NONLINEAR EFFECTS IN ANTIFERROMAGNETS. "LATENT" ANTIFERROMAGNETISM

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The field expansion of the magnetic moment of antiferromagnetic substances may contain quadratic (and in general even) terms with respect to H, $m = \chi H + bH^2 + cH^3 + \ldots$, in contrast with the expansion for paramagnetic substances which never has even powers. It is shown that, depending on the symmetry of the substance and on the type of antiferromagnetic transition, the forces responsible for the appearance of even powers may be of an exchange as well as of a relativistic nature. Some concrete examples are considered. The existence of ferromagnetic substances possessing a peculiar type of "latent" ferromagnetism is mentioned. In such substances the mean ionic magnetic moments differ with respect to their magnitude as well as to their direction, although, in distinction to ferrites, all magnetic ions in them are the same and are located at crystallographically equivalent positions. This "latent" antiferromagnetism changes the temperature dependence of the spontaneous moment near the ferromagnetic transition point.

1. INTRODUCTION

IT is known that for paramagnetic substances the expansion of the magnetic moment in the field H contains only odd powers of H: $m = \chi H + cH^3 + \ldots$. This is because the magnetic symmetry group of the paramagnet always contains the time reversal operator R, which changes the signs of the magnetic moments and fields. The situation changes for antiferromagnets. The magnetic symmetry group of an antiferromagnetic crystal may either not contain the element R at all or may have it only in combinations with other symmetry elements. Then, in general, the appearance of even powers of H is not forbidden, and we may write for m an expansion in the general form:

$$m_i = \chi_{ik}H_k + b_{ikl}H_kH_l + c_{iklm}H_kH_lH_m + \ldots . \quad (1)$$

Sirotin [1] has established the general form of the terms quadratic in H for all 122 magnetic point groups. Unfortunately, the formal analysis has nothing to say about the order of magnitude of the coefficients b nor about what kind of forces—exchange or relativistic—cause the appearance of the quadratic terms. The latter determines whether it is possible to observe nonlinear effects experimentally. In fact, if the quantities b are due to exchange, then they are of order $b \sim \chi/H_e$, where χ is the usual susceptibility and H_e is the so-called exchange field (according to existing experimental data $H_e \sim 5 \times 10^5$—10^6 Oe). The

quantities c are always of exchange nature and are of order $c \sim \chi/H_e^2$. Thus, in fields of 10^4 to 5×10^4 Oe the corrections associated with the quadratic terms amount to $H/H_e \sim 1$ to 10% and can be detected. Corrections from terms cubic in the field do not exceed 1% under these conditions and can be neglected.

Another situation arises when the quantities b are of relativistic nature. Then $b \sim \alpha\chi/H_e$, where α is the ratio of the relativistic energy to the exchange energy and usually does not exceed 10^{-2}. In this case, in fields of 5×10^4 to 10^5 Oe the corrections from the quadratic terms ($\sim \alpha H/H_e$) are surely less than 1%, and it is scarcely possible to observe them at the present time.

In Sec. 3 we shall show that among antiferromagnetic substances there is at least one, namely UO_2, in which the coefficient b is due to exchange forces. In the two other antiferromagnets known to the authors in which the expansion of m contains quadratic terms—$FeCO_3$ and the low temperature modification of α-Fe_2O_3—the coefficient b has a relativistic origin.

In this paper (Sec. 2) we also consider a phenomenon, in principle highly significant in ferromagnetic substances, which can be called "latent" antiferromagnetism. In such a ferromagnet the mean magnetic moments of the ions differ both in magnitude and in direction, although, in contrast to ferrites, the magnetic ions in it are

the same and are distributed among crystallographically equivalent positions. The presence of "latent" antiferromagnetism alters the temperature dependence of the spontaneous moment close to the ferromagnetic transition point. We shall consider "latent" antiferromagnetism in the example of a cubic face-centered crystal having the symmetry corresponding to close packing (space group O_h^5 [2]).

2. "LATENT" ANTIFERROMAGNETISM

We shall consider a cubic face-centered crystal the magnetic ions of which form a cubic face-centered lattice; the specific positions of the nonmagnetic ions is of no consequence to us (they should, however, not destroy the symmetry of the lattice formed by the magnetic ions, i.e., O_h^5). At some temperature T_C let there take place a transition from the paramagnetic state to a ferro- or antiferromagnetic state, during which the cubic face-centered Bravais lattice is converted to a simple cubic one with the same edge length (naturally, the volume of the unit cell is doubled). After such a transition, the crystal in the magnetic sense becomes a system of four interpenetrating simple cubic sublattices, each of which is formed by ions of the type (000), (0 $\frac{1}{2}$ $\frac{1}{2}$), ($\frac{1}{2}$ 0 $\frac{1}{2}$), and ($\frac{1}{2}$ $\frac{1}{2}$ 0), respectively.

The magnetic structure of the crystal is completely determined if the spins of the ions belonging to each sublattice are given. We shall symbolize the spins of the ions situated respectively on the sublattices of type (000), (0 $\frac{1}{2}$ $\frac{1}{2}$), ($\frac{1}{2}$ 0 $\frac{1}{2}$), and ($\frac{1}{2}$ $\frac{1}{2}$ 0) by s_1, s_2, s_3, and s_4.

Close to the transition point the spins s_i are small, and the thermodynamic potential Φ can be expanded as a power series in their components. The form of the expansion is determined from the condition of its invariance with respect to the symmetry group of the paramagnetic phase of the crystal, i.e., with respect to the crystallographic group O_h^5 plus the transformation of time reversal (transformation R).

The 12-dimensional representation based on the vectors s_i is reducible. To find the irreducible representations we introduce the vector m, equal to the sum $s_1 + s_2 + s_3 + s_4$, and three "vectors" l_1, l_2, l_3:

$$\begin{aligned}
m &= s_1 + s_2 + s_3 + s_4 & s_1 &= \tfrac{1}{4}(m + l_1 + l_2 + l_3), \\
l_1 &= s_1 + s_2 - s_3 - s_4 & s_2 &= \tfrac{1}{4}(m + l_1 - l_2 - l_3), \\
l_2 &= s_1 - s_2 + s_3 - s_4 & s_3 &= \tfrac{1}{4}(m - l_1 + l_2 - l_3), \\
l_3 &= s_1 - s_2 - s_3 + s_4 & s_4 &= \tfrac{1}{4}(m - l_1 - l_2 + l_3).
\end{aligned} \tag{2}$$

The vector m, which represents the total magnetic moment of a unit cell after the phase transition, transforms according to an irreducible representation. The 9-dimensional representation given by the three "vectors" l_i is reducible. It decomposes into two irreducible ones, a three dimensional one: l_{1x}, l_{2y}, l_{3z}, and a six-dimensional one: $l_{1y}, l_{1z}, l_{2x}, l_{2z}, l_{3x}, l_{3y}$.

The expansion of the thermodynamic potential Φ to terms of fourth order in m and l_i has the form

$$\begin{aligned}
\Phi &= \tfrac{1}{2}A\,(l_1^2 + l_2^2 + l_3^2) + \tfrac{1}{2}Bm^2 + \tfrac{1}{2}a\,(l_{1x}^2 + l_{2y}^2 + l_{3z}^2) \\
&\quad + \tfrac{1}{4}C\,(l_1^2 + l_2^2 + l_3^2)^2 + \tfrac{1}{4}D\,(l_1^4 + l_2^4 + l_3^4) + \tfrac{1}{2}E\,((l_1 l_2)^2 \\
&\quad + (l_1 l_3)^2 + (l_2 l_3)^2) + F\,((m l_1)\,(l_2 l_3) + (m l_2)\,(l_1 l_3) \\
&\quad + (m l_3)\,(l_1 l_2)) + \tfrac{1}{2}Gm^2\,(l_1^2 + l_2^2 + l_3^2) \\
&\quad + \tfrac{1}{2}I\,((m l_1)^2 + (m l_2)^2 + (m l_3)^2) + \tfrac{1}{4}Km^4. \tag{3}
\end{aligned}$$

Here we omit relativistic terms of the fourth order, which are not significant for what follows, while keeping a single relativistic invariant of the second order: $l_{1x}^2 + l_{2y}^2 + l_{3z}^2$.

In the paramagnetic phase the coefficients A and B are greater than zero, and l_i and m equal to zero correspond to a minimum in Φ. The transition to the antiferromagnetic or ferromagnetic state happens either at the point where A goes to zero (or A + a, a < 0) or where B vanishes. In the latter case, however, the substance will be an ordinary ferromagnet below the transition point with $m \neq 0$ and $l_i = 0$, and we shall not consider it further, assuming henceforth that B > 0.

At temperature $T = T_C$, where A vanishes (or A + a, if a < 0), the components of l_i first become non-zero. As always in the theory of second-order phase transitions at temperatures near T_C, the quantities $l_i \sim (T_C - T)^{1/2}$. Since the expansion (3) contains an invariant linear in m, a non-zero spontaneous moment m will arise, in general, simultaneously with the appearance of l_i. Obvious estimates show that thereby $m \sim l_i^3 \sim (T_C - T)^{3/2}$. Thus, we have to do here with an unusual ferromagnetic transition in which the dependence of m on temperature is different from the usual $m \sim (T_C - T)^{1/2}$. (Actually, owing to the presence in (3) of the relativistic term $a(l_{1x}^2 + l_{2y}^2 + l_{3z}^2)$ the situation is somewhat more complicated (see below).)

Close to the transition point, where $l_i \sim (T_C - T)^{1/2}$, $m \sim (T_C - T)^{3/2}$, the last three terms in (3) are small compared to Bm^2, so that for m we obtain the expression

$$m = -(F/B)\,\{l_1\,(l_2 l_3) + l_2\,(l_1 l_3) + l_3\,(l_1 l_2)\}. \tag{4}$$

On the other hand, since terms in (3) that contain

m are small in comparison with expressions that do not contain m, for the determination of the l_i it suffices to minimize the expression

$$\Phi' = \tfrac{1}{2}A(l_1^2 + l_2^2 + l_3^2) + \tfrac{1}{2}a\,(l_{1x}^2 + l_{2y}^2 + l_{3z}^2)$$
$$+ \tfrac{1}{4}C\,(l_1^2 + l_2^2 + l_3^2)^2 + \tfrac{1}{4}D\,(l_1^4 + l_2^4 + l_3^4)$$
$$+ \tfrac{1}{2}E\,\{(l_1 l_2)^2 + (l_1 l_3)^2 + (l_2 l_3)^2\}. \tag{5}$$

We shall begin with the case of temperatures not too close to the transition point, when we can neglect the second term in (5), which is due to relativistic interactions, in comparison with the first, an exchange term. Since $a \sim \varepsilon_0^2 v^2/T_C c^2$, where v is a velocity of the order of atomic velocities, c is the speed of light, and ε_0 is a quantity of the order of atomic energies, the corresponding temperature region is determined by the inequality $T_C - T \gg \varepsilon_0^2 v^2/T_C c^2$. On the other hand, we naturally assume that the condition $T_C - T \ll T_C$ is fulfilled: this is necessary for the validity of the expansion (5) in powers of the l_i. Since the magnitude of $\varepsilon_0^2 v^2/T_C^2 c^2$ does not as a rule exceed 0.01, there is a region where the inequality is fulfilled.

Depending on the ratio between D and E, there are three possible states that fit the minimum condition for Eq. (5) without the relativistic term:

I. $D > 0$, $E > 0$: $l_1 \perp l_2 \perp l_3$, $l_1^2 = l_2^2 = l_3^2$;

II. $D < 0$, $E > D$: $l_2 = l_3 = 0$, $l_1 \neq 0$;

III. $E < 0$, $E < D$: $l_1 = \pm l_2 = \pm l_3$.

The orientation of the vectors l_i relative to the crystallographic axes is determined by the relativistic terms in the expansion of Φ; in particular, for a < 0, by the term $\tfrac{1}{2}a(l_{1x}^2 + l_{2y}^2 + l_{3z}^2)$, so that in this case in state I, l_1 is directed along the x axis, l_2 along y, and l_3 along z; in states II and III all non-zero l_i are directed along one of the four-fold axes.

It can be seen at once from (4) that in states I and II the spontaneous moment is absent. In state III the spontaneous moment lies along the same four-fold axis, as does l_i, and has the modulus

$$m = L^3 |F|/B, \qquad L^2 = l_1^2 + l_2^2 + l_3^2. \tag{6}$$

Thus, for E < 0, E < D the crystal at these temperatures will be ferromagnetic with a spontaneous moment m that depends on temperature according to the law $\sim L^3 \sim (T_C - T)^{3/2}$, $m \ll L \sim (T_C - T)^{1/2}$. Upon further cooling, when T becomes of the order of T_C, Eq. (6) loses validity, and m is comparable to l_i in order of magnitude. The crystal is converted, consequently, to the usual ferromagnet (in the sense of the magnitude

of its spontaneous moment); however, the average spins of the ions in the magnetic unit cell, even though directed along one axis, will differ in absolute magnitude and in sign. In particular, when $l_1 = l_2 = l_3$ it follows from (2) that

$$s_1 = \tfrac{1}{4}(m + 3l_1), \qquad s_2 = s_3 = s_4 = \tfrac{1}{4}(m - l_1).$$

It is important at this point to emphasize that in contrast to ferrites, all the magnetic ions are the same and, in the paramagnetic state, are to be found in crystallographically equivalent positions.[1] Hence, to distinguish the phenomenon described from ferrimagnetism, it is convenient to call it "latent" antiferromagnetism. The unique temperature dependence of the spontaneous moment established above (see Fig. 1) can serve as the macroscopic distinction of the latter from pure ferromagnetism and the ferromagnetism of ferrites.
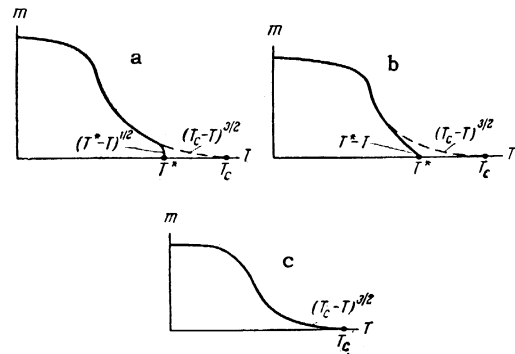

FIG. 1

At temperatures such that $T_C - T \lesssim \varepsilon_0^2 v^2/T_C c^2$, the contribution of the relativistic interactions becomes important. If a < 0 (and for simplicity we limit ourselves to this case only), the transition from the paramagnetic state occurs at the point where A + a vanishes. Below the transition point only l_{1x}, l_{2y}, l_{3z} will differ from zero, whereby either $l_{1x}^2 = l_{2y}^2 = l_{3z}^2 = L^2/3$ (state I), if D > 0, or $l_{2y} = l_{3z} = 0$, $l_{1x}^2 = L^2$ (state II), if D < 0. In both these states, the spontaneous moment is equal to zero, as can also be seen from Eq. (4). The transition to the ferromagnetic state (state III) takes place upon further lowering of the temperature by means of still another transition of the second kind (if, of course, the conditions E < 0, E < D are fulfilled). Without giving the calculations, we shall present the final results.

For D > 0 the transition to the ferromagnetic state occurs at the temperature T* at which the

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[1] Actually, in the ferromagnetic region there occurs a magnetostrictive deformation of the cubic cell along its body diagonal and the ions (000) and (½½0) ... become unequivalent.

quantity $EL^2 - a$ becomes zero. Since $L^2 \sim L_0^2(T_C - T)/T_C$, where L_0 is the value of L at $T = 0$, then $T^* - T_C \sim \varepsilon_0^2 v^2/T_C c^2$. The spontaneous magnetic moment that emerges at $T = T^*$, is equal in order of magnitude to

$$m \sim m_0 \frac{v^2}{c^2} \frac{\varepsilon_0^2}{T_c^2} \left(\frac{T^* - T}{T_c}\right)^{1/2}, \qquad (7)$$

where m_0 is the spontaneous moment at $T = 0$. Therefore, in this case the temperature dependence of the spontaneous moment in the immediate vicinity of T^* ($T^* - T \ll T^* - T_C \sim \varepsilon_0^2 v^2/T_C^2 c^2$) is just the same as in the usual ferromagnetic transition (see Fig. 1a). Unlike the latter, however, there is present the small coefficient $\varepsilon_0^2 v^2/T_C^2 c^2$ in Eq. (7). Upon further lowering of the temperature the dependence on T will follow the law obtained above, $m \sim (T_C - T)^{3/2}$ (for $T_C - T \gg \varepsilon_0^2 v^2/T_C c^2$).

For $D > 0$ the transition from the antiferromagnetic state (II) to the ferromagnetic takes place at the point T^* where the quantity $(E - D)L^2 - a$ vanishes. The temperature dependence of m for $T^* - T \ll \varepsilon_0^2 v^2/T_C c^2$ has the form (see Fig. 1b)

$$m \sim m_0 \frac{v}{c} \frac{\varepsilon_0}{T_c} \frac{T^* - T}{T_c}, \qquad (8)$$

which is different from the law $m \sim (T^* - T)^{1/2}$ in the case of ordinary ferromagnetic transitions. It is also characteristic that in Eq. (8) the small coefficient $(\varepsilon_0/T_C)v/c$ again shows up.

We note that the unusual situation in which the transition to the ferromagnetic state proceeds by means of two second-order phase transitions close together in temperature, in such a way that the substance first undergoes a transition to a pure antiferromagnetic state, is completely bound up with the structure of the relativistic terms in the thermodynamic potential. Hence we do not exclude the simpler possibility, when the substance makes a transition directly to the ferromagnetic state with "latent" antiferromagnetism. Then the dependence of m on the temperature will follow the law $m \sim (T_C - T)^{3/2}$ over the entire transition region (Fig. 1c).

3. NONLINEAR EFFECTS IN ANTIFERROMAGNETS

We shall first consider the antiferromagnets $FeCO_3$ and α-Fe_2O_3. They are crystallographically isomorphous and belong to the rhombohedral system. At low temperatures $FeCO_3$ and α-Fe_2O_3 are also isomorphous in the magnetic sense. Their class of magnetic symmetry consists of all the transformations of the usual point group D_{3d} and does not contain the transformation R at all (see [3]). To this magnetic symmetry belongs an expansion of the thermodynamic potential in powers of the field of the following form (the x axis is directed along one of the two-fold axes):

$$\widetilde{\Phi} = -\tfrac{1}{4}\chi_\parallel H_z^2 - \tfrac{1}{2}\chi_\perp(H_x^2 + H_y^2)$$
$$+ b[(H_x + iH_y)^3 + (H_x - iH_y)^3] + O(H^4). \qquad (9)$$

The structure of the cubic term in H in Eq. (9) obviously betrays its relativistic origin. Hence, in view of what was said in the introduction, we shall not dwell further on this case and proceed directly to a consideration of antiferromagnetic UO_2, for which the corresponding cubic term has exchange character.

Antiferromagnetic UO_2 is a face-centered cubic crystal with the symmetry of close packing (group O_h^5). The uranium ions occupy the points of the Bravais face-centered cubic lattice. Neutron diffraction experiments [4] have shown that the magnetic unit cell is a simple cube with the same edge length as the original cube of the crystallographic cell (i.e., the very same case we considered in the preceding section), and the spins of the ions of type (000), $(\tfrac{1}{2}\tfrac{1}{2}0)$, $(\tfrac{1}{2}0\tfrac{1}{2})$, and $(0\tfrac{1}{2}\tfrac{1}{2})$ are directed along the four different body diagonals of the cube. It is not difficult to show, using (2), that this structure coincides with the structure of state I for $a < 0$.

With the object in mind of obtaining formulas useful at all temperatures and not only near the temperature of the antiferromagnetic transition, we shall consider the absolute magnitudes and the mutual orientation of the vectors l_1, l_2, l_3 of the preceding section as given. We therefore introduce three unit vectors $\gamma_1, \gamma_2, \gamma_3$ in the directions respectively of l_1, l_2, l_3 and stipulate the condition $(\gamma_1 \cdot \gamma_2) = (\gamma_1 \cdot \gamma_3) = (\gamma_2 \cdot \gamma_3) = 0$. Of course, this limitation will be valid only under the condition that the magnetic energy is small in comparison with the exchange energy: $H \ll H_e$, where H_e is the exchange field mentioned in the Introduction.

We now write down the expansion of the thermodynamic potential in powers of the angles that the vectors γ_i make with the crystallographic axes and in powers of the magnetic field. It is easily shown, using the results of the preceding section, that taking into account the mutual perpendicularity of the vectors γ this expansion has the form

$$\widetilde{\Phi} = -\tfrac{1}{2}\chi H^2 - b(\gamma_1 H)(\gamma_2 H)(\gamma_3 H)$$
$$+ \tfrac{1}{2}a(\gamma_{1x}^2 + \gamma_{2y}^2 + \gamma_{3z}^2) + O\{H^4, \gamma^4\}. \qquad (10)$$

Here we retain the largest relativistic term $\gamma_{1x}^2 + \gamma_{2y}^2 + \gamma_{3z}^2$ and the single cubic exchange term. As has been mentioned in the introduction, the coefficient b is of the order of magnitude χ/H_e, where χ is the susceptibility.

We first consider the case of weak fields in which the cubic term is much smaller than the anisotropy energy, i.e., when $H^3 \ll aH_e/\chi$ or' $H \ll H_e(\varepsilon_0^2 v^2/T_c^2 c^2)^{1/3}$. In such fields only the components $\gamma_{1x}, \gamma_{2y}, \gamma_{3z}$ are non-zero ($a < 0$). Their sign for equilibrium magnetization will be determined from the minimum condition on $\tilde{\Phi}$, i.e., from the condition $b(\gamma_1 H)(\gamma_2 H)(\gamma_3 H) > 0$. Hence, the field dependent part of $\tilde{\Phi}$ can be written in the form

$$\tilde{\Phi}' = -\tfrac{1}{2}\chi H^2 - |b||H_x H_y H_z|,$$

whence

$$m_x = \chi H_x + |b||H_y H_z|\,\text{sign}\,H_x,$$

$$m_y = \chi H + |b||H_x H_z|\,\text{sign}\,H_y,$$

$$m_z = \chi H_z + |b||H_x H_y|\,\text{sign}\,H_z.$$

We shall not here discuss hysteresis phenomena, which are very complicated.

In considering the equilibrium magnetization of a polycrystal it is necessary to take into account that in each crystallite the signs of γ_{1x}, γ_{2y}, and γ_{3z} are always given by the equilibrium condition. Hence in averaging over the orientations of the crystallites, or what is the same thing, over the directions of the vectors γ_i, it is necessary to integrate only over the region where the products $\gamma_{1x}\gamma_{2y}\gamma_{3z}$ have a specific sign (it makes no difference which). Since $\gamma_1 \perp \gamma_2 \perp \gamma_3$ this averaging is equivalent to an average of Eq. (11) over the directions of H in the region where $H_x H_y H_z$ is positive. As a result we obtain

$$\tilde{\Phi}_{av} = -\frac{1}{2}\chi H^2 - H^3|b|/4\pi, \tag{12}$$

$$m = H(\chi + 3|b|H/4\pi).$$

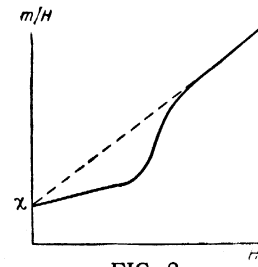We consider, finally, the case of strong fields,

FIG. 2

when $bH^3 \gg a$ or

$$H_e \gg H \gg H_e\,(\varepsilon_0^2 v^2/T_c^2 c^2)^{1/3}$$

and it is possible in general to neglect the anisotropy energy. Since $\gamma_1 \perp \gamma_2 \perp \gamma_3$, the problem of finding a minimum in $\tilde{\Phi}$ for given H is equivalent to determining the minimum of the expression $-bH_x H_y H_z$ for a given H^2. From this we find at once

$$\tilde{\Phi} = -\frac{1}{2}\chi H^2 - 3^{-3/2}|b|H^3,$$

$$m = H(\chi + 3^{1/2}|b|H). \tag{13}$$

Equations (13) are, to be sure, useful for both poly- and monocrystals. Comparing (12) and (13), we see that the curve of the dependence of m/H on field for a polycrystalline sample consists of two straight-line portions whose slopes are in the ratio $4\pi/3^{3/2} \approx 2.4$ (Fig. 2).

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