

# A THERMODYNAMIC THEORY OF “WEAK” FERROMAGNETISM OF ANTIFERROMAGNETICS

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**Abstract**—A thermodynamic theory of “weak” ferromagnetism of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{MnCO}_3$  and  $\text{CoCO}_3$  is developed on the basis of LANDAU’s theory of phase transitions of the second kind. It is shown that the “weak” ferromagnetism is due to the relativistic spin-lattice and the magnetic dipole interactions. A strong dependence of the properties of “weak” ferromagnetics on the magnetic crystalline symmetry is noted and the behaviour of these ferromagnetics in a magnetic field is studied.

CERTAIN antiferromagnetic crystals, e.g.  $\alpha\text{-Fe}_2\text{O}_3$  and the carbonates  $\text{MnCO}_3$  and  $\text{CoCO}_3$ , exhibit spontaneous magnetization. The magnitude of their magnetic moment is, however, extremely small and varies between the limits of  $10^{-2}$ – $10^{-5}$  of the nominal value. In  $\alpha\text{-Fe}_2\text{O}_3$  it represents 0.02 per cent according to NÉEL and PAUTHENET’s measurements<sup>(1)</sup> and in the carbonates, according to BOROVIK-ROMANOV and ORLOVA,<sup>(2)</sup> 0.2 per cent for  $\text{MnCO}_3$ , and  $\cong 2$  per cent for  $\text{CoCO}_3$ . The smallness of the spontaneous moments indicates that we are not dealing here with the usual exchange ferromagnetism when, except in the vicinity of the Curie point, the spontaneous moment is of the same order of magnitude as the nominal value.

In a recent work of YIN-YUAN LI<sup>(3)</sup> this effect is explained by antiferromagnetic domains with magnetized walls. The author himself points out that the formation of such domains is not energetically advantageous and that it would be possible only due to non-uniformities and impurities in a crystal. These ferromagnetic properties of the crystal would then depend strongly on its purity and uniformity, they would vary from sample to sample and, would disappear completely in an ideal crystal.

The work reported in reference 2 was carried out with very pure crystals and showed that ferromagnetism is still retained and therefore the connexion between the weak ferromagnetism and

any non-uniformities seems very unlikely. It will be shown that many properties of the “weak” ferromagnetics follow directly from thermodynamics and may be fully explained in terms LANDAU’s theory<sup>(4,5)</sup> of phase transitions of the second kind by their magnetic symmetry.

## MAGNETIC SYMMETRY

Besides the smallness of the spontaneous magnetic moment the “weak” ferromagnetism is very sensitive to the crystal symmetry.

We shall consider two isomorphous antiferromagnetics  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . Both belong to the

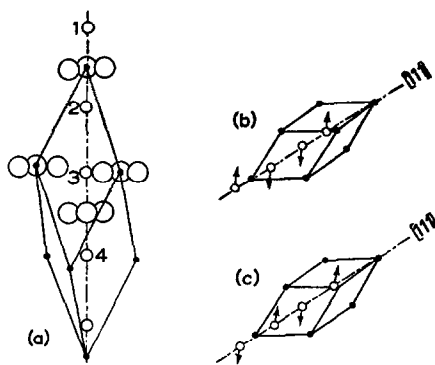


FIG. 1. (a)—Unit cells of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . The large circles represent the oxygen ions, the small ones ferric ions. (b)—Antiferromagnetic structure of  $\alpha\text{-Fe}_2\text{O}_3$ . (c)—Antiferromagnetic structure of  $\text{Cr}_2\text{O}_3$ .

rhombohedral system and the distribution of their atoms possesses  $D_{3d}^6$  space group symmetry.<sup>(6)</sup> In their unit cell there are four  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  ions, distributed along the space diagonal of the rhombohedron (Fig. 1). Neutron diffraction studies of SHULL *et al.*<sup>(7)</sup> and BROCKHOUSE<sup>(8)</sup> showed that in the antiferromagnetic state the magnetic unit cell is identical with the space one. Spins of the ions 1, 2, 3 and 4 differ in sign only and their sum in the cell is equal to zero, and in  $\alpha\text{-Fe}_2\text{O}_3$   $s_1 = -s_2 = -s_3 = s_4$  while in  $\text{Cr}_2\text{O}_3$   $s_1 = -s_2 = s_3 = -s_4$  (Fig. 1a and b). Direction of the spins with respect to the crystalline axes was not determined for  $\text{Cr}_2\text{O}_3$ . Depending on temperature  $\alpha\text{-Fe}_2\text{O}_3$  may occur in two different antiferromagnetic states: at  $T < 250^\circ\text{K}$  the spins are along the crystal axis (state I), and at  $250^\circ\text{K} < T < 950^\circ\text{K}$  they lie in one of the vertical planes of symmetry making a small angle with the basal plane (111) (state II).

It appears that  $\text{Cr}_2\text{O}_3$  is not ferromagnetic at all and  $\alpha\text{-Fe}_2\text{O}_3$  is ferromagnetic only in the state II. When, with lowering of temperature,  $\alpha\text{-Fe}_2\text{O}_3$  changes from the II state into the I state its spontaneous magnetic moment disappears.

Let us assume that we know the symmetry of the antiferromagnetic distribution of the spins when their sum in the unit cell is equal to zero. A question then arises: is ferromagnetism possible with this symmetry? In other words, is it possible to change the spin direction or magnitude, without departing from the symmetry of the original distribution, in such a way as to make the sum of the spins in the unit cell non-zero in value?

Thus, for example, in the II state  $\alpha\text{-Fe}_2\text{O}_3$  ferromagnetism would arise if all spins leave the symmetry plane and rotate towards one another (Fig. 2). The possibility of such a rotation depends

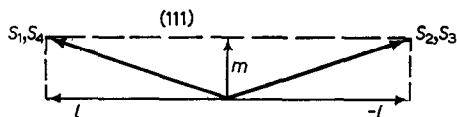


FIG. 2. Projection of ion spins on (1) for  $\alpha\text{-Fe}_2\text{O}_3$ .

on whether the magnetic symmetry of the II state and the symmetry with the spins rotated are identical.

The symmetry of a magnetic crystal is deter-

mined not only by the distribution of its atoms but also by the average value of the spin at every point  $s(x, y, z)$ . It is known<sup>(6)</sup> that the vector quantity  $s(x, y, z)$  may possess in addition to the usual symmetry transformations, i.e. axes of rotation, symmetry planes and translations, also a symmetry element  $R$  consisting of the change of the spin sign  $s(x, y, z) \rightarrow -s(x, y, z)$ . This is due to the invariance of the equations of mechanics with respect to simultaneous change of the sign of time and the sign of magnetic fields and spins.

If the spin distribution possesses  $R$  by itself, then  $s(x, y, z) = -s(x, y, z) = 0$  and the crystal is paramagnetic. A non-zero value of  $s(x, y, z)$  may be, however, invariant with respect to various combinations of  $R$  with axes of rotation, planes of symmetry and translations. Thus in addition to the 230 known space groups, which describe all the possible types of symmetry of the distribution of atoms in crystals, new "magnetic" space groups arise which describe symmetry of the spin distribution.

All groups obtainable in this way have not yet been constructed. However, to describe the symmetry of a ferromagnetic body we need not know the corresponding space group. The symmetry of the ferromagnetic and, in general, all macroscopic, properties is determined by the symmetry class, i.e. by the point group obtained from the corresponding space group by replacement of translations by identical transformations, and helical axes and glide surfaces by rectilinear axes and planes. All the possible "magnetic" classes were described by TAVGER and ZAITSEV.<sup>(9)</sup> It was found that, in addition to the usual 32 classes which possess the element  $R$  by itself, there are also 58 special "magnetic" classes.

We shall find the classes of symmetry of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  in the antiferromagnetic state. As shown earlier,  $\alpha\text{-Fe}_2\text{O}_3$  may occur in two antiferromagnetic states: with spins directed along the crystal axis (state I) and with spins lying in one of the planes of symmetry (state II). From considerations of symmetry we should also discuss another possible spin orientation, along one of the second-order axes (state III).

Using the description of the space group  $D_{3d}^6$  given in reference 10 we can easily find to which classes the states I, II and III of  $\alpha\text{-Fe}_2\text{O}_3$

belong. We shall now write down the elements of symmetry which form the respective classes:\*

$$C_3, U_2, I, S_6, \sigma_d \quad (\text{I})$$

$$U_2, I, \sigma_d \quad (\text{II})$$

$$U_2R, I, \sigma_dR. \quad (\text{III})$$

A spontaneous magnetic moment  $\mathbf{m}$  may exist only when it is invariant under the action of all transformations of the symmetry of the class. In the I state  $\mathbf{m}$  is zero since the corresponding class contains a third-order axis and a second-order one perpendicular to it. In the states II and III a non-zero spontaneous moment may exist and it is directed along a second-order axis in the II state and in the III state it lies in a plane of symmetry.

The experimental observation that  $\alpha\text{-Fe}_2\text{O}_3$  is ferromagnetic in the II state and not in the I state is a direct consequence of the magnetic symmetry. Symmetry considerations make it also possible to determine the direction of the spontaneous magnetic moment. In this case it is directed along that one of the second-order axes, perpendicular to a plane of symmetry, in which the antiferromagnetic components of the spins lie.

We shall now consider  $\text{Cr}_2\text{O}_3$ . As shown earlier, spins of the  $\text{Cr}^{3+}$  ions differ only in their sign, and  $s_1 = -s_2 = s_3 = -s_4$ . Such an antiferromagnetic structure possesses element of symmetry  $IR$ . It therefore follows that  $\text{Cr}_2\text{O}_3$  cannot be ferromagnetic at all. We find on applying the element  $IR$  to the magnetic moment vector  $\mathbf{m}$  that

$$\mathbf{m} = -\mathbf{m} = 0.$$

The above considerations make it possible to decide whether ferromagnetism is possible in a given antiferromagnetic structure of a crystal and to find directions of a spontaneous magnetic moment that are permissible in given structural symmetry. The symmetry does not limit in any way the magnitude of the magnetic moment. For example, in  $\alpha\text{-Fe}_2\text{O}_3$  in the II state it is possible, without affecting the symmetry, to rotate the spins about the crystal axis to make their

directions coincide and the crystal would then be a pure ferromagnetic. To explain the smallness of the spontaneous magnetization and to show the close relationship between the "weak" ferromagnetism and antiferromagnetism it is necessary to apply the thermodynamic theory of transitions of the second kind.

#### LANDAU'S THEORY OF PHASE TRANSITIONS OF THE SECOND KIND<sup>(4,5)</sup>

The state of a magnetic crystal is described by the average density of the spin distribution  $s(x, y, z)$ . If in a unit cell there are several magnetic ions which cannot be reduced by translations then the average spin of each type of ions is described by its own function  $s_a(x, y, z)$ . The symmetry of a magnetic crystal is identical with the symmetry of the vector function  $s(x, y, z)$  and is given by one of the "magnetic" space groups.<sup>†</sup> In a phase transition of the second kind the spin density  $s(x, y, z)$ , i.e. the magnitude and the orientation of the spins in the crystal, varies continuously but its symmetry changes suddenly, and at the transition point itself the symmetries of both phases are identical.

We shall discuss the transition from a paramagnetic into an antiferromagnetic state. In the paramagnetic phase  $s(x, y, z) = 0$  and its "magnetic" symmetry is described by one of the 230 "magnetic" groups with the element  $R$  by itself.<sup>‡</sup> In the antiferromagnetic phase  $s(x, y, z) \neq 0$  (but the integral  $\int s dV$  of the spin density in the unit cell is equal to zero) and its symmetry is the same as the symmetry of the  $s(x, y, z)$  function.

From group theory it is known that any function can be represented as a linear combination of functions which transform one into another under all transformations of the group. Let  $\phi_1(x, y, z)$ ,  $\phi_2(x, y, z)$ , ... transform one into another under all transformations of the symmetry group of the paramagnetic phase. Then the spin density in the antiferromagnetic phase may be represented by

$$s_a(x, y, z) = \sum_i a_{ai} c_i \phi_i(x, y, z)$$

\* Here  $C_3$  denotes a vertical axis of third order,  $U_2$  = a horizontal axis of second order,  $\sigma_d$  = a vertical plane of symmetry,  $S_6$  = a mirror-rotation axis of sixth order and  $I$  = an inversion operation.

† The atomic distribution symmetry can be obtained from the average spin distribution symmetry if in the appropriate magnetic group the element  $R$  is regarded as an identical transformation.

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

where  $a_{\alpha i}$  are temperature- and pressure-independent coefficients chosen so that the components of the spin density  $s_{\alpha}(x, y, z)$  transform as pseudovector components.

In this expansion instead of the functions  $\phi_i$  we may of course use any linear combination of them. It is always possible to select  $\phi_i$  so that they can be resolved into a series of sets, containing a minimum number of functions, such that in all transformations of the symmetry group the functions of each set transform one into another. Each such set is an irreducible representation of the symmetry group. In terms of these functions the expansion of  $s(x, y, z)$  has the form

$$s_{\alpha}(x, y, z) = \sum_n \sum_i a_{\alpha i}^{(n)} c_i^{(n)} \phi_i^{(n)}(x, y, z) \quad (1)$$

where  $n$  = the number of an irreducible representation and  $i$  = the number of a function in its base.

The symmetry group of a paramagnetic crystal contains  $R$  by itself. Since  $R^2 \equiv 1$  and  $R$  is interchangeable with all axes of rotation, planes of symmetry and translations, therefore all the irreducible representations of the group can be divided into two types of representations: the first type with functions which do not change under the action of  $R$ , and those of the second type with functions which change their sign. Since  $s(x, y, z)$  itself changes its sign under the action of  $R$ , the above expansion would contain only those functions which change their sign under the action of  $R$ .

The thermodynamic potential  $\Phi$  of a crystal with spin density  $s(x, y, z)$  depends on temperature, pressure and the coefficients  $c_i^{(n)}$ . Dependence of  $c_i^{(n)}$  themselves on  $p, T$ , and therefore the symmetry of the crystal in the antiferromagnetic phase are determined thermodynamically from the condition of minimum of  $\Phi$ .

In the paramagnetic phase all  $c_i^{(n)}$  are equal to zero. Since the change of state of a crystal at a phase transition of the second kind is continuous therefore the coefficients  $c_i^{(n)}$  become zero at the phase-transition point, and they have very small values in the antiferromagnetic phase near the transition point. It follows that near the transition point the potential  $\Phi$  can be expanded into a power series of  $c_i^{(n)}$ .

In the expansion (1) we regarded  $c_i^{(n)}$  as constant and  $\phi_i^{(n)}(x, y, z)$  as changeable under trans-

formations of the group. We can equally well regard  $\phi_i^{(n)}$  to be constant and  $c_i^{(n)}$  transformable in the same way as  $\phi_i^{(n)}$  earlier. Since  $\Phi$  is invariant under transformations of the symmetry, its expansion in terms of  $c_i^{(n)}$  should contain only invariant combinations of the latter.

As shown earlier, all  $c_i^{(n)}$  change their sign under the  $R$  transformation, and therefore in the expansion of  $\Phi$  we can only have invariants composed of even powers of  $c_i^{(n)}$ . From group theory we know that from quantities transforming in irreducible representation we can form only one invariant of the second order which is a positive definite quadratic form always expressible as a sum of squares.

Consequently, retaining only the square terms, the expansion of the thermodynamic potential  $\Phi$  has the form

$$\Phi = \Phi_0 + \sum_n A^{(n)} \sum_i c_i^{(n)2}$$

where  $A^{(n)}$  are functions of  $p$  and  $T$ , and  $\Phi_0$  is the potential of the paramagnetic phase.

In the paramagnetic phase when  $\Phi$  is minimum  $c_i^{(n)} = 0$  and consequently all  $A^{(n)} > 0$ . Transition to the antiferromagnetic phase occurs when one of the functions  $A^{(n)}$  changes its sign (at the transition point itself  $A^{(n)} = 0$ ). Then  $c_i^{(n)}$  of the corresponding irreducible representation are no longer zero. The crystal symmetry now changes and is given by the symmetry of the average spin density

$$s_{\alpha}(x, y, z) = \sum_i a_{\alpha i}^{(n)} c_i^{(n)} \phi_i^{(n)}(x, y, z).$$

To find the actual form of the symmetry we must take into account terms with the fourth power of  $c_i^{(n)}$ . Introducing

$$\eta^2 = \sum_i c_i^2, \quad c_i = \gamma_i \eta$$

(we are omitting index  $n$  for the sake of brevity) we can write the expansion of  $\Phi$  as

$$\Phi = \Phi_0(p, T) + \eta^2 A(p, T) + \eta^4 \sum_k B_k(p, T) f_k^{(4)}(\gamma_i)$$

where  $f_k^{(4)}(\gamma_i)$  are invariants of the fourth order which can be made up of  $\gamma_i$ .

On finding  $\gamma_i$  from the minimum condition for  $\Phi$  we can write  $\Phi$  in the form usual in the theory of phase transitions of the second kind:

$$\Phi = \Phi_0(p, T) + \eta^2 A(p, T) + \eta^4 B(p, T)$$

from which in the usual way we find the dependence of  $\eta^2$  on  $p$  and  $T$ .

The quantities  $\eta^2$  and  $\gamma_i$  found in this way determine the symmetry of the average spin density  $s_\alpha = \eta^2 \sum_i a_{\alpha i} \gamma_i \phi_i$  and, simultaneously, the crystal symmetry in the antiferromagnetic phase.

The magnetic transition in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> occurs without a change of the unit cell. In this case the theory put forward above is greatly simplified. Now the average spin density  $s_\alpha(x, y, z)$  of each of the four ions of Fe<sup>3+</sup> or Cr<sup>3+</sup> (Fig. 1), since we are interested only in changes of the symmetry, may be regarded to be independent of co-ordinates, and the magnetic symmetry of the crystal is determined simply by the average values of the spins of each of the ions:  $s_1, s_2, s_3, s_4$ . In the expansion (1) there is no need now to distinguish the coefficients  $c_i^{(n)}$  and the functions  $\phi_i^{(n)}$ , and by their product  $c_i^{(n)}\phi_i^{(n)}$  we now understand a linear combination of the components of  $s_1, s_2, s_3, s_4$  transforming according to the corresponding irreducible representation of the crystal symmetry group in the paramagnetic phase. For  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> this group consists of all the elements of symmetry of their space group  $D_{3d}^6$ , the transformation  $R$  and all possible combinations of  $R$  with transformations of  $D_{3d}^6$ . Such a group is called a direct product of  $D_{3d}^6$  and  $R$  and is usually written  $D_{3d}^6 \times R$ .

Near the transition point the average ionic spins  $s_1, s_2, s_3, s_4$  are small and the thermodynamic potential  $\Phi$  may be expanded as a power series of their components. As before only the even-powered terms enter the expansion since  $\Phi$  should be invariant under the transformation  $R$  of replacement of all  $s$  by  $-s$ . The expansion should be also invariant under all transformations of the symmetry of the space group  $D_{3d}^6$  of the crystal. Since the transition occurs without a change of the unit cell all translations by a whole period of the lattice should be regarded as identical transformations. The group  $D_{3d}^6$  goes over into a group which we shall call  $\tilde{D}_{3d}^6$ , isomorphous with the point group  $D_{3d}$  which determines the crystal class, and which differs from the  $D_{3d}^6$  by replacement of certain rotation axes and symmetry planes by helical axes and glide surfaces. The distribution of the elements of symmetry of  $\tilde{D}_{3d}^6$  in the crystal cell is given in.<sup>(10)</sup>

Axial vectors  $s_1, s_2, s_3, s_4$  form a reducible

representation of the  $\tilde{D}_{3d}^6$  group. To break it up into irreducible representations we shall introduce instead of  $s$  vectors  $m, l_1, l_2, l_3$  given by

$$\begin{aligned} m &= s_1 + s_2 + s_3 + s_4 & s_1 &= \frac{1}{4}(m + l_1 + l_2 + l_3) \\ l_1 &= s_1 - s_2 - s_3 + s_4 & s_2 &= \frac{1}{4}(m - l_1 - l_2 + l_3) \\ l_2 &= s_1 - s_2 + s_3 - s_4 & s_3 &= \frac{1}{4}(m - l_1 + l_2 - l_3) \\ l_3 &= s_1 + s_2 - s_3 - s_4 & s_4 &= \frac{1}{4}(m + l_1 - l_2 - l_3) \end{aligned}$$

The vector  $m$  is simply the average magnetic moment of a unit cell.

In all transformations of the symmetry vectors  $m$  and  $l$  transform independently. The components  $m_x, l_{1x}, l_{2x}, l_{3x}$  transform according to unidimensional representations  $A_{2g}, A_{1g}, A_{1u}, A_{2u}$  of the point group  $D_{3d}$  (for tables of characters of irreducible representations see reference 11). The  $x$ - and  $y$ -components of the vectors  $m$  and  $l_1$  transform according to the same two-dimensions representation  $E_g$  and the same components of the vectors  $l_2$  and  $l_3$  according to  $E_u$ .

Knowing the irreducible representations according to which the components of  $m$  and  $l$  transform we can write down the most general form of the expansion permitted by the symmetry of the crystal. Limiting ourselves to the second-order terms we have for  $\Phi$ :\*

$$\left. \begin{aligned} \Phi &= \frac{A_1}{2} l_1^2 + \frac{A_2}{2} l_2^2 + \frac{A_3}{2} l_3^2 + \frac{B}{2} m^2 + \frac{\alpha_1}{2} l_{1z}^2 \\ &\quad + \frac{\alpha_2}{2} l_{2z}^2 + \frac{\alpha_3}{2} l_{3z}^2 + \frac{b}{2} m_z^2 + \\ &\quad + \beta_1 (l_{1x} m_y - l_{1y} m_x) + \\ &\quad + \beta_2 (l_{2x} l_{3y} - l_{2y} l_{3x}). \end{aligned} \right\} \quad (2)$$

In the expression (2) there are various magnetic energy terms corresponding to different types of the spin interaction. Terms of the type  $Al^2$  do not depend on the orientation of the vector  $l$  and the spins  $s$  relative to the crystal axes, and they represent exchange interactions; terms of the type  $\alpha l_z^2, (l_x m_y - l_y m_x)$  arise from the relativistic spin-lattice interactions and from the magnetic dipole interaction and determine the magnetic

\* We shall use a rectilinear system of co-ordinates with the  $z$ -axis directed along the crystal axis and the  $x$ -axis along one of the second-order axes.

anisotropy of the crystal. The ratio  $\alpha/A$  of the magnetic isotropy energy to that of the exchange energy is proportional to the square of the ratio  $(v/c)^2$  of the velocity of electrons in the crystal to the velocity of light and lies usually between  $10^{-2}$  and  $10^{-5}$ .

An important peculiarity of the crystals with the symmetry we are discussing now is the occurrence of "mixed" terms  $l_{1x}m_y - l_{1y}m_x$  and  $l_{2x}l_{3y} - l_{2y}l_{3x}$  in the expansion of the thermodynamic potential. From the mathematical point of view they arise because the  $x$ - and  $y$ -components of vectors  $\mathbf{m}$  and  $\mathbf{l}_1$  (or  $\mathbf{l}_2$  and  $\mathbf{l}_3$ ) are transformed according to the same representations. We shall see later that the first of the above "mixed" terms is responsible for the ferromagnetism of  $\alpha\text{-Fe}_2\text{O}_3$ .

In the case of the paramagnetic phase all  $A > 0$  and  $B > 0$  and the state in which all  $\mathbf{l}$  and  $\mathbf{m}$  are zero corresponds to the minimum of the thermodynamic potential. The transition occurs at the point where one of  $A$ 's becomes zero.\* If the spin interaction in the crystal is purely of the exchange type, then below the transition point only the vector  $\mathbf{l}$  which stands by the negative  $A$  is non-zero, and consequently in crystals with the symmetry considered here one of the following three types of antiferromagnetic structure occurs:

$$(1) l_1 \neq 0, l_2 = l_3 = \mathbf{m} = 0, s_1 = -s_2 = -s_3 = s_4$$

which is the structure of  $\alpha\text{-Fe}_2\text{O}_3$ ;

$$(2) l_2 \neq 0, l_1 = l_3 = \mathbf{m} = 0, s_1 = -s_2 = s_3 = -s_4$$

which is the structure of  $\text{Cr}_2\text{O}_3$ ; and

$$(3) l_3 \neq 0, l_1 = l_2 = \mathbf{m} = 0, s_1 = s_2 = -s_3 = -s_4$$

In the actual crystal, owing to the relativistic interactions which yield the term  $l_{1x}m_y - l_{1y}m_x$ , in  $\alpha\text{-Fe}_2\text{O}_3$  a small vector  $\mathbf{m}$  arises in addition to the basic antiferromagnetic spin distribution described by the vector  $\mathbf{l}_1$ , and the crystal becomes ferromagnetic. This ferromagnetism will be of relativistic, and not exchange, nature.

For the same reason the antiferromagnetic structure of  $\text{Cr}_2\text{O}_3$  is determined by the vectors  $\mathbf{l}_2$  and  $\mathbf{l}_3$  taken together (for the structure of  $\text{Cr}_2\text{O}_3$  see below).

\* We shall assume that  $B$  is always greater than zero, since otherwise our crystal would be the usual exchange ferromagnetic.

### FERROMAGNETISM OF $\alpha\text{-Fe}_2\text{O}_3$

We shall now consider the magnetic structure of  $\alpha\text{-Fe}_2\text{O}_3$  in greater detail. Near the transition point  $\mathbf{l}_1$  and  $\mathbf{m}$  are small and to calculate them it is sufficient to take into account in the expansion for the thermodynamic potential the second-order terms together with the exchange term proportional to  $l_1^4$  since the remaining fourth-order terms are small compared with the latter. Then  $\Phi$  can be written as:

$$\Phi = \frac{A}{2}l^2 + \frac{B}{2}m^2 + \frac{\alpha}{2}l_z^2 + \frac{b}{2}m_z^2 + \beta(l_xm_y - l_y m_x) + \frac{C}{4}l^4$$

with the subscript 1 of the vectors  $\mathbf{l}$  omitted.

The minimum of  $\Phi$  for a constant  $|\mathbf{l}|$  is determined by the equations:

$$\begin{aligned} \beta m_y &= \lambda l_x & B m_x - \beta l_y &= 0 \\ -\beta m_x &= \lambda l_y & B m_y + \beta l_x &= 0 & l_x^2 + l_y^2 + l_z^2 &= l^2 \\ \alpha l_z &= \lambda l_z & (B + b)m_z &= 0. \end{aligned}$$

This group of equations has two solutions:

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

$$(II) \quad l_z = m_z = 0, m_x = (\beta/B)l_y, m_y = -(\beta/B)l_x.$$

In the I state the ion spins are directed along the crystal axis and ferromagnetism is absent. In the II state the spins lie in the Plane (111), and the spontaneous magnetic moment has the magnitude  $\mathbf{m} = (|\beta|/B)\mathbf{l}$  and is perpendicular to  $\mathbf{l}$ . As pointed out earlier  $|\beta|/B \cong 10^{-2} - 10^{-5}$ , therefore  $m/l \cong 10^{-2} - 10^{-5}$  in agreement with the experimental value  $m/l = 2 \times 10^{-4}$ . In the II state the spins  $s_1, s_4$  and  $s_2, s_3$  no longer cancel out but they are rotated with respect to one another by a small angle of the order of  $10^{-4}$  (Fig. 2).

The direction of the vector  $\mathbf{l}$  in the plane (111) is not determined by the second-order terms in the expansion of  $\Phi$ . For this we must have an invariant of the lowest order which may be constructed from  $l_x$  and  $l_y$ . Such an invariant is  $(l_x + il_y)^6 + (l_x - il_y)^6$  and depending on its coefficient the vector  $\mathbf{l}$  will lie either along one of the second-order axes or in one of the planes of symmetry. All these results are in full agreement with the results obtained earlier from considerations of symmetry.

Of the two possible structures I and II the one which has the lowest thermodynamic potential will actually exist.

In the I state

$$\Phi_I = \frac{A}{2}l^2 + \frac{\alpha}{2}l^2 + \frac{C}{4}l^4$$

and in the II state

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

Minimizing them with respect to  $l^2$  we find that

$$\Phi_I = -\frac{1}{4} \frac{(A+\alpha)^2}{C},$$

$$\Phi_{II} = -\frac{1}{4} \frac{(A-\beta^2/B)^2}{C}, \quad l^2 \cong -\frac{A}{C}.$$

Since  $\alpha \sim \beta \sim (v/c)^2$ , then neglecting the terms of the order of  $(v/c)^4$  we finally obtain

$$\Phi_I \cong -\frac{1}{4} \frac{A^2}{C} - \frac{A\alpha}{2C}, \quad \Phi_{II} = -\frac{1}{4} \frac{A^2}{C}.$$

Consequently one or the other state will arise depending on the sign of  $\alpha$ . SHULL *et al.*<sup>(7)</sup> have shown that at  $250^\circ\text{K} < T < 950^\circ\text{K}$  the spins lie in the (111) plane, and at  $T < 250^\circ\text{K}$  in the [111] direction, and therefore  $\alpha > 0$  at  $250^\circ\text{K} < T < 950^\circ\text{K}$  (we note that  $A < 0$ ) and  $\alpha > 0$  at  $T < 250^\circ\text{K}$ .

To find the temperature dependence of  $l$  and  $m$  near the transition point, we shall assume, as usual, that  $A = \lambda(T - T_c)$  and therefore

$$l = \sqrt{\left[\frac{\lambda}{C}(T_c - T)\right]}, \quad m = \frac{|\beta|}{B}l = \frac{|\beta|}{B} \times \sqrt{\left[\frac{\lambda}{C}(T_c - T)\right]}.$$

Away from the transition point the value of  $l$  is no longer small and its power expansion is in general, not longer valid. It is possible however, to expand in powers of a unit vector  $\gamma$  in the direction of  $l$  (it can be easily seen that this expansion is equivalent to an expansion in powers of  $(v/c)^2$ ). The expansion in powers of  $m$  is still possible because of  $m$ 's smallness.

We shall write down invariants of fourth order in  $\gamma$  and  $m$ , which contain  $m$  of power not higher than the second (invariants with higher powers of  $m$  are negligibly small). As before we should distinguish between the pure exchange invariants, those of mixed nature, and the relativistic invariants. The ratio of the energy corresponding to the mixed invariants to the energy of the exchange ones is proportional to  $(v/c)^2$ , and the ratio of the energy corresponding to the relativistic invariants to the exchange ones to  $(v/c)^4$ , and for this reason the relativistic invariants are sometimes called doubly relativistic.

For a crystal with the symmetry of  $\alpha\text{-Fe}_2\text{O}_3$  there is only one exchange invariant of the fourth order:

$$(m\gamma)^2$$

two mixed ones:

$$(m\gamma)m_z\gamma_z, \quad \gamma_z^2m^2$$

and five doubly relativistic ones:

$$\begin{aligned} &\gamma_z[(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3], \\ &m_z[(\gamma_x + i\gamma_y)^3 + (\gamma_x - i\gamma_y)^3] \\ &\gamma_z^4, (\gamma_x m_y - \gamma_y m_x)^2, \gamma_z^2(\gamma_x m_y - \gamma_y m_x). \end{aligned}$$

For our purpose only the one exchange invariant and the first three relativistic ones are important, since the rest, as we shall find later, are small compared with them. We shall also need one triply relativistic invariant  $(\gamma_x + i\gamma_y)^6 + (\gamma_x - i\gamma_y)^6$ ; the ratio of the energy corresponding to this invariant to the exchange energy is proportional to  $(v/c)^6$ .

Finally the thermodynamic potential can be written as

$$\Phi = \left. \begin{aligned} &\frac{a}{2}\gamma_z^2 + \frac{B}{2}m^2 + g(\gamma_x m_y - \gamma_y m_x) + \\ &+ \frac{b}{2}m_z^2 + \frac{D}{2}(\gamma m)^2 + \frac{d}{2i}\gamma_z[(\gamma_x + i\gamma_y)^3 - \\ &- (\gamma_x - i\gamma_y)^3] + \frac{f}{2}m_z[(\gamma_x + i\gamma_y)^3 + (\gamma_x - i\gamma_y)^3] + \\ &+ \frac{e}{2}[(\gamma_x + i\gamma_y)^6 + (\gamma_x - i\gamma_y)^6] + \frac{g}{4}\gamma_z^4. \end{aligned} \right\} \quad (3)$$

We shall now find the magnetic structure of

$\alpha\text{-Fe}_2\text{O}_3$  at temperatures between the point of transition into the paramagnetic state and the point of the  $\text{I} \rightleftharpoons \text{II}$  state transition, but not too near these points. In this region  $a \gg d, e, f, g$ , since  $d/a \sim f/a \sim g/a \sim (v/c)^2$ ,  $e/a \sim (v/c)^4$ .

We shall re-write equation (3) for  $\Phi$  using polar co-ordinates for the vector  $\gamma$  and omitting the term  $(g/4)\gamma_z^4$ , since the latter is, as shown later, negligible in this region:

$$\left. \begin{aligned} \Phi = & \frac{a}{2} \cos^2 \theta + \frac{B}{2} m^2 + \\ & + q \sin \theta (m_y \cos \phi - m_x \sin \phi) + \\ & + \frac{b}{2} m^2 + \frac{D}{2} [m_z \cos \theta + \\ & + \sin \theta (m_x \cos \phi + m_y \sin \phi)]^2 + \\ & + d \cos \theta \sin^3 \theta \sin^3 \phi + e \cos 6\phi \sin^6 \theta + \\ & + f m_z \sin^3 \theta \cos 3\phi. \end{aligned} \right\} \quad (3a)$$

Minimizing  $\Phi$  with respect to  $m$  for given values of  $\theta$  and  $\phi$ , we find

$$\left. \begin{aligned} m_x = & \frac{q}{B} \sin \theta \sin \phi \\ m_y = & -\frac{q}{B} \sin \theta \cos \phi \\ m_z = & -\frac{f}{B} \sin^3 \theta \cos 3\phi. \end{aligned} \right\} \quad (4)$$

At the minimum of  $\Phi$  we can have the following three sets of values of

$$\left. \begin{aligned} \text{(I)} \quad & \theta = 0, \quad m = 0 \\ \text{(II)} \quad & \theta \cong \frac{\pi}{2} - \frac{d}{a}, \quad \phi = \pi/2, \quad m_x = \frac{q}{B}, \\ & m_y = m_z = 0 \\ \text{(III)} \quad & \theta = \frac{\pi}{2}, \quad \phi = 0, \quad m_y = -\frac{q}{B}, \\ & m_z = -\frac{f}{B}, \quad m_x = 0. \end{aligned} \right\} \quad (5)$$

Thus, at not too small values of  $a$ , the  $\alpha\text{-Fe}_2\text{O}_3$  crystal may exist in three magnetic states. In the I state all the spins are directed along the  $[111]$  axis

and there is no ferromagnetism. In the II state the antiferromagnetic component of the spins lies in one of the planes of symmetry making a small ( $\cong d/a \sim (v/c)^2$ ) angle with the  $(111)$  plane, the spontaneous magnetic moment  $m_0 = |q|/B \sim (v/c)^2$  is directed along a second-order axis perpendicular to the antiferromagnetic spin component. In the III state the antiferromagnetic component of the spins is directed along one of the second-order axes; the spontaneous magnetic moment is of the same magnitude as in the II state, i.e.  $m_0 = |q|/B$ , and it lies in the plane of symmetry which is perpendicular to the second-order axis of the antiferromagnetic component making a small angle (of the order of  $f/q \sim (v/c)^2$ ) with the  $(111)$  plane.

Once more the results obtained are in full agreement with those found earlier from the considerations of symmetry.

According to NÉEL and PAUTHENET,<sup>(1)</sup>  $m_0 = 0.4$  c.g.s. e.m.u.; the reciprocal of the magnetic susceptibility in the paramagnetic phase\* is  $B = 5 \times 10^4$ . Hence we find that  $q = 2 \times 10^4$  c.g.s. e.m.u.

At a given temperature and pressure of the three states the one with the lowest value of  $\Phi$  will exist. Using equation (5) we find

$$\Phi_{\text{I}} = \frac{a}{2}, \quad \Phi_{\text{II}} = -\frac{q^2}{2B} - \frac{d^2}{4a} - e, \quad \Phi_{\text{III}} = -\frac{q^2}{2B} + e.$$

Since, in general  $|a| \gg q^2/2B, d^2/4|a|, e$ , then at  $a > 0$  the state II will exist provided  $e > -d^2/8a$  (which according to reference 7 occurs at  $250^\circ\text{K} < T < 950^\circ\text{K}$ ), while the state III will exist if  $e < -d^2/8a$ . When  $a < 0$  the state I exists (according to references 1, 7 this occurs at  $T < 250^\circ\text{K}$ ).

At a certain value of  $a$  close to zero the transition between the I state and the II (or III) state occurs. The character of this transition can be found from the considerations of symmetry without solving the appropriate equations. From LANDAU's theory it follows that a transition of the second kind is possible only between two states in which the symmetry group of one is the subgroup of the symmetry group of the other. In the section

\* Actually in the paramagnetic phase the thermodynamical potential  $\Phi$  has the form  $\Phi = Bm^2/2 + bm_z^2/2$ . Therefore, since  $\partial\Phi/\partial m = H$ , we find  $m_x = H_x/B$ ,  $m_y = H_y/B$ ,  $m_z = H_z/(B+b)$  for  $b/B \ll 1$ .



on magnetic symmetry we found the symmetry classes of the states I, II and III. It is clear that a transition of the second kind is impossible between the states I and III, and the states II and III. The symmetry class of the II state is a subgroup of the symmetry class of the I state. For a transition of the second kind between the states I and II to be possible absence of third-order terms<sup>(4,5)</sup> in the expansion of the thermodynamic potential near the transition point is also necessary. In the I to II state transition the  $x$ - and  $y$ -components of the vector  $\gamma$ , which occur in the  $\Phi$  expansion, are small. It can be easily verified that the magnetic symmetry of the I state permits the existence of a third-order invariant  $(\gamma_x + i\gamma_y)^3 - (\gamma_x - i\gamma_y)^3$ , and consequently the I  $\rightleftharpoons$  II transition is also a transition of the first kind.

We shall consider now the behaviour of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> near the point of transition of the first kind from the II to the I state. In this case in the expansion of the thermodynamic potential in equation (3) it is sufficient to retain only the following terms:

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

Expressing  $m$  in terms of  $\gamma$  and introducing polar co-ordinates for  $\gamma$ , we find

$$\Phi = -\frac{q^2}{2B} + \frac{a'}{2}\cos^2\theta + \frac{g}{4}\cos^4\theta + d\cos\theta\sin^3\theta\sin 3\phi$$

where

$$a' = a + \frac{q^2}{B}.$$

In the I state  $\cos\theta = 1$  and in the II state  $\sin 3\phi = \pm 1$ , therefore, for  $\theta < \pi/2$ , we have

$$\Phi_I = -\frac{q^2}{2B} + \frac{a'}{2} + \frac{g}{4}$$

$$\Phi_{II} = \Phi_I - \frac{a'}{2}\sin^2\theta - \frac{g}{4} \times$$

$$\times (1 + \cos^2\theta)\sin^2\theta - |d|\cos\theta\sin^3\theta.$$

The angle  $\theta$  is found from the following equation

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

At the transition point  $\Phi_I = \Phi_{II}$ ,  $\partial\Phi_{II}/\partial\theta = 0$ , and these conditions yield the following two equations for determination of the angle  $\theta_c$  and the quantity  $a'_c$

$$|d|\tan^3\theta_c - a'_c\tan^2\theta_c - 3|d|\tan\theta_c - a'_c - g = 0,$$

$$\left(a'_c + \frac{g}{2}\right)\tan^2\theta_c + 2|d|\tan\theta_c + a'_c + g = 0$$

and therefore

$$|d|\tan^2\theta_c + \frac{g}{2}\tan\theta_c - |d| = 0$$

and

$$\tan\theta_c = -g/4|d| + \sqrt{(g^2/16d^2 + 1)}.$$

We shall now calculate the spontaneous magnetic moment  $m_c$  at the transition point and the entropy of the transition. Using equation (4) we find

$$m_c = \frac{|g|}{B}\sin\theta_c$$

or

$$\sin\theta_c = \frac{m_c}{m_0}$$

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

The change of entropy is

$$\Delta S_{I,II} = -\frac{\partial}{\partial T}(\Phi_I - \Phi_{II}) = -\frac{1}{2}\left(\frac{da'}{dT}\right)_c \sin^2\theta_c$$

and the heat of the transition is

$$q_{I,II} = -\frac{T_c}{2}\left(\frac{da'}{dT}\right)_c \left(\frac{m_c}{m_0}\right)^2.$$

We can now describe fully the behaviour of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal with change of temperature.

At temperatures  $T > 950^\circ\text{K}$  the crystal is paramagnetic. At the point  $T_* = 950^\circ\text{K}$  there is a transition into the state in which the spins of the Fe<sup>3+</sup> ions differ, as a first approximation, in sign

only:  $s_1 = -s_2 = -s_3 = s_4$ , and they are directed along the line of intersection of the plane (111) and one of the planes of symmetry. In a higher approximation the spins  $s_1, s_4$  and  $s_2, s_3$  are found to be rotated towards one another about the crystal axis [111] by a small angle of the order of  $10^{-4}$ , as shown in Fig. 2, and this produces a spontaneous magnetic moment whose magnitude is 0.04 per cent of the nominal value and which is directed along a second-order axis. Such an explanation for occurrence of ferromagnetism was first put forward by BOROVIK-ROMANOV and ORLOVA.<sup>(2)</sup> Also the spins do not actually lie in the (111) plane, but make with it a small angle of the order of  $(v/c)^2$

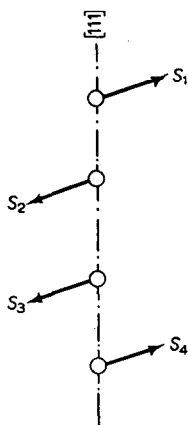


FIG. 3. Projections of the  $\alpha\text{-Fe}_2\text{O}_3$  spins on a symmetry plane.

(Fig. 3). On approaching  $T_c = 250^\circ\text{K}$  from the direction of high temperatures the angle between the spins and the [111] axis begins to decrease rapidly. At  $T_c = 250^\circ\text{K}$  it reaches a certain critical value  $\theta_c$  and the spontaneous magnetic moment falls to a value  $m_c$ . At  $T_c = 250^\circ\text{K}$  a transition of the first kind occurs when the spins suddenly change their direction to that of [111] and the spontaneous magnetic moment disappears. At  $T < 250^\circ\text{K}$  the crystal becomes antiferromagnetic with the spins oriented along the crystal axis; ferromagnetism is absent in this state.

#### BEHAVIOUR OF $\alpha\text{-Fe}_2\text{O}_3$ IN MAGNETIC FIELDS

Behaviour of the ferromagnetic modification of  $\alpha\text{-Fe}_2\text{O}_3$  in magnetic fields is of great interest since

its magnetic properties in the antiferromagnetic state I are those of a usual antiferromagnetic.

We shall limit ourselves to not too strong fields so that  $H^2 \ll aB$ , since at fields  $H^2 \cong aB$  there may occur a transition from the II into the I state accompanied by destruction of ferromagnetism. For this to occur in known antiferromagnetics at temperatures of the order of hundreds of degrees fields of about  $10^5$ – $10^6$  oersted are required.

In the presence of an external magnetic field the thermodynamic potential has the form:<sup>†</sup>

$$\tilde{\Phi} = \Phi - mH = \frac{a}{2} \cos^2 \theta + \frac{B}{2} m^2 + \left. \begin{aligned} & + \frac{b}{2} m_z^2 + q \sin \theta (m_y \cos \phi - \\ & - m_x \sin \phi) + \frac{D}{2} [m_z \cos \theta + \\ & + \sin \theta (m_x \cos \phi + m_y \sin \phi)]^2 + \\ & + d \cos \theta \sin^3 \theta \sin 3\phi + e \sin^6 \theta \cos 6\phi + \\ & + f m_z \sin^3 \theta \cos^3 \phi - mH. \end{aligned} \right\} \quad (6)$$

We shall first consider the limiting case of very weak fields whose intensity is small compared with the energy of anisotropy in the (111) plane. The latter is given by the terms  $d \cos \theta \sin^3 \theta \sin 3\phi$  and  $e \sin^6 \theta \cos 6\phi$ . When  $H^2 \ll aB$  the value of  $\cos \theta$  is still small and of the order of  $d/a$ , and therefore the energy of anisotropy is of the order of  $e + d^2/a$ . The energy of the applied magnetic field is on the whole due to the energy of the spontaneous magnetic moment  $m_0 = |q|/B$  and is therefore  $H|q|/B$ . The criterion of weakness of the applied magnetic field can therefore be expressed as

$$H|q|/B \ll e^2 + d/a \text{ or } H \ll H^* = 6B(e + d^2/4a)/|q|$$

(we shall find useful later the quantity  $H^*$ ).

In absence of a magnetic field the crystal is in the II state. Its spontaneous magnetic moment is then directed along the  $x$ -axis,  $\phi = \pi/2$  and

<sup>†</sup>  $\Phi$  is the thermodynamic potential in terms of the variables  $p, T, m$ , while  $\tilde{\Phi}$  is this potential in terms of  $p, T, H$ , i.e.  $(d\tilde{\Phi})p, T = -mdH$ , and it is  $\tilde{\Phi}$  that should be minimized at a given value of  $H$ .

$\theta = \pi/2 - d/a$ . In a weak magnetic field the thermodynamic potential  $\tilde{\Phi}$  is a quadratic function of the field intensity components, and the quantities  $m_x - |q|/B$ ,  $m_y$ ,  $m_z$ ,  $\pi/2 - \phi$ ,  $\pi/2 - d/a - \theta$  are linear functions of the field intensity. Introducing the quantities

$$m_x' = m_x - |q|/B, \quad \kappa = \pi/2 - \phi, \quad \alpha = \pi/2 - d/a - \theta$$

we expand  $\tilde{\Phi}$  neglecting powers higher than the squares of these quantities:

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

We also introduce  $m_y' = m_y - (q/B)\kappa$  in place of  $m_y$ . Then  $\tilde{\Phi}$  becomes:

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

where  $e' = e + d^2/4a$  and the constant terms are omitted.

Determining  $\alpha$ ,  $\kappa$ ,  $m_x'$ ,  $m_y'$ ,  $m_z$  from the condition of minimum of  $\Phi$  we obtain the following system of equation:

$$\begin{aligned} \alpha + dqm_x'/a &= 0, \\ Bm_x' + dq\alpha/a - H_x &= 0, \\ 36e'\kappa + qH_y/B - 3fm_z &= 0, \\ (B+D)m_y' + Ddm_z/a - H_y &= 0, \\ (B+b)m_z + Ddm_y'/a - 3f\kappa - H_z &= 0, \end{aligned}$$

from which by a simple calculation, retaining only the largest terms, we find for  $\kappa$  and  $\alpha$ :

$$\left. \begin{aligned} \kappa &= -qH_y/36e'B + fH_z/12e'B, \\ \alpha &= -dqH_x/a^2B, \end{aligned} \right\} \quad (7)$$

for the components of the magnetic moment:

$$\left. \begin{aligned} m_x &= \frac{|q|}{B} + \frac{H_x}{B}, \\ m_y &= \frac{q^2 H_y}{36e'B^2} - \frac{qf}{12e'B^2} H_z, \\ m_z &= \frac{H_z}{B+b} - \frac{qf}{12e'B^2} H_y, \end{aligned} \right\} \quad (8)$$

and for the magnetic susceptibility:

$$\begin{aligned} \chi_{xx} &= \frac{1}{B}, \quad \chi_{yy} = \frac{q^2}{36e'B^2}, \quad \chi_{yz} \\ &= -\frac{qf}{12e'B^2}, \quad \chi_{zz} = \frac{1}{B+b}, \quad \chi_{xy} = \chi_{xz} = 0. \end{aligned}$$

$\chi_{xx}$ ,  $\chi_{zz}$ ,  $\chi_{yy}$  are of the same order as the susceptibility,  $1/B$  in the paramagnetic phase, but  $\chi_{yz}$  has a much larger value of the order  $(v/c)^{-2}$ .

It is not by accident that  $\chi_{xy}$  and  $\chi_{xz}$  are equal to zero. The thermodynamic potential  $\tilde{\Phi}$ , as a function of the field intensity components, should remain invariant under all transformations of the crystal symmetry. We found earlier that the symmetry group of the II state consists of the elements  $U_2$ ,  $I$ ,  $\sigma_d$ . The most general combination of  $H_x$ ,  $H_y$ ,  $H_z$  invariant under these three transformations is

$$\begin{aligned} \tilde{\Phi} = & -m_0 H_x - \frac{1}{2} \chi_{xx} H_x^2 - \frac{1}{2} \chi_{yy} H_y^2 - \\ & - \frac{1}{2} \chi_{zz} H_z^2 - \chi_{yz} H_y H_z \end{aligned}$$

from which we obtain for the magnetic moment an expression of the type given in equation (8).

We shall consider the other limiting case of fields  $H \gg H^*$ . In this case the terms representing the anisotropy energy in the expression for the thermodynamic potential can be neglected. Also, since we are assuming that  $H^2 \ll aB$ , we can neglect the small departure of the angle  $\theta$  from the right angle. Now  $\tilde{\Phi}$  has the following form:

$$\begin{aligned} \tilde{\Phi} = & \frac{B}{2} m^2 + \frac{b}{2} m_z^2 + q(m_y \cos \phi - m_x \sin \phi) + \\ & + \frac{D}{2} (m_x \cos \phi + m_y \sin \phi)^2 - mH. \end{aligned}$$

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

$$\begin{aligned} m_x &= \frac{q}{B} \sin \phi + \frac{H_x}{B} - \frac{D}{B(B+D)} \times \\ &\quad \times (H_x \cos \phi + H_y \sin \phi) \cos \phi, \\ m_y &= -\frac{q}{B} \cos \phi + \frac{H_y}{B} - \frac{D}{B(B+D)} \times \\ &\quad \times (H_x \cos \phi + H_y \sin \phi) \sin \phi, \\ m_z &= \frac{H_z}{B+b}. \end{aligned}$$

In the plane  $xy$  we introduce polar co-ordinates for  $H_x$  and  $H_y$ :  $H_x = H_t \cos \psi$  and  $H_y = H_t \sin \psi$  and resolve  $\mathbf{m}$  in the direction of  $\mathbf{H}_t$  and at right angles to the latter:

$$\left. \begin{aligned} m_{\parallel} &= -\frac{q}{B} \sin(\psi - \phi) + \frac{H_t}{B} - \frac{DH_t}{B(B+D)} \times \\ &\quad \times \cos^2(\psi - \phi) \\ m_{\perp} &= \frac{q}{B} \cos(\psi - \phi) - \frac{DH_t}{B(B+D)} \times \\ &\quad \times \cos(\psi - \phi) \sin(\psi - \phi) \end{aligned} \right\} \quad (9)$$

Excluding  $\mathbf{m}$  from the expression for the thermodynamic potential and omitting the terms not dependent on  $\phi$ , we find:

$$\tilde{\Phi} = \frac{[q^2]}{B} H_t \sin(\psi - \phi) + \frac{DH_t^2}{2B(B+D)} \cos^2(\psi - \phi). \quad (10)$$

The angle  $\phi$  as a function of  $\mathbf{H}_t$  is found from the following equation:

$$\begin{aligned} \frac{\partial \tilde{\Phi}}{\partial \phi} &= -\frac{q}{B} H_t \cos(\psi - \phi) + \\ &+ \frac{DH_t^2}{B(B+D)} \cos(\psi - \phi) \sin(\psi - \phi) = 0, \end{aligned}$$

which has two solutions:

$$\begin{aligned} (1) \quad &\cos(\psi - \phi) = 0 \\ (2) \quad &\sin(\psi - \phi) = \frac{q(B+D)}{DH_t}. \end{aligned}$$

The following values of the thermodynamic potential correspond to the above two solutions:

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

and the sign of the difference of the above two values

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

is determined by the sign of  $D$ .

Thus in fields  $H \gg H^*$  the crystal may exist in two states depending on the sign of  $D$ . If  $D > 0$ , then

$$\phi = \psi + \frac{\pi}{2}$$

and

$$m_{\parallel} = |q|/B + H_t/B, \quad m_{\perp} = 0, \quad m_z = H_z/(B+b).$$

The spontaneous magnetic moment which lies in the  $xy$ -plane is oriented along the field and the antiferromagnetic components of the spins perpendicularly to the field. In contrast to the usual antiferromagnetics the susceptibility is now practically isotropic. This was noted for  $\alpha\text{-Fe}_2\text{O}_3$  by NÉEL and PAUTHENET<sup>(1)</sup> and therefore favours the positive sign of  $D$ .

For  $D < 0$  we find from equation (9) that

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

The susceptibility is now strongly anisotropic in the direction of the crystal axis and there is no spontaneous magnetic moment, i.e. the crystal becomes a usual antiferromagnetic. Figs. 4(a) and 4(b) show the dependence of  $m_{\parallel}$  on the field for various signs of  $D$ .

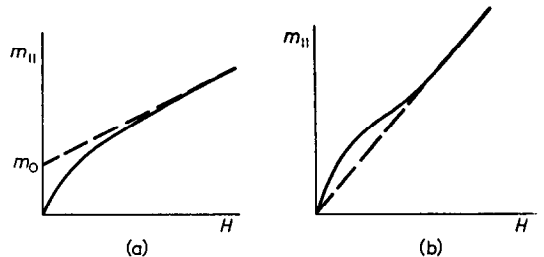


FIG. 4. Magnetization curves: (a)— $D > 0$ . (b)— $D < 0$ .

We shall finally consider the region of fields when  $H \cong H^*$ . In this case simple but tedious calculations show that we must add an anisotropy energy term  $e' \cos 6\phi$  to the thermodynamic potential given by equation (10):

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

The magnetic moment is still given by equation (9).

For  $H_t \gtrsim H^*$  the second term in equation (11) is small compared with the first, since  $H^* = 6Be'/|q|$  and  $qH^*/B \sim (v/c)^6$ , while  $H^{*2}/B \sim (v/c)^8$ . Thus  $\tilde{\Phi}$  can now be written as:

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

and the equation, which determines  $\phi$ , as:

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

The above equation and equation (12) may be reduced to a non-dimensional form on replacing  $H_t$  by  $h = H_t/H^*$

$$\left. \begin{aligned} \tilde{\Phi}/e' &= 6h \sin(\psi - \phi) + \cos 6\phi \\ h \cos(\psi - \phi) + \sin 6\phi &= 0. \end{aligned} \right\} \quad (13)$$

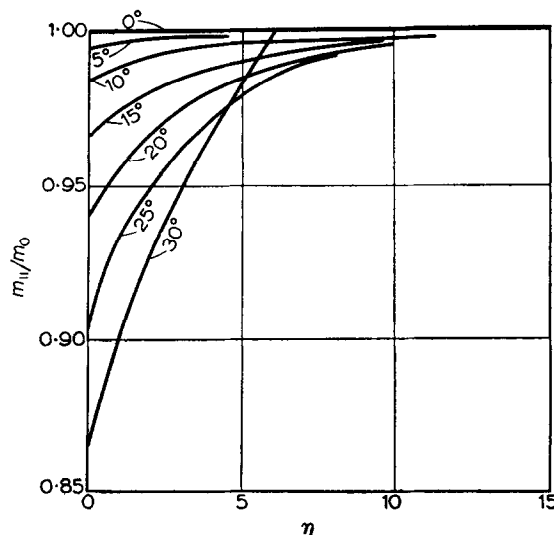


FIG. 5. Equilibrium magnetization curves for various external field directions. Figures denote value of  $\psi$ .

Fig. 5 shows equilibrium curves of magnetization calculated by numerical solution of equations (13). The ordinate axis gives values of  $m_{||} - H_t/B$  in units of the spontaneous magnetic moment  $m_0 = |q|/B$ .

In addition to the equilibrium solutions equations (13) contain also non-equilibrium solutions of the hysteresis type. The region outside which hysteresis is always impossible is given by the two conditions  $\partial \tilde{\Phi}/\partial \phi = \partial^2 \tilde{\Phi}/\partial \phi^2 = 0$  which yield the equations of the bounding curve in a parametric form

$$\left. \begin{aligned} h \cos(\psi - \phi) + \sin 6\phi &= 0 \\ h \sin(\psi - \phi) + 6 \cos 6\phi &= 0. \end{aligned} \right\} \quad (14)$$

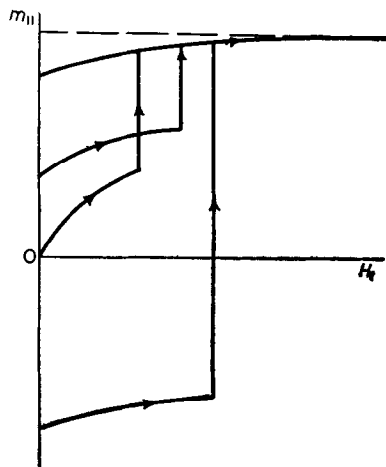


FIG. 6. Typical hysteresis curves.

Fig. 6 shows typical hysteresis curves given by equations (13) and the conditions (14).

### $\text{Cr}_2\text{O}_3$

We shall briefly consider the antiferromagnetic structure of  $\text{Cr}_2\text{O}_3$ . The spin distribution for the  $\text{Cr}^{3+}$  ions is described by the vectors  $\mathbf{l}_2$  and  $\mathbf{l}_3$ . It was shown earlier that the components of  $\mathbf{l}_2$  and  $\mathbf{l}_3$  transform in the crystal symmetry transformations in the same way as those of  $\mathbf{l}_1$  and  $\mathbf{m}$ , which describe the magnetic structure of  $\alpha\text{-Fe}_2\text{O}_3$ , except that  $\mathbf{l}_2$  and  $\mathbf{l}_3$  change their sign in inversion transformations while  $\mathbf{l}_1$  and  $\mathbf{m}$  do not. Since in the thermodynamic potential expansion  $\mathbf{l}_2$  and  $\mathbf{l}_3$  occur only in the even powers their inversion properties

will not affect the expansion and  $\Phi$  for  $\text{Cr}_2\text{O}_3$  may be obtained from  $\Phi$  for  $\alpha\text{-Fe}_2\text{O}_3$  by replacing  $l_1$  by  $l_2$  and  $m$  by  $l_3$ . Without repeating the calculations we can now describe the thermodynamically possible antiferromagnetic structures of  $\text{Cr}_2\text{O}_3$ .

As a first approximation the structure of  $\text{Cr}_2\text{O}_3$  may be described by the vector  $l_2$ . All the four  $\text{Cr}^{3+}$  ions possess spins of the same magnitude and direction, and  $s_1 = -s_2 = s_3 = -s_4$  (Fig. 1c). As before, three states are possible which differ by the orientation of the spins  $s$  with respect to the crystal axes. In the I state the spins are directed along the  $[111]$  crystal axis, in the II state the spins lie along the line of intersection of one of the symmetry planes with the  $(111)$  plane, and in the III state the spins are directed along one of the second-order axes.

In a higher approximation the spins  $s_1, s_2$  and the spins  $s_3, s_4$  in the II and the III states rotate about the  $[111]$  axis towards one another by a small angle as shown in Fig. 7. Their sum still remains

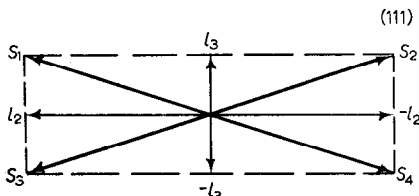


FIG. 7. Projections of the  $\text{Cr}_2\text{O}_3$  spins on  $(111)$ .

equal to zero so that no ferromagnetism arises here [more exactly  $s_1 = \frac{1}{4}(l_2 + l_3)$ ,  $s_2 = \frac{1}{4}(-l_2 + l_3)$ ,  $s_3 = \frac{1}{4}(l_2 - l_3)$ ,  $s_4 = -\frac{1}{4}(l_2 + l_3)$ ].

The magnetic properties of  $\text{Cr}_2\text{O}_3$  will not differ from those of usual antiferromagnetics and we shall not discuss them.

#### $\text{MnCO}_3$ , $\text{CoCO}_3$ , $\text{FeCO}_3$

In the isomorphous antiferromagnetic crystals  $\text{MnCO}_3$ ,  $\text{CoCO}_3$  and  $\text{FeCO}_3$  the weak ferromagnetism is exhibited by  $\text{MnCO}_3$  and  $\text{CoCO}_3$  but not by  $\text{FeCO}_3$  which is a pure antiferromagnetic.

Ferromagnetism of  $\text{MnCO}_3$  and  $\text{CoCO}_3$  was studied in detail by BOROVIK-ROMANOV and ORLOVA.<sup>(2)</sup> According to their measurements the spontaneous magnetic moment of  $\text{MnCO}_3$  is 0.2 per cent of the nominal value and that of  $\text{CoCO}_3$ , 2 per cent.  $\text{FeCO}_3$  was studied by BIZETTE<sup>(12)</sup> who found that in the antiferromagnetic state the spins

of the  $\text{Fe}^{2+}$  ions are directed along the  $[111]$  crystal axis.

The properties of these crystals can be explained if we assume that the antiferromagnetic transition occurs in them without a change of the unit cell.  $\text{MnCO}_3$ ,  $\text{CoCO}_3$  and  $\text{FeCO}_3$  belong to the rhombohedral system and their symmetry is given by the space group  $D_{3d}^6$ ,<sup>(6)</sup> i.e. by the same group as  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . The two metal ions in the unit cell lie on the volume diagonal of the rhombohedron at the points  $(1/4, 1/4, 1/4)$  and  $(3/4, 3/4, 3/4)$ .

As before we shall describe the magnetic structure in terms of the ion spins  $s_1$  and  $s_2$ . We shall introduce vectors  $m = s_1 + s_2$  and  $l = s_1 - s_2$ . It can be easily shown that under all the symmetry transformations  $m$  and  $l$  transform independently of one another,  $m_x$  and  $l_x$  transform according to unidimensional representations  $A_{2g}$  and  $A_{1g}$  of the point group  $D_{3d}$  and their  $x$ - and  $y$ -components according to one representation  $E_g$ , that is the vectors  $m$  and  $l$  here transform in the same way as the vectors  $m$  and  $l$  of  $\alpha\text{-Fe}_2\text{O}_3$ .

It follows therefore that the magnetic properties of the crystals considered in this section are identical with those of  $\alpha\text{-Fe}_2\text{O}_3$  and therefore all the results obtained earlier apply here.

In particular the fact that  $\text{FeCO}_3$  does not exhibit ferromagnetism is fully explained by the direction of the  $\text{Fe}^{2+}$  ions spins along the crystal axis (the I state).

From the occurrence of ferromagnetism in  $\text{MnCO}_3$  and  $\text{CoCO}_3$  we can conclude that they exist in the states (II or III) with their spins in the  $(111)$  plane.

All calculations of the magnetic properties of  $\alpha\text{-Fe}_2\text{O}_3$  are fully applicable for the ferromagnetic  $\text{MnCO}_3$  and  $\text{CoCO}_3$ .

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#### REFERENCES

1. NÉEL L. and PAUTHENET R. *C.R. Acad. Sci., Paris* **234**, 2172 (1952).
2. BOROVIK-ROMANOV A. S. and ORLOVA M. P. *Zh. Eksp. Teor. Fiz.* **31**, 579 (1956).

3. YIN-YUAN LI *Phys. Rev.* **101**, 1450 (1956).
4. LANDAU L. D. *Phys. Z. Sowjet.* **11**, 26, 545 (1937).
5. LANDAU L. D. and LIFSHITZ E. M. *Statistical Physics* (in Russian) Moscow (1951).
6. WYCKOFF R. W. G. *The Structure of Crystals*. New York (1931).
7. SHULL C. G., STRAUSSER W. A. and WOLLAN E. O. *Phys. Rev.* **83**, 333 (1951).
8. BROCKHOUSE B. N. *J. Chem. Phys.* **21**, 961 (1953).
9. TAVGER B. A. and ZAITSEV V. M. *Z. Exp. Theor. Phys.* **30**, 564 (1956).
10. *Internationale Tabellen zur Bestimmung von Kristallstrukturen* Vol. 1. (1935).
11. ROSENTHAL J. and MURPHY G. *Rev. Mod. Phys.* **8**, 317 (1936).
12. BIZETTE H. *J. Phys. Radium* No. **12**, 161 (1951).