on the photoconductivity of Ge and Si. It follows directly from Eq. (46) that, within the framework of the theory presented here, we have succeeded qualitatively in eliminating the above discrepancy with experiment. We have also indicated what must be done for an accurate quantitative calculation. The question of competing mechanisms of recombination[18] will be investigated separately.

In conclusion I wish to express my gratitude to Iu. E. Perlin, M. F. Deigen and V. A. Moskalenko for discussions of the results of this work.

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291

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THE MAGNETIC STRUCTURE OF FLUORIDES OF THE TRANSITION METALS

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The method of Ref. 1 is applied to the problem of the magnetic structure of the antiferromagnetic crystals MnF_2, CoF_2, FeF_2, and NiF_2. It is shown that crystals with such symmetry may possess a weak ferromagnetism.

IN Ref. 1 the problem of the weak ferromagnetism of certain antiferromagnetic substances was treated on the basis of Landau's theory of phase transitions of the second kind. In the present work the same method is used to study the magnetic structure of MnF_2, CoF_2, FeF_2, and NiF_2.

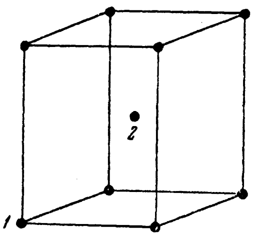


FIG. 1. Unit cell of MnF_2. Only the Mn^{++} ions are shown.

These crystals are isomorphic; they have a simple tetragonal lattice and the symmetry of space group D_{4h}^{14}.[2] In their unit cell there are two metallic ions in positions (000) and $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ (cf. Fig. 1; here only the metallic ions are represented). The magnetic structure of the substances under consideration was studied neutronographically by Erickson.[3] It was found that they are all antiferromagnetic; the spins of the ions located at the centers of the crystal cells are equal in magnitude, and opposite in sign, to the spins of the ions located at the lattice points. In the case of MnF_2, CoF_2, and FeF_2, the spins are directed along the crystal axis. In the case of NiF_2, the small intensity of the magnetic scattering by the nickel ions makes it impossible to determine with great certainty the direction of the spins; Erickson himself concluded that the picture that agrees best with the observed intensities is one in which the spins make an angle of about 10° with the crystal axis.

It follows from Erickson's work that the antiferromagnetic transition, in all four fluorides, occurs without change of the unit cell; therefore their magnetic structure is described by the mean magnitudes $\mathbf{s}_1$ and $\mathbf{s}_2$ of the spins of the two metallic ions located in the unit cell. As in Ref. 1, we expand the thermodynamic potential Φ of the crystal as a power series in the components of $\mathbf{s}_1$ and $\mathbf{s}_2$. For this purpose it is convenient to introduce the vector $\mathbf{m} = \mathbf{s}_1 + \mathbf{s}_2$, representing the magnetic moment of the unit cell, and $\boldsymbol{l} = \mathbf{s}_1 - \mathbf{s}_2$. It is easily verified that in all transformations of the symmetry group D_{4h}^{14}, the vectors $\mathbf{m}$ and $\boldsymbol{l}$ transform independently of each other. With a view to consideration of the behavior of a crystal over a wide temperature range, rather than specifically in the neighborhood of the transition, we shall write the expansion of Φ in powers of the magnetic moment $\mathbf{m}$ and of the unit vector $\boldsymbol{\gamma}$ in the direction of $\boldsymbol{l}$.

The thermodynamic potential consistent with the crystal symmetry, to terms of the fourth order, has the form

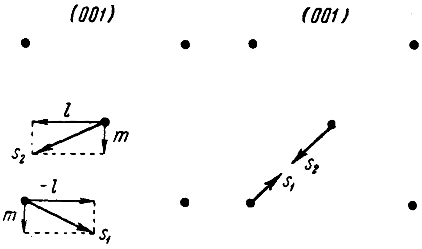
$$\Phi = \frac{a}{2}\gamma_z^2 + \frac{B}{2}\mathrm{m}^2 + \frac{b}{2}m_z^2 + e(\gamma_x m_y + \gamma_y m_x) + \frac{D}{2}(\mathrm{m}\gamma)^2 + 2d(\mathrm{m}\gamma)\gamma_x\gamma_y + \frac{f}{4}\gamma_z^4 + \frac{g}{2}\gamma_x^2\gamma_y^2.$$

The terms in $\mathbf{m}^2$ and $(\mathbf{m}\boldsymbol{\gamma})^2$ correspond to exchange interaction of the spins. The coefficients a, e, d stand in front of terms that represent relativistic interaction of the spins, and they are therefore proportional to the small quantity $(v/c)^2$, where v is the electron speed; the coefficients f and g are proportional to $(v/c)^4$. The presence of the term $\gamma_x m_y + \gamma_y m_x$ in the expansion of the thermodynamic potential leads, as in Ref. 1, to the result that the crystal in some states may possess a small spontaneous moment, of the order of $(v/c)^2$ times the nominal.

Crystals of the symmetry under consideration can exist in three magnetic states; one or another corresponds to a minimum of Φ, according to the relation among a', f, and g', where

$$a' = a + e^2/B, \quad g' = g + 2e^2D/B(B+D) + 2d^2/(B+D).$$

Namely, in the case in which $2a' + f < 0 < g'$ or $2a' + f < g' < 0$, the spins of the two metallic ions are equal and of opposite signs and are directed along the crystal axis (state I). Such an antiferromagnetic structure was observed by Erickson in MnF_2, CoF_2, and FeF_2. In the case $g' > 0$, $2a' + f > 0$ (state II_1), the spins of the two ions, in the first approximation, are compensated and are directed along the [100] (or [010]) axis of the tetragonal cell. In the next approximation, however, they are rotated toward one another about the crystal axis, remaining in the (001) plane, so that there results a spontaneous magnetic moment $m_0 = |e|/B\,(\sim(v/c)^2)$, directed along the [010] (or [100]) axis, i.e., perpendicular to the vector $\boldsymbol{\gamma}$ (Fig. 2a). Finally, in the case $g' < 0$, $2a' + f > g'$ (state II_2), the spins, in the first approximation, are likewise compensated, but are directed along one of the [110] axes. In the next approximation there arises a spontaneous moment $m_0 = |e + d|/(B + D)$, directed along the same [110] axis; that is, the spins of the metallic ions become unequal in magnitude without change of direction (Fig. 2b).



a b

FIG. 2. a—orientation of the spins in state II_1; b—orientation of the spins in state II_2.

All three antiferromagnetic states, I, II_1, and II_2, can originate directly by a phase transition of the second kind from the paramagnetic state. Transitions between them occur in the range where the coefficient a' is approaching zero. When a' becomes small $(\sim (v/c)^4)$ [in general $a' \sim (v/c)^2$], two additional states are possible, besides those already indicated. For $-f < a' < 0 < g'$ (state III_1), the vector γ lies in the (010) [or (100)] plane at a small angle θ to the crystal axis, with $\cos\theta = \sqrt{-a'/f}$; then there is a spontaneous magnetic moment $m_0 = |e|\sqrt{1 + a'/f}/B$, directed along [100] (or [010]). In state III_2 $(-f < a' < g' < 0)$, γ and m lie in one of the (110) planes; m in this case has a oomponent along the crystal axis. We shall not give the unwieldy formulas for θ and M_0 that apply to this case.

We now ask: between which of the states of the crystal mentioned above are phase transitions of the second kind possible? According to Landau's theory, a phase transition between two states can occur only if the symmetry group of the one state is a symmetry subgroup of the other. We write the symmetry elements that describe the magnetic symmetry classes of the various possible states of our crystal: *

I. $C_2,\ 2C_4R,\ 2U_2,\ 2U'_2R,\ I,\ \sigma_h,\ 2S_4R,\ 2\sigma_v,\ 2\sigma'_vR$
II_1. $C_2R,\ U_2R,\ U_2,\ I,\ \sigma_hR,\ \sigma_vR,\ \sigma_v$
II_2. $C_2R,\ U'_2R,\ U'_2,\ I,\ \sigma_hR,\ \sigma'_vR,\ \sigma'_v$
III_1. $U_2,\ I,\ \sigma_v$
III_2. $U'_2R,\ I,\ \sigma'_vR$.

It is easily seen that only the following transitions of the second kind are possible:

$$I \longleftrightarrow III_1,\ III_2;\quad II_1 \longleftrightarrow III_1;\ II_2 \longleftrightarrow III_2.$$

Furthermore, it can be shown that in the expansions of the thermodynamic potential that correspond to these transitions, third-order terms are absent, so that according to Landau's theory the indicated transitions are actually allowed.

States III_1 and III_2 are realized, as has already been pointed out, in a very narrow temperature range, where the coefficient a' is approaching zero; that is, in the ranges where transitions between states II_1 and I, or between states II_2 and I, occur. Let us consider, for example, how a continuous transition between states II_1 and I occurs. In state II_1 the spins of the two ions in the unit cell are arranged as is shown in Fig. 2a. At some temperature T'_c a transition occurs between states II_1 and III_1. With further change of temperature, the spins leave the (001) plane and begin to approach the crystal axis. The spontaneous magnetic moment thereupon decreases in magnitude, retaining the direction [100]. Finally, at some other temperature T''_c a continuous transition occurs from III_1 to I. At this point the spins of the ions lie along the direction of the crystal axis, and the spontaneous magnetic moment is equal to zero. Thus the transition between states II_1 and I occurs by two successive transitions of the second kind.

The measurements of Erickson, who found in the case of NiF_2 and angle of 10° between the spins and the axis, show that at T = 25°K the NiF_2 crystal is in one of the transitional states (III_1 or III_2). However, as was mentioned above, Erickson's experiment has too low precision. Measurements of Stout and Matarrese,[4] who observed a spontaneous magnetic moment in NiF_2, show that NiF_2 at this temperature cannot be in state I.

I express my thanks to E. M. Lifshitz for discussion of the work.

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292

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*Here C_2 denotes a vertical twofold axis, C_4 a vertical fourfold axis, U_2 a horizontal twofold axis directed along [100] or [010], U'_2 a twofold axis directed along [100] or [1$\bar{1}$0], S_4 a fourfold reflection-rotation axis, σ_v and σ'_v vertical symmetry planes perpendicular respectively to axes U_2 and U'_2, σ_h a horizontal plane, I the operation of inversion, and R the operation of change of sign of the spins.