry of the antiferromagnetic distribution of the spins, with their sum over the unit cell equal to zero. Then the question arises, does or does not the given symmetry permit ferromagnetism? In other words, is it possible to

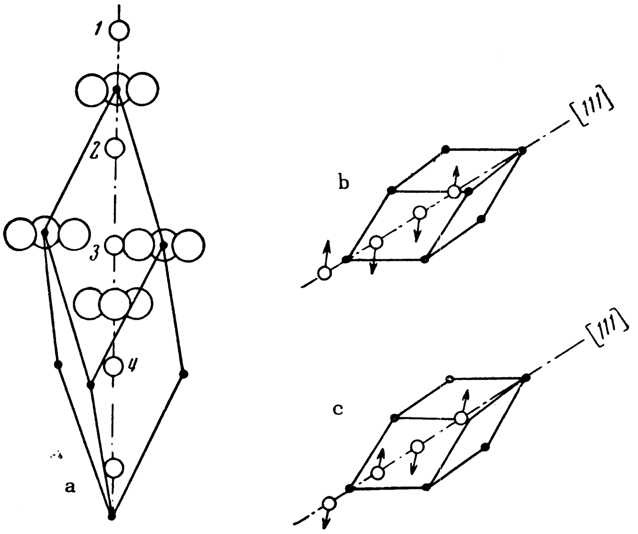

FIG. 1. (a) Unit cell of α-Fe_2O_3 and Cr_2O_3: the large circles denote oxygen ions, the small circles metallic ions. (b) Antiferromagnetic structure of α-Fe_2O_3. (c) Antiferromagnetic structure of Cr_2O_3.

change the directions or magnitudes of the spins, without disturbing the symmetry of their original distribution, in such a way as to make the sum of the spins over the unit cell different from zero?

For example, in state II of α-Fe_2O_3, ferromagnetism would appear if all the spins were to leave the planes of symmetry and turn toward one another (Fig. 2). The possiblity of such a rotation actually depends on whether the magnetic symmetry of state II and the symmetry of the state with rotated spins coincide.

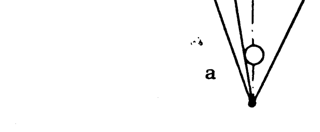

FIG. 2. Projection of the spins of the ions in α-Fe_2O_3 on the (111) plane.

The symmetry of a magnetic crystal is determined not only by the distribution of its atoms but also by the value of the mean spin $\mathbf{s}(x, y, z)$ at each point. As is known,[5] the vector quantity $\mathbf{s}(x, y, z)$ may possess, in addition to the usual symmetry transformations (that is, axes of rotation, planes of symmetry, and translations), also a singular element of symmetry R, consisting of a change of its sign: $\mathbf{s}(x, y, z) \rightarrow -\mathbf{s}(x, y, z)$. This is a consequence of the invariance of the equations of mechanics with respect to a simultaneous change of the sign of time and the sign of the magnetic field and the spins.

If the spin distribution by itself possesses the element R, then $\mathbf{s}(x, y, z) = -\mathbf{s}(x, y, z) = 0$, and the crystal will be paramagnetic. Any $\mathbf{s}(x, y, z)$ different from zero may, however, be invariant with respect to various combinations of R with axes of rotation, planes of symmetry, and translations. Therefore, along with the known 230 space groups, which describe all the possible types of symmetry of the distribution of atoms in a crystal, there arise new specifically "magnetic" space groups, which describe the symmetry of the distribution of spins.

The groups obtainable by this method have not yet all been constructed. However, in order to describe the symmetry of a ferromagnetic body it is not necessary to know the corresponding space group. The symmetry of the ferromagnetic properties, as in general of all macroscopic properties, is determined by the symmetry class, *i.e.*, by the point group that is obtained from the corresponding space group by replacing translations by identity transformations, and screw axes and glide planes by simple axes and planes. All the possible "magnetic" classes were constructed by Tavger and Zaitsev.[9] It was found that besides the usual 32 classes that by themselves contain the element R, there exist also 58 specifically "magnetic" classes.

We shall determine the symmetry classes of α-Fe_2O_3 and Cr_2O_3 in the antiferromagnetic state. As has already been mentioned, α-Fe_2O_3 can exist in two antiferromagnetic states: with the spins directed along the crystal axis (state I), and with the spins lying in one of the symmetry planes (state II). From symmetry considerations we must also examine one other possible orientation of the spins, namely along one of the twofold axes (state III).

By using the standard description of space group D_{3d}^6,[10] it is easy to find to which class each of the states I, II, and III belongs for α-Fe_2O_3. We write the symmetry elements that generate the corresponding classes:*

$$\begin{array}{ll} \mathrm{I} & 2C_3,\ 3U_2,\ I,\ 2S_6,\ 3\sigma_d, \\ \mathrm{II} & U_2,\ I,\ \sigma_d, \\ \mathrm{III} & U_2R,\ I,\ \sigma_dR. \end{array} \qquad (1)$$

A spontaneous magnetic moment **m** can obviously exist only if it remains invariant under the action of all the symmetry transformations of the class. In state I, **m** is identically equal to zero, since the corresponding class contains a threefold axis and a twofold axis perpendicular to it. In states II and III, a spontaneous moment different from zero can exist; in II it is directed along a twofold axis, in III it lies in a symmetry plane.

Thus the experimental fact that α-Fe_2O_3 is ferromagnetic in state II and nonferromagnetic in state I is simply a consequence of the magnetic symmetry of the states. Furthermore, symmetry considerations permit determination of the direction of the spontaneous magnetic moment: it is directed along one of the twofold axes, perpendicular to the symmetry plane in which the antiferromagnetic components of the spins lie.

We turn to Cr_2O_3. As has already been mentioned, the spins of the Cr^{+3} ions differ only in sign, with $\mathbf{s}_1 = -\mathbf{s}_2 = \mathbf{s}_3 = -\mathbf{s}_4$. It is easy to see that such an antiferromagnetic structure possesses the symmetry element IR. From this it follows directly that Cr_2O_3 in general cannot be ferromagnetic. In fact, upon applying the element IR to the magnetic moment vector **m**, we find $\mathbf{m} = -\mathbf{m} = 0$.

The considerations that we have presented enable us to tell whether ferromagnetism is possible for a given antiferromagnetic structure, and to find the directions of spontaneous magnetic moment that are allowed by its symmetry. However, symmetry does not impose any limitations on the magnitude of the magnetic moment. For example, in the case of α-Fe_2O_3 in state II it is possible, without violating the symmetry, to rotate the spins about the crystal axis toward one another in such a way that their directions coincide, and the crystal becomes a pure ferromagnetic. In order to explain the fact that the spontaneous magnetization is small and to show the intimate connection of "weak" ferromagnetism with antiferromagnetism, we must turn to the thermodynamic theory of phase transitions of the second kind.

LANDAU'S THEORY OF PHASE TRANSITIONS OF THE SECOND KIND

The state of a magnetic crystal is described by the mean density of the spin distribution, $\mathbf{s}(x, y, z)$. If there are in the unit cell several magnetic ions that cannot be transformed one to another by translations, then the mean spin of each type of ion will be described by its own function $\mathbf{s}_a(x, y, z)$. The symmetry of the magnetic crystal coincides with the symmetry of the vector function $\mathbf{s}(x, y, z)$ and is determined by one of the "magnetic" space groups.* In a phase transition of the second kind, the spin density $\mathbf{s}(x, y, z)$, that is the magnitude and orientation of the spins in the crystal, changes in a continuous manner, but its symmetry changes jumpwise; at the transition point itself, the symmetries of the two phases coincide.

Consider, for instance, a change from a paramagnetic to an antiferromagnetic state. In the paramagnetic phase $\mathbf{s}(x, y, z) = 0$, and its symmetry is described by one of the 230 "magnetic" groups that by themselves contain the element R.† In the antiferromagnetic phase $\mathbf{s}(x, y, z) \neq 0$ (but the integral of the spin density over the unit cell, $\int \mathbf{s}dV$, is equal to zero), and its symmetry coincides with the symmetry of the function $\mathbf{s}(x, y, z)$. The transition from the paramagnetic to the antiferromagnetic state in α-Fe_2O_3 and Cr_2O_3 proceeds without change of the unit cell. In this case the general theory of Landau[4,5] is considerably simplified. Namely, the magnetic structure of the crystals in question is now fully determined by assigning the mean spin of each of the four Fe^{+3} or Cr^{+3} ions, $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, and $\mathbf{s}_4$ (*cf.* Fig. 1). Near the transition point, the mean spins $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, and $\mathbf{s}_4$ of the ions are small, and the thermodynamic potential Φ can be expanded as a series in powers of their components. Only even

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*Here C_3 denotes a vertical threefold axis, U_2 a horizontal twofold axis, σ_d a vertical symmetry plane, S_6 a sixfold rotation-reflection axis, and I the operation of inversion.

*The symmetry of the distribution of atoms is obtained from the symmetry of the distribution of mean spin by regarding the element R in the corresponding magnetic group as the identity transformation.

†If the ordinary space group of the crystal is G, then in the paramagnetic state its magnetic group is $G \times R$.

powers will occur in the expansion, since Φ must obviously be invariant with respect to the transformation R, replacement of every $\mathbf{s}$ by $-\mathbf{s}$. Further, the expansion must remain invariant under the action of all the symmetry transformations of the ordinary space group of the crystal, D_{3d}^6. However, since we deal here with a transition without change of the unit cell, all translations by a whole period of the lattice may be treated as identity transformations.

Instead of the vectors $\mathbf{s}$, we introduce vectors $\mathbf{m}$, $\mathbf{l}_1$, $\mathbf{l}_2$, and $\mathbf{l}_3$ determined by the equalities

$$\begin{aligned} \mathbf{m} &= \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4, & \mathbf{s}_1 &= {}^1/_4\,(\mathbf{m} + \mathbf{l}_1 + \mathbf{l}_2 + \mathbf{l}_3), \\ \mathbf{l}_1 &= \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4, & \mathbf{s}_2 &= {}^1/_4\,(\mathbf{m} - \mathbf{l}_1 - \mathbf{l}_2 + \mathbf{l}_3), \\ \mathbf{l}_2 &= \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4, & \mathbf{s}_3 &= {}^1/_4\,(\mathbf{m} - \mathbf{l}_1 + \mathbf{l}_2 - \mathbf{l}_3), \\ \mathbf{l}_3 &= \mathbf{s}_1 + \mathbf{s}_2 - \mathbf{s}_3 - \mathbf{s}_4, & \mathbf{s}_4 &= {}^1/_4\,(\mathbf{m} + \mathbf{l}_1 - \mathbf{l}_2 - \mathbf{l}_3). \end{aligned}$$

The vector $\mathbf{m}$, obviously, is simply the mean magnetic moment of the unit cell.*

It is now easy to write the most general form of the expansion of Φ consistent with the symmetry of the crystal. For the present we write only terms of the second order in the expansion of Φ:†

$$\begin{aligned} \Phi = A_1\mathbf{l}_1^2 + A_2\mathbf{l}_2^2 + A_3\mathbf{l}_3^2 + B\mathbf{m}^2 \\ + \alpha_1 l_{1z}^2 + \alpha_2 l_{2z}^2 + \alpha_3 l_{3z}^2 \qquad (2) \\ + bm_z^2 + \beta_1(l_{1x}m_y - l_{1y}m_x) + \beta_2(l_{2x}l_{3y} - l_{2y}l_{3x}). \end{aligned}$$

In the expression (2) for the magnetic energy there are terms of different structure, corresponding to different types of spin interaction. The terms of the form $A\mathbf{l}^2$ do not depend on the orientation of the vector $\mathbf{l}$, and by the same token of the spin $\mathbf{s}$, with respect to the crystal axis; they represent exchange interactions. The terms of the form αl_z^2 and $\beta(l_x m_y - l_y m_x)$ arise because of relativistic spin-lattice interactions and magnetic dipole interaction and determine the magnetic anisotropy of the crystal. The ratio α/A of the magnetic anisotropy energy to the exchange energy is proportional to the square of the ratio of the speed of the electrons in the crystal to the speed of light, $(v/c)^2$, and ordinarily lies in the range 10^{-2} to 10^{-5}.

An important property of crystals of the symmetry under consideration is the presence, in the expansion of the thermodynamic potential, of the "mixed" terms $l_{1x}m_y - l_{1y}m_x$ and $l_{2x}l_{3y} - l_{2y}l_{3x}$. From the mathematical point of view they appear because the x and y components of the vectors $\mathbf{m}$ and $\mathbf{l}_1$ (or $\mathbf{l}_2$ and $\mathbf{l}_3$) transform according to identical representations. As we shall see, the first of these terms also leads to the ferromagnetism of α-Fe_2O_3.

In the paramagnetic phase every $A > 0$ and $B > 0$, and the minimum of the thermodynamic potential corresponds to the state in which all the $\mathbf{l}$'s and $\mathbf{m}$ are equal to zero. A transition occurs at the point where one of the $\mathbf{A}$'s becomes zero.* If the interaction of the spins in the crystal were purely exchange, then below the transition point only that vector $\mathbf{l}$ would be different from zero that has a negative A; consequently, in crystals of the contemplated symmetry there could arise one of the following three types of antiferromagnetic structure:

1) $\mathbf{l}_1 \neq 0$, $\mathbf{l}_2 = \mathbf{l}_3 = \mathbf{m} = 0$, $\mathbf{s}_1 = -\mathbf{s}_2 = -\mathbf{s}_3 = \mathbf{s}_4$,

α-Fe_2O_3 in fact has such a structure.

2) $\mathbf{l}_2 \neq 0$, $\mathbf{l}_1 = \mathbf{l}_3 = \mathbf{m} = 0$, $\mathbf{s}_1 = -\mathbf{s}_2 = \mathbf{s}_3 = -\mathbf{s}_4$,

this is the structure of Cr_2O_3;

3) $\mathbf{l}_3 \neq 0$, $\mathbf{l}_1 = \mathbf{l}_2 = \mathbf{m} = 0$, $\mathbf{s}_1 = \mathbf{s}_2 = -\mathbf{s}_3 = -\mathbf{s}_4$.

In actuality, however, because of the relativistic interactions that lead to the appearance of a term $l_{1x}m_y - l_{1y}m_x$, to the basic antiferromagnetic spin distribution in α-Fe_2O_3, described by the vector $\mathbf{l}_1$, there is added a small vector $\mathbf{m}$, and the crystal becomes ferromagnetic. This ferromagnetism, clearly, is not of exchange but of relativistic nature.

For the same reason the antiferromagnetic structure of Cr_2O_3 will be determined jointly by the vectors $\mathbf{l}_2$ and $\mathbf{l}_3$ (on the structure of Cr_2O_3, *cf.* below).

THE FERROMAGNETISM OF α-Fe_2O_3

We shall study the magnetic structure of α-Fe_2O_3 in more detail. Near the transition point $\mathbf{l}$ and $\mathbf{m}$ are

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*It is easily seen that in all symmetry transformations, the vectors $\mathbf{l}$ and $\mathbf{m}$ transform independently of each other. The components m_z, l_{1z}, l_{2z}, l_{3z} transform according to the one-dimensional representations A_{2g}, A_{1g}, A_{1u}, A_{2u} of the point group D_{3d} (for tables of types of representation not cited *cf.*, for instance, Ref. 11). The x and y components of the vectors $\mathbf{m}$ and $\mathbf{l}_1$ transform according to the same two-dimensional representation E_g; of the vectors $\mathbf{l}_2$ and $\mathbf{l}_3$, according to E_u.

†We shall use a rectangular system of coordinates with the z axis along the crystal axis, and with the x axis along one of the twofold axes.

*We shall assume B always greater than zero; for in the contrary case the crystal would be an ordinary exchange ferromagnetic.

small, and for determining them it is sufficient to consider only second-order terms in the expansion of the thermodynamic potential, with the addition of an exchange term proportional to $\mathbf{l}_1^4$, since the other fourth-order terms are small in comparison with it. Then Φ takes the form

$$\Phi = \frac{A}{2}\mathbf{l}^2 + \frac{B}{2}\mathbf{m}^2 + \frac{\alpha}{2}l_z^2 + \frac{b}{2}m_z^2$$

$$+ \beta(l_x m_y - l_y m_x) + \frac{C}{4}\mathbf{l}^4,$$

where we have omitted the index 1 on all the letters. The minimum of Φ for given l is determined by the equations

$$\beta m_y = \lambda l_x, \quad -\beta m_x = \lambda l_y, \quad \alpha l_z = \lambda l_z;$$

$$Bm_x - \beta l_y = 0, \quad Bm_y + \beta l_x = 0; \quad (B + b) m_z = 0;$$

$$l_x^2 + l_y^2 + l_z^2 = \mathbf{l}^2.$$

This system has two solutions:

$$\text{I)} \quad \mathbf{m} = 0, \quad l_x = l_y = 0;$$

$$\text{II)} \quad l_z = 0, \quad m_z = 0, \quad m_x = (\beta/B)\, l_y,$$

$$m_y = -(\beta/B)\, l_x.$$

In the state I, the spins of the ions are directed along the crystal axis, and ferromagnetism is absent. In the state II, the spins lie in the (111) plane, and there appears a spontaneous magnetic moment perpendicular to the vector l and of magnitude $m = (|\beta|/B)l$. As we have already said, $|\beta|/B \sim 10^{-2}$ to 10^{-5}, whence it follows that $m/l \sim 10^{-2}$ to 10^{-5}, in agreement with the experimental value $m/l = 2\times 10^{-4}$. Thus in the state II the spins $\mathbf{s}_1$, $\mathbf{s}_4$ and $\mathbf{s}_2$, $\mathbf{s}_3$ no longer compensate each other, but are turned with respect to each other through a small angle of order 10^{-4}, as is shown in Fig. 2.

The direction of the vector l in the (111) plane is not determined by second-order terms in the expansion of Φ. For this purpose it is necessary to consider the lowest-order invariant that can be constructed out of l_x and l_y. This is $(l_x + il_y)^6 + (l_x - il_y)^6$; and depending on its coefficient, l will lie either along one of the twofold axes or in one of the symmetry planes. All these results, of course, are in complete agreement with the results obtained above from symmetry considerations.

Of the two possible structures I and II, that one actually exists that corresponds to the minimum value of the thermodynamic potential. In case I

$$\Phi_{\mathrm{I}} = \frac{A}{2}l^2 + \frac{\alpha}{2}l^2 + \frac{C}{4}l^4,$$

and in case II

$$\Phi_{\mathrm{II}} = \frac{A}{2}l^2 - \frac{\beta^2}{2B}l^2 + \frac{C}{4}l^4.$$

On minimizing these with respect to l^2, we get

$$\Phi_{\mathrm{I}} = -\frac{(A+\alpha)^2}{4C}, \quad \Phi_{\mathrm{II}} = -\frac{(A-\beta^2/B)^2}{4C}, \quad l^2 \cong -\frac{A}{C}.$$

Since $\alpha \sim \beta \sim (v/c)^2$, we finally get, by neglecting terms of order $(v/c)^2$,

$$\Phi_{\mathrm{I}} \cong -A^2/4C - A\alpha/C, \quad \Phi_{\mathrm{II}} \cong -A^2/4C.$$

Consequently, the one or the other modification emerges according to the sign of α. Shall *et al.* have established that for 250°K < T < 950° K the spins lie in the (111) plane, and that for T < 250° K they lie in the [111] direction; hence $\alpha > 0$ for 250° K < T_0 < 950° K (we recall that $A < 0$), and $\alpha < 0$ for T < 250° K.

To determine the dependence of l and m on temperature near the transition point, we set $A = \lambda(T - T_k)$ as usual, whence

$$l = \sqrt{\lambda(T_k - T)/C}, \quad m = (|\beta|/B)\sqrt{\lambda(T_k - T)/C}.$$

Far from the transition point, l is no longer small, and an expansion in its powers is, in general, incorrect. However, an expansion in powers of the unit vector $\boldsymbol{\gamma}$ in the direction of l still has meaning (it is easy to see that such an expansion is equivalent to an expansion in powers of $(v/c)^2$). An expansion in powers of m, of course, is always possible in view of its smallness.

We write the invariants of fourth order in $\boldsymbol{\gamma}$ and m that contain m only in powers no higher than the second (invariants in which m enters to higher powers are negligibly small). Here as earlier we must distinguish the pure exchange invariants, the invariants of mixed nature, and finally the relativistic invariants. The ratio of the mixed-invariant energy to the exchange is proportional to $(v/c)^2$, and the ratio of the relativistic-invariant energy to the exchange is proportional to $(v/c)^4$; therefore we shall sometimes call the last "twice relativistic."

For a crystal with the symmetry of α-Fe_2O_3 there are always one exchange invariant of fourth order, $(\mathbf{m}\gamma)^2$, two mixed invariants, $(\mathbf{m}\gamma)m_z\gamma_z$ and $\gamma_z^2 m_z^2$, and five twice relativistic invariants,

$$[(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3]\,\gamma_z,\ [(\gamma_y + i\gamma_y)^3 + (\gamma_x - i\gamma_y)^3]\,m_z,$$
$$\gamma_z^4,\ (\gamma_x m_y - \gamma_y m_x)^2,\ \gamma_z^2(\gamma_x m_y - \gamma_y m_x).$$

Of these, only the exchange invariant and the first three relativistic invariants will be important for us; the rest are small in comparison with them, as can be extablished *a posteriori.* In addition, we shall need one thrice relativistic invariant $(\gamma_x + i\gamma_y)^6 + (\gamma_x - i\gamma_y)^6$; the ratio of the energy corresponding to it to the exchange energy is proportional to $(v/c)^6$.

The thermodynamic potential Φ finally takes the form

$$\Phi = \frac{a}{2}\gamma_z^2 + \frac{B}{2}\mathbf{m}^2 + q(\gamma_x m_y - \gamma_y m_x) + \frac{b}{2}m_z^2 + \frac{D}{2}(\gamma\mathbf{m})^2 + \frac{d}{2i}[(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3]\,\gamma_z$$
$$+ \frac{f}{2}[(\gamma_x + i\gamma_y)^3 + (\gamma_x - i\gamma_y)^3]\,m_z + \frac{e}{2}[(\gamma_x + i\gamma_y)^6 + (\gamma_x - i\gamma_y)^6] + \frac{g}{4}\gamma_z^4. \qquad (3)$$

We shall determine the magnetic structure of α-Fe_2O_3 at temperatures between the point of transition to the paramagnetic state and the point of transition from state I to state II, but not too close to these points. In this region $a \gg d,\ e,\ f$, and g, since $d/a \sim f/a \sim g/a \sim (v/c)^2$, and since $e/a \sim (v/c)^4$. We rewrite the expression (3) for Φ, introducing polar coordinates for the vector γ and discarding the term $\frac{1}{4}g\gamma_z^4$, which – as can be established *a posteriori* – is unimportant in this region.

$$\Phi = \frac{a}{2}\cos^2\theta + \frac{B}{2}m^2 + q\sin\theta\,(m_y\cos\varphi - m_x\sin\varphi)$$
$$+ \frac{b}{2}m_z^2 + \frac{D}{2}[m_z\cos\theta + \sin\theta\,(m_x\cos\varphi + m_y\sin\varphi)]^2 \qquad (3a)$$
$$+ d\cos\theta\sin^3\theta\sin 3\varphi + e\cos 6\varphi\sin^6\theta + fm_z\sin^3\theta\cos 3\varphi.$$

On minimizing Φ with respect to $\mathbf{m}$ for given values of the angles φ and θ, we find

$$m_x = \frac{q}{B}\sin\theta\sin\varphi,\quad m_y = -\frac{q}{B}\sin\theta\cos\varphi,\quad m_z = -\frac{f}{B}\cos 3\varphi\sin^3\theta. \qquad (4)$$

For a minimum of the thermodynamic potential Φ there are three choices of the values of $\mathbf{m}$, θ, and φ:

$$\begin{aligned}&\text{I)}\ \theta = 0,\ \mathbf{m} = 0.\\ &\text{II)}\ \theta \approx \pi/2 - d/a,\ \varphi = \pi/2,\ m_x = q/B,\ m_y = m_z = 0.\\ &\text{III)}\ \theta = \pi/2,\ \varphi = 0,\ m_y = -q/B,\ m_z = -f/B,\ m_x = 0.\end{aligned} \qquad (5)$$

Thus when a is not too small, and α-Fe_2O_3 crystal may be in any of three magnetic states. In state I, all the spins are directed along the [111] axis, and ferromagnetism is absent. In state II, the antiferromagnetic part of the spins lies in one of the symmetry planes at a small angle $[\sim d/a \sim (v/c)^2]$ to the (111) plane; a spontaneous magnetic moment $m_0 = |q|/B \sim (v/c)^2$ is directed along a twofold axis, perpendicular to the antiferromagnetic part of the spins. In state III, the antiferromagnetic part of the spins is directed along one of the twofold axes; the spontaneous magnetic moment has the same value as in state II, $m_0 = |q|/B$, and lies in a symmetry plane, perpendicular to the twofold axis mentioned, at a small angle [of order $f/q \sim (v/c)^2$] to the (111) plane.

It is easy to see that the solutions found are in complete agreement with the results obtained earlier from symmetry considerations.

According to the measurements of Néel and Pauthenet,[1] $m_0 = 0.4$ CGS emu, and $B = 5 \times 10^4$ (B is the reciprocal of the magnetic susceptibility in the paramagnetic phase*). Hence we get for q the value 2×10^4 CGS emu.

Actually, at a given temperature and pressure, the one of the three states realized is that corresponding to the smallest value of Φ. By use of (5), we find

$$\Phi_{\mathrm{I}} = a/2, \quad \Phi_{\mathrm{II}} = (-q^2/2B) - (d^2/4a) - e, \quad \Phi_{\mathrm{III}} = (-q^2/2B) + e.$$

In general $|a| \gg q^2/2B$, $d^2/4|a|$, and $|e|$; therefore for $a > 0$, state II is realized if $e > -d^2/8a$ (according to Ref. 7 this takes place for 250° K $< T <$ 950° K) and state III if $e < -d^2/8a$. For $a < 0$, state I is realized (according to Refs. 1 and 7 this takes place for $T <$ 250° K).

At some value of a near zero, a transition occurs between state I and state II (or III). The character of this transition can be determined on the basis of symmetry considerations, without resort to solution of the corresponding equations. In fact, from Landau's theory, presented above, it follows that a transition of the second kind is possible only between two states such that the symmetry group of the one is a subgroup of the symmetry group of the other. In the section on magnetic symmetry we found the symmetry classes of states I, II, and III. It is immediately evident that a transition of the second kind between states I and III or between states II and III is impossible. The symmetry class of state II is a subgroup of the symmetry class of state I. However, in order that a transition of the second kind between these states may actually occur, it is necessary that in the expansion of the thermodynamic potential near the transition point there be no third-order terms.[4,5] In the case of a transition from state I to state II, the small quantities in which Φ is expanded are the x and y components of the vector $\boldsymbol{\gamma}$. It is easily verified that the magnetic symmetry of state I requires the presence of the third-order invariant $(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3$, and consequently the transition $\mathrm{I} \rightleftarrows \mathrm{II}$ is also a transition of the first kind.

Let us consider the behavior of an α-Fe_2O_3 crystal near the transition point of the first kind from state II to state I. In this case it is sufficient to keep, in the expansion (3) of the thermodynamic potential, the terms

$$\Phi = \frac{a}{2}\gamma_z^2 + \frac{B}{2}m^2 + q(\gamma_x m_y - \gamma_y m_x) + \frac{D}{2}(\mathbf{m}\gamma)^2 + \frac{d}{2i}[(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3]\gamma_z + \frac{g}{4}\gamma_z^4.$$

On expressing $\mathbf{m}$ in terms of $\boldsymbol{\gamma}$ and again introducing polar coordinates for $\boldsymbol{\gamma}$, we get

$$\Phi = -\frac{q^2}{2B} + {}^1/_2 a' \cos^2\theta + {}^1/_4 g \cos^4\theta + d \cos\theta \sin^3\theta \sin 3\varphi,$$

where $a' = a + q^2/B$. In state I, $\cos\theta = \pm 1$; and in state II, $\sin 3\varphi = \pm 1$. Therefore, assuming that $\theta < \pi/2$, we have

$$\Phi_{\mathrm{I}} = -\frac{q^2}{2B} + {}^1/_2 a' + {}^1/_4 g,$$

$$\Phi_{\mathrm{II}} = \Phi_{\mathrm{I}} - {}^1/_2 a' \cos^2\theta - {}^1/_4 g (1 + \cos^2\theta)\sin^2\theta - |d| \cos\theta \sin^3\theta.$$

The angle θ is determined by the equation

$$a' \cos\theta + g\cos^3\theta - |d| \sin^3\theta + 3|d| \cos^2\theta \sin\theta = 0$$

At the transition point itself, $\Phi_{\mathrm{I}} = \Phi_{\mathrm{II}}$ and $\partial\Phi_{\mathrm{II}}/\partial\theta = 0$, which gives the following two equations for determination of the angle θ_k and the quantity a_k':

---

*Actually, in the paramagnetic phase the thermodynamic potential has the form $\Phi = \frac{1}{2}Bm^2 + \frac{1}{2}bm_z^2$. Hence, since $\partial\Phi/\partial\mathbf{m} = \mathbf{H}$, we have

$$m_x = H_x/B, \quad m_y = H_y/B, \quad m_z = H_z/(B + b),$$

with $b/B \ll 1$.

$$|d|\ \tan^3\theta_k - a'_k \tan^2\theta_k - 3|d| \tan\theta_k - a'_k - g = 0,$$
$$(a'_k + \tfrac{1}{2}g)\ \tan^2\theta_k + 2|d| \tan\theta_k + a'_k + a'_k + g = 0,$$

Hence

$$|d| \tan^2\theta_k + \tfrac{1}{2}g\ \tan\theta_k - |d| = 0,\ \tan\theta_k = -g/4|d| + \sqrt{(g/4d)^2 + 1}.$$

We further compute the value of the spontaneous magnetic moment m_k at the transition point and the entropy of the transition. By use of (4) we find

$$m_k = (|q|/B) \sin\theta_k, \quad \text{or} \quad \sin\theta_k = m_k/m_0,$$

where m_0 is the value of the magnetic moment far from the transition point. Further,

$$\Delta S = -\frac{\partial}{\partial T}(\Phi_\mathrm{I} - \Phi_\mathrm{II}) = -{}^1/_2 \left(\frac{da'}{dT}\right)_k \sin^2\theta_k$$

and the heat of transition is

$$q = -{}^1/_2\, T_k\, (da'/dT)_k\, (m_k/m_0)^2.$$

Now we are able to describe completely the behavior of an α-Fe_2O_3 crystal with change of temperature. At temperatures $T > 950°$ K, the crystal is in the paramagnetic state. At the point $T = 950°$ K there occurs a transition to a state in which, to the first approximation, the spins of the Fe^{+3} ions differ only in sign, with $\mathbf{s}_1 = -\mathbf{s}_2 = -\mathbf{s}_3 = \mathbf{s}_4$, and are directed along the line of intersection of the (111) plane and of one of the symmetry planes. In the next approximation, the spins $\mathbf{s}_1$, $\mathbf{s}_4$ and $\mathbf{s}_2$, $\mathbf{s}_3$ are rotated toward one another about the crystal axis [111] by a small angle, of order 10^{-4}, as in Fig 2; in consequence of this there arises a spontaneous magnetic moment, amounting to 0.04% of the nominal moment and directed along a twofold axis.* Furthermore the spins actually do not lie in the (111) plane but make a small angle, of order $(v/c)^2$, with it (*cf.* Fig. 3). Upon cooling to $T = 250°$ K, the angle between the spins and the [111] axis begins to decrease rapidly. At $T = 250°$ K it reaches a certain critical value θ_k, and the spontaneous magnetic moment falls to a value m_k. At $T = 250°$ K there occurs a phase transition of the first kind, in which the spins change discontinuously to the [111] direction, and the spontaneous magnetic moment disappears. For $T < 250°$ K the crystal is in an antiferromagnetic state, with the spins oriented along the crystal axis; in this state ferromagnetism is absent.

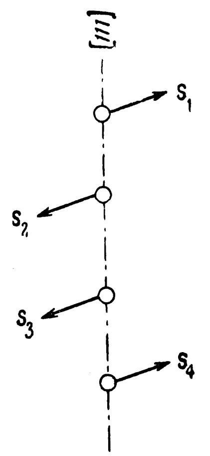

FIG. 3. Projection of the spins of α-Fe_2O_3 on a symmetry plane.

BEHAVIOR OF α-Fe_2O_3 IN A MAGNETIC FIELD

The greatest interest attaches to the behavior in a magnetic field of the ferromagnetic modification of α-Fe_2O_3; for its magnetic properties in the purely antiferromagnetic state I are the usual ones for any antiferromagnetic.

We restrict ourselves to the consideration of not-too-large magnetic fields, $H^2 \ll aB$; for at fields for which $H^2 \sim aB$, a transition from state II to state I may occur, with destruction of the ferromagnetism. The fields necessary for this, for the known antiferromagnetics at temperatures of the order of 100 degrees, have values from 10^5 to 10^6 Oersted.

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*Such a representation of the origin of weak ferromagnetism in $MnCO_3$ and $CoCO_3$ was first proposed by Borovik-Romanov and Orlova.[2]

In the presence of an external magnetic field, the thermodynamic potential has the form*

$$\begin{aligned}\tilde{\Phi} = \Phi - \mathbf{mH} = {}^1/_2\, a\cos^2\theta + {}^1/_2\, Bm^2 + {}^1/_2\, bm_z^2 + q\sin\theta\,(m_y\cos\varphi \\ - m_x\sin\varphi) + {}^1/_2\, D\,[m_z\cos\theta + \sin\theta\,(m_x\cos\varphi + m_y\sin\varphi)]^2 \\ + d\cos\theta\sin^3\theta\sin 3\varphi + e\cos 6\varphi\sin^6\theta + fm_z\sin^3\theta\cos 3\varphi - \mathbf{mH}.\end{aligned} \tag{6}$$

We examine first the limiting case of very weak fields, whose intensity is small in comparison with the anisotropy energy in the (111) plane. The latter is described by the terms $d\cos\theta\sin^3\sin 3\varphi$ and $e\cos 6\varphi\sin^6\theta$. Under the condition $H^2 \ll aB$, $\cos\theta$ as before remains a small quantity of order d/a; therefore the anisotropy energy is in order of magnitude equal to $e + d^2/a$. The magnetic field energy consists basically of the energy $H|q|/B$ of the spontaneous magnetic moment $m_0 = |q|/B$ in the field. Thus the criterion for weakness of the field can be expressed in the following form:

$$\frac{H\,|q|}{B} \ll \frac{d^2}{a} + e \quad \text{or} \quad H \ll H_k = \frac{6B}{|q|}\left(e + \frac{d^2}{4a}\right)$$

(we have introduced directly for H_k a quantity convenient for later calculations).

In the absence of the field, the crystal is in state II. Then its spontaneous magnetic moment is directed along the x axis; $\varphi = \pi/2$, and $\theta = \pi/2 - d/a$. In a weak magnetic field the thermodynamic potential will be a quadratic function of the components of intensity, and the quantities $m_x - |q|/B$, m_y, m_z, $\pi/2 - \varphi$, and $\pi/2 - d/a - \theta$ will be linear functions of the intensity. We introduce the notation

$$m_x' = m_x - \frac{|q|}{B}, \quad \varkappa = \frac{\pi}{2} - \varphi, \quad \alpha = \frac{\pi}{2} - d/a - \theta$$

and expand $\tilde{\Phi}$ to the second degree in these quantities:

$$\begin{aligned}\tilde{\Phi} = -\frac{q^2}{2B} - \frac{d^2}{2a} - e + \frac{a}{2}\alpha^2 + \frac{dq}{a}\alpha m_x' + \left(\frac{q^2}{2B} + \frac{Dq^2}{2B^2} + \frac{9}{2}\frac{d^2}{a} + 18e\right)\varkappa^2 \\ + q\left(1 + \frac{D}{B}\right)\varkappa m_y + \left(\frac{Dqd}{Ba} - 3f\right)\varkappa m_z + \frac{B}{2}m_x'^2 + \frac{B+D}{2}m_y^2 \\ + \frac{B+b}{2}m_z^2 + \frac{Dd}{a}m_y m_z - H_x m_x' - H_y m_y - H_z m_z.\end{aligned}$$

We further introduce, instead of m_y, the quantity $m_y' = m_y + q\varkappa/B$. Then $\tilde{\Phi}$ can be rewritten in the form

$$\begin{aligned}\tilde{\Phi} = \frac{a}{2}\alpha^2 + \frac{dq}{a}\alpha m_x' + \frac{B}{2}m_x'^2 - H_x m_x' + \frac{B+D}{2}m_y'^2 \\ + \frac{B+b}{2}m_z^2 + \frac{Dd}{a}m_z m_y' - 3f\varkappa m_z + \frac{q}{B}H_y\varkappa + 18e'\varkappa^2 - H_z m_z - H_y m_y',\end{aligned}$$

where we have denoted the quantity $e + d^2/4a$ by e' and have dropped nonessential constant terms.

Upon using the condition that $\tilde{\Phi}$ be a minimum to determine α, $\varkappa$, m_x', m_y', and m_z, we get the system of equations

$$a\alpha + \frac{dq}{a}m_x' = 0, \quad Bm_x' + \frac{dq}{a}\alpha - H_x = 0, \quad 36e'\varkappa + \frac{q}{B}H_y - 3fm_z = 0,$$

$$(B + D)\,m_y' + \frac{Dd}{a}m_z - H_y = 0, \quad (B + b)\,m_z + \frac{Dd}{a}m_y' - 3f\varkappa - H_z = 0,$$

hence, after some calculation, with retention only of the terms of largest order of magnitude, we find for $\varkappa$ and α

---

*Φ is the thermodynamic potential corresponding to variables p, T, and m; the potential $\tilde{\Phi}$ corresponds to the variables p, T, and H. Therefore $(d\tilde{\Phi})_{T,p} = -\mathbf{m}\,d\mathbf{H}$ and, in particular, $\tilde{\Phi}$ must be a minimum for a given value of H.

$$\varkappa = -\frac{q}{36e'B}H_y + \frac{f}{12e'B}H_z, \quad \alpha = -\frac{dq}{a^2B}H_x, \tag{7}$$

for the components of magnetic moment

$$\begin{gathered} m_x = |q|/B + H_x/B, \\ m_y = q^2H_y/36e'B^2 - qfH_z/12e'B^2, \\ m_z = H_z/(B+b) - qfH_y/12e'B^2 \end{gathered} \tag{8}$$

and for the magnetic susceptibilities

$$\chi_{xx} = \frac{1}{B}, \quad \chi_{zz} = \frac{1}{B+b}, \quad \chi_{yy} = \frac{q^2}{36e'B^2}, \quad \chi_{yz} = -\frac{qf}{12e'B^2}.$$

It is to be noted that whereas χ_{xx}, χ_{zz}, and χ_{yz} are equal in order of magnitude to the susceptibility $1/B$ in the paramagnetic phase, χ_{yy} has – as is easily established – a much greater value, of order $(v/c)^{-2}$.

The vanishing of χ_{xy} and χ_{xz} is not accidental. The thermodynamic potential, as a function of the components of field intensity, must remain invariant with respect to all symmetry transformations of the crystal. We established above that the symmetry group of state II consists of the elements U_2, I, and σ_d. The most general combination of H_x, H_y, and H_z that is invariant with respect to these transformations is

$$\tilde{\Phi} = -m_0H_x - {}^1\!/_2\chi_{xx}H_x^2 - {}^1\!/_2\chi_{yy}H_y^2 - {}^1\!/_2\chi_{zz}H_z^2 - \chi_{yz}H_yH_z,$$

whence one obtains an expression of the type (8) for the magnetic moment.

We pass on to the opposite limiting case of a field $H \gg H_k$. In this case the anisotropy-energy terms in in the expression for the thermodynamic potential can be neglected. Furthermore, since we are assuming $H^2 \ll aB$, the small deviation of the angle θ from a right angle may be neglected. Then Φ can be written in the form

$$\tilde{\Phi} = \frac{B}{2}m^2 + \frac{b}{2}m_z^2 + q\,(m_y\cos\varphi - m_x\sin\varphi) + \frac{D}{2}(m_x\cos\varphi + m_y\sin\varphi)^2 - \mathbf{mH}.$$

We express the magnetic moment $\mathbf{m}$ in terms of the external field and the angle φ:

$$\begin{gathered} -q\sin\varphi + D\,(m_x\cos\varphi + m_y\sin\varphi)\cos\varphi + Bm_x = H_x, \\ q\cos\varphi + D\,(m_x\cos\varphi + m_y\sin\varphi)\sin\varphi + Bm_y = H_y, \\ (B+b)\,m_z = H_z \end{gathered}$$

and furthermore

$$\begin{gathered} m_x = \frac{q}{B}\sin\varphi + \frac{H_x}{B} - \frac{D}{B+D}(H_x\cos\varphi + H_y\sin\varphi)\cos\varphi, \\ m_y = -\frac{q}{B}\cos\varphi + \frac{H_y}{B} - \frac{D}{B+D}(H_x\cos\varphi + H_y\sin\varphi)\sin\varphi, \\ m_z = H_z/(B+b). \end{gathered}$$

In the xy plane, we introduce polar coordinates for H_x and H_y, $H_x = H_t\cos\psi$ and $H_y = H_t\sin\psi$, and we resolve m along and perpendicular to the direction of $\mathbf{H}_t$:

$$\begin{gathered} m_{\parallel} = -\frac{q}{B}\sin(\psi-\varphi) + \frac{H_t}{B} - \frac{DH_t}{B(B+D)}\cos^2(\psi-\varphi), \\ m_{\perp} = \frac{q}{B}\cos(\psi-\varphi) - \frac{DH_t}{B(B+D)}\cos(\psi-\varphi)\sin(\psi-\varphi), \\ m_z = H_z/(B+b). \end{gathered} \tag{9}$$

We now eliminate m from the expression for the thermodynamic potential, and in it we drop the terms independent of φ:

$$\widetilde{\Phi} = \frac{q}{B} H_t \sin(\psi - \varphi) + \frac{DH_t^2}{2B(B+D)} \cos^2(\varphi - \psi). \tag{10}$$

φ is determined as a function of H_t by the equation

$$\frac{\partial \widetilde{\Phi}}{\partial \varphi} = -\frac{q}{B} H_t \cos(\psi - \varphi) + \frac{DH_t^2}{B(B+D)} \cos(\psi - \varphi) \sin(\psi - \varphi) = 0,$$

which has two solutions,

1) $\cos(\psi - \varphi) = 0$,
2) $\sin(\psi - \varphi) = \dfrac{q(B+D)}{DH_t}$.

To these correspond the values of the chemical potential

$$\widetilde{\Phi}_1 = -\frac{|q|}{B} H_t \text{ and } \widetilde{\Phi}_2 = \frac{DH_t^2}{2B(B+D)} + \frac{q^2(B+D)}{2BD},$$

the sign of the difference

$$\widetilde{\Phi}_2 - \widetilde{\Phi}_1 = \frac{D}{2B(B+D)} \left(H_t + \frac{|q|(B+D)}{D}\right)^2.$$

coincides with the sign of D.

Thus in fields $H \gg H_k$, the crystal can be in either of two states, according to the sign of D. In the first,

$$D > 0, \quad \varphi = \psi + \pi/2 \text{ and}$$
$$m_\parallel = |q|/B + H_t/B, \quad m_\perp = 0, \quad m_z = H_z/(B+b).$$

The spontaneous magnetic moment lies in the xy plane and is directed along the field; the antiferromagnetic components of the spins are directed perpendicular to it. In contrast to ordinary antiferromagnetics, the magnetic susceptibility is practically isotropic. This situation in α-Fe_2O_3 was encountered in the work of Néel and Pauthenet, a fact that affords evidence for the positiveness of D.

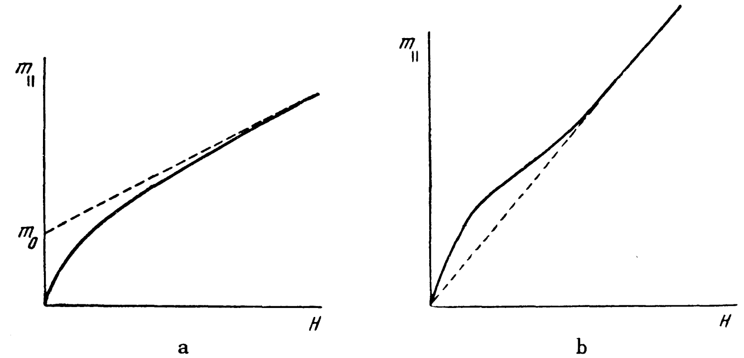
In the second state, $D < 0$. From (9) we get

$$m_\parallel = H_t/(B+D), \quad m_\perp = 0, \quad m_z = H_z/(B+b).$$

The susceptibility is sharply anisotropic in the direction of the crystal axis, and the spontaneous magnetic moment in general is absent; that is, the crystal behaves like an ordinary antiferromagnetic. Figs. 4 *a* and *b* depict schematically the dependence of $m_\parallel$ on the field for different signs of D.

Finally, we consider the range of magnetic fields $H \sim H_k$. In this case, as can be shown by simple but laborious calculations, expression (10) for the thermodynamic potential must be supplemented with a term e' cos 6φ representing anisotropy energy:

$$\widetilde{\Phi} = \frac{q}{B} H_t \sin(\varphi - \varphi) + \frac{DH_t^2}{2B(B+D)} \cos^2(\psi - \varphi) + e' \cos 6\varphi. \tag{11}$$



a b

FIG. 4. Magnetization curve: (a) in the base $D > 0$; (b) in the case $D < 0$.

Expression (9) for the magnetic moment remains valid as before.

When $H_t \sim H_k$, the second term in (11) is small in comparison with the first, since $H_k = 6Be'/|q|$ and $|q|H_k/B \sim (v/c)^6$, whereas $H_k^2/B \sim (v/c)^8$. Thus, finally, we can write the expression for $\tilde{\Phi}$

$$\tilde{\Phi} = \frac{q}{B} H_t \sin(\psi - \varphi) + e' \cos 6\varphi \tag{12}$$

and the equation that determines φ

$$qH_t \cos(\psi - \varphi) + 6e'B \sin 6\varphi = 0.$$

The last equation and the expression (12) can be put into dimensionless form by introducing, instead of H_t, the variable $h = H_t/H_k$:

$$\begin{gathered} \tilde{\Phi}/e = 6h \sin(\psi - \varphi) + \cos 6\varphi, \\ h \cos(\psi - \varphi) + \sin 6\varphi = 0. \end{gathered} \tag{13}$$

Fig. 5 shows equilibrium magnetization curves obtained by numerical solution of Eq. (13). Plotted along the ordinate axis is the quantity $m_{\parallel} - H_t/B$, measured in units of the spontaneous magnetic moment $m_0 = |q|/B$.

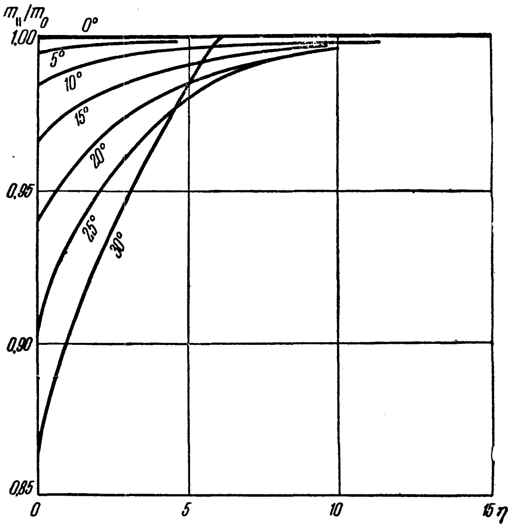


FIG. 5. Equilibrium magnetization curves for various directions of the external field. The numbers on the curves show the values of ψ.

Besides the equilibrium solutions, Eqs. (13) have nonequilibrium solutions of hysteretic type. The region outside of which hysteresis, in each case, is impossible is determined by the two known conditions $\partial\tilde{\Phi}/\partial\varphi = \partial^2\tilde{\Phi}/\partial\varphi^2 = 0$; this gives the equations of the limiting curve in the parametric form

$$\begin{gathered} h \cos(\psi - \varphi) + \sin 6\varphi = 0, \\ h \sin(\psi - \varphi) + 6 \cos 6\varphi = 0. \end{gathered} \tag{14}$$

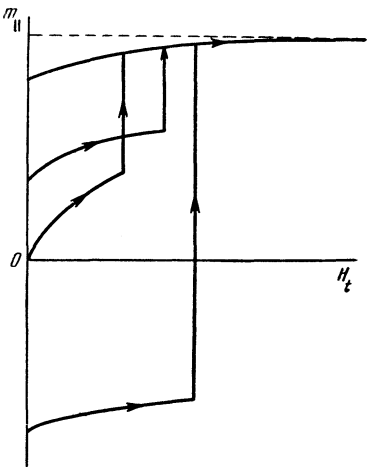


FIG. 6. Typical hysteresis curves.

In Fig. 6 are schematically represented typical hysteresis curves, given by Eqs. (13) and the conditions (14).

Cr_2O_3

We shall treat briefly the antiferromagnetic structure of Cr_2O_3. The distribution of the spins of the Cr^{+3} ions is described by the vectors $\mathbf{l}_2$ and $\mathbf{l}_3$. It was explained above that the components of $\mathbf{l}_2$ and $\mathbf{l}_3$ transform, in the symmetry transformations of the crystal, as do the $\mathbf{l}_1$ and $\mathbf{m}$ that describe the magnetic structure of α-Fe_2O_3, with this difference only: $\mathbf{l}_2$ and $\mathbf{l}_3$ change sign in the inversion transformation, whereas $\mathbf{l}_1$ and $\mathbf{m}$ do not. In the expansion of the thermodynamic potential, $\mathbf{l}_2$ and $\mathbf{l}_3$ enter only in even powers; therefore their properties with respect to inversion have no bearing on the form of this expansion, and Φ for Cr_2O_3 can be obtained from Φ for α-Fe_2O_3 by replacing $\mathbf{l}_1$ by $\mathbf{l}_2$ and $\mathbf{m}$ by $\mathbf{l}_3$. Therefore it is possible to describe the thermodynamically possible antiferromagnetic structures of Cr_2O_3 without repeating the calculations.

In the first approximation, the antiferromagnetic structure of Cr_2O_3 is described by the vector $\mathbf{l}_2$. All four Cr^{+3} ions have spins of the same magnitude and direction, except that $\mathbf{s}_1 = -\mathbf{s}_2 = \mathbf{s}_3 = -\mathbf{s}_4$ (*cf.* Fig. 1c). As before, three states are possible, with dif-

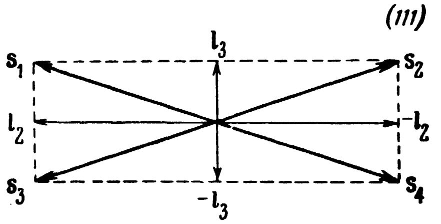


FIG. 7. Projection of the spins of Cr_2O_3 on the (111) plane

ferent directions of the spins **s** with respect to the crystalline axes. In state I, the spins are directed along the crystal axis [111]; in state II, the spins lie along the line of intersection of one of the symmetry planes with the (111) plane; and in state III, the spins are directed along one of the twofold axes.

In the next approximation, the spins $\mathbf{s}_1$ and $\mathbf{s}_2$ and the spins $\mathbf{s}_3$ and $\mathbf{s}_4$, in states II and III, are rotated toward one another through a small angle about the [111] axis, as is shown in Fig. 7. In this process, however, their sum remains equal to zero, so that ferromagnetism does not arise; more precisely,

$$\mathbf{s}_1 = {}^1/_4 (\mathbf{l}_2 + \mathbf{l}_3), \quad \mathbf{s}_2 = {}^1/_4 (-\mathbf{l}_2 + \mathbf{l}_3),$$

$$\mathbf{s}_3 = {}^1/_4 (\mathbf{l}_2 - \mathbf{l}_3), \quad \mathbf{s}_4 = -{}^1/_4 (\mathbf{l}_2 + \mathbf{l}_3),$$

that is

$$\mathbf{s}_1 = -\mathbf{s}_4, \quad \mathbf{s}_2 = -\mathbf{s}_3.$$

The magnetic properties of Cr_2O_3 will not differ from those of ordinary antiferromagnetics, and we will not dwell on them.

$MnCO_3$, $CoCO_3$, $FeCO_3$

The isomorphic antiferromagnetic crystals $MnCO_3$, $CoCO_3$, and $FeCO_3$ are also remarkable in this respect, that two – $MnCO_3$ and $CoCO_3$ – exhibit a "weak" ferromagnetism, while $FeCO_3$ is a pure antiferromagnetic.

The ferromagnetism of $MnCO_3$ and $CoCO_3$ was studied in detail by Borovik-Romanov and Orlova.[2] According to their measurements the spontaneous magnetic moment of $MnCO_3$ amounts to 0.2% of the nominal, and that of $CoCO_3$ to about 2%. $FeCO_3$ was investigated by Bizette;[12] it was found that in the antiferromagnetic state the spins of the Fe^{+2} ions are directed along the crystal axis [111].

These properties can be explained in a natural way by supposing that the antiferromagnetic transition occurs in these materials without change of the unit cell. $MnCO_3$, $CoCO_3$, and $FeCO_3$ belong to the rhombohedral system, and their symmetry is described by the space group D_{3d}^6 (Ref. 6) – that is, the same group as for α-Fe_2O_3 and Cr_2O_3. The unit cell contains two metallic ions located on the body diagonal of the rhombohedron at the sites (¼¼¼) and (¾¾¾).

As before, we shall describe their magnetic structure by means of the ionic spins $\mathbf{s}_1$ and $\mathbf{s}_2$. We introduce the vectors $\mathbf{m} = \mathbf{s}_1 + \mathbf{s}_2$ and $\mathbf{l} = \mathbf{s}_1 - \mathbf{s}_2$. It is easily verified that in all the symmetry transformations, **m** and **l** transform independently of each other; m_z and l_z transform according to the one-dimensional representations A_{2g} and A_{1g} of point group D_{3d}, and the x and y components transform according to the single representation E_g, that is according to the same representation as do the vectors **m** and $\mathbf{l}_1$ for α-Fe_2O_3.

Thus the magnetic symmetry properties of these crystals coincide completely with those of α-Fe_2O_3, and therefore all the results obtained for the latter may be carried over to this case.

In particular, the fact that $FeCO_3$ exhibits no ferromagnetism is fully explained by the fact that the spins of the Fe^{+2} ions are directed along the crystal axis (state I).

Contrariwise, from the presence of ferromagnetism in $MnCO_3$ and $CoCO_3$ we can and must conclude that they are in states with spins lying in the (111) plane (state II or III).

All the calculations relating to the magnetic properties of α-Fe_2O_3 are completely applicable to ferromagnetic $MnCO_3$ and $CoCO_3$.

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Electron-Positron Pair Production in Collisions Between Fast π-Mesons and Nucleons

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The cross section is calculated for pair production in collisions between high-energy π-mesons and nucleons.

LANDAU AND POMERANCHUK[1] have considered gamma-radiation processes in the collision of high-energy π-mesons with nucleons. Their method can be used also for treating electron-positron pair production.

The cross section for this process, naturally, will be α^2 times less than that for gamma-radiation. Owing, however, to the experimental difficulties in the detection and energy measurement of photons, it may be found experimentally simpler to deal with electron-positron pairs. Thus a theoretical investigation of electron-positron pair production is of interest.

The method used is based on the fact that at high π-meson energies the nucleon appears as an opaque sphere, so that the meson ψ-function outside the radius of action of the nuclear forces is a superposition of a plane wave and a diffracted wave. It turns out that in order to calculate the cross section for photon or pair production, it is sufficient to know the meson wave function outside the radius of action of the nuclear forces.

The two cases of pair production accompanying meson diffraction and absorption (stopping) must be considered separately. In the second case the final π-meson state is an ingoing wave, and we have a "sink" for particles. This leads to a situation in which the transition currents do not satisfy a continuity equation, and it becomes necessary to introduce an additional transition charge density in order to obtain charge conservation. This method was first applied by Tisza[2] to pair production in β-decay.

Landau and Pomeranchuk performed their calculation with the aid of a Green function. In the present work we make use of the transition-current method, since this makes it easier to account for the "disappearance" of charge. This "disappearance" effect does not have to be treated in considering gamma-radiation, since the interaction Hamiltonian of the meson and the electromagnetic field contains only the vector potential, so that the introduction of an additional transition charge density does not change its form.

The interaction of mesons with the electron-positron field is given by*

$$\hat{V} = e\left[(\boldsymbol{\alpha},\ \mathbf{A}(\mathbf{r})) - \varphi(\mathbf{r})\right], \tag{1}$$

where A and φ are the meson transition potentials.

The matrix element corresponding to production of a pair with total momentum $\mathbf{k}_0 = \mathbf{k} + \mathbf{k}'$ and total energy $\varepsilon_0 = \varepsilon + \varepsilon'$, is

$$U = e\left[(u^*_{k'}, \alpha \mathbf{A}_{k_0,\,\varepsilon_0} v_k) - (u^*_{k'} v_k)\, \varphi_{k_0,\,\varepsilon_0}\right], \tag{2}$$

where $\mathbf{A}_{k_0,\,\varepsilon_0}$ and $\varphi_{k_0,\,\varepsilon_0}$ are the Fourier components of the transition potentials, given by

$$\begin{aligned} \mathbf{A}_{k_0,\,\varepsilon_0} &= \int \mathbf{A}_{\varepsilon_0}(\mathbf{r})\, e^{-i\mathbf{k}_0\mathbf{r}}\, d\mathbf{r}, \\ \varphi_{k_0,\,\varepsilon_0} &= \int \varphi_{\varepsilon_0}(r)\, e^{-i\mathbf{k}_0\mathbf{r}}\, d\mathbf{r}; \end{aligned} \tag{3}$$

The index ε_0 indicates that the transition takes

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* Throughout we have set $\hbar = c = 1$.