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Magnetic "order-order" and "order-alien disorder" phase transitions

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For an isotropic magnetic material with non-Heisenberg exchange, the possibility is demonstrated of a new type of "order-disorder" phase transition, in which the short-range order above the transition point is of a different type from the long-range order below the transition point (an "order-alien disorder" phase transition). Thus the paramagnetic Curie temperature may be positive in an isotropic antiferromagnet and negative in a ferromagnet. The reason for this is the different temperature dependence of the Heisenberg and of the non-Heisenberg exchange, as a result of which the high-temperature properties may be determined by the former and the low-temperature properties by the latter. For the same reason, phase transitions of the "ferromagnet-antiferromagnet" type are possible; and such a purely magnetic mechanism of "order-order" phase transitions is in many cases much more realistic than the Kittel exchange inversion. In particular, this mechanism permits the occurrence of a whole series of phase transitions between commensurable collinear structures (from a two-sublattice antiferromagnet to a three-sublattice ferrimagnet to a four-sublattice antiferromagnet to a paramagnet), observed in EuSe. By analysis of the experimental data for EuSe it is shown also that the last of these transitions is of the "order-alien disorder" type. If a ferromagnetic state is possible, then three-spin exchange enhances the singularity of the susceptibility at T_C as compared with a Heisenberg magnet.

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INTRODUCTION

It is usually considered self-evident that upon heating, an isotropic antiferromagnet (AF) transforms to a paramagnetic (PM) state with a negative PM Curie temperature Θ, and a ferromagnet (FM) to a state with a positive Θ. The sign of Θ is the same as that of the binary spin correlators of neighboring atoms, which describe the short-range magnetic order. Therefore a negative sign means that after breakdown of the long-range AF order in the crystal, there remains in it short-range AF order; a positive Θ means that the short-range order is ferromagnetic. Similarly in other cases also in which we have to do with order-disorder phase transitions (PT), it is supposed that the short-range order above the transition point is of the same type as the long-range order below it.

One of the basic results of our paper is the demonstration of the existence of a new type of order-disorder phase transition, for which the short-range order above the transition point is of a different type from the long-range order below it. For example, if such a transition occurs in an isotropic antiferromagnet, its PM Curie temperature is not negative but positive1); if in a ferromagnet, then Θ is negative. Such order-strange disorder phase transitions are necessarily of first order, whereas PT with retention of the type of short-range order (order-ordinary disorder) may be either of first or of second order.

The question of the nature of the short-range order above the point where the long-range order disappears is very important, since many properties of crystals are determined not by the long- but by the short-range order. One example has already been given: the PM susceptibility of strong magnets. This includes also the electrical and optical properties. In particular, the position of the optical absorption edge in magnetic semiconductors and insulators depends very strongly on the short-range order; and this fact is used by us below, together with other experimental data, to establish the occurrence of FM short-range order after disappearance of long-range AF order in EuSe. Thus the paper presents not only a theoretical but also an experimental demonstration of the existence of an order-alien disorder phase transition.

The theoretical demonstration of the existence of an order-alien disorder PT is given for a model of a magnet with isotropic many-spin exchange.2) What has been investigated so far in the literature is the effect on an order-disorder phase transition of biquadratic exchange[2,3] $[\sim(S_1S_2)^2]$ and of four-spin exchange[4] $[\sim(S_1S_2)\times(S_3S_4)]$. In these papers it was established that addition of such terms to the Heisenberg Hamiltonian may produce a discontinuous phase transition from the FM state to the PM. But as will be clear from what follows, a Hamiltonian with biquadratic exchange[2,3] permits only an order-ordinary disorder PT. A four-spin Hamiltonian, for a certain choice of its parameters, allows one to obtain an order-alien disorder PT, but this possibility went unnoticed earlier.[4]

In the model used in the present paper, a fundamental role is played by competition of the Heisenberg exchange with the three-spin $[\sim(\mathbf{S}_1\mathbf{S}_2)(\mathbf{S}_2\mathbf{S}_3)]$, for which it is necessary that, for some reason or other, the Heisenberg exchange between neighbor atoms should be anomalously weak. Petrich and Kasuya[5] expressed the idea that three-spin exchange, like biquadratic, can transform a continuous order-disorder PT to a discontinuous; but the possibility of an order-alien disorder PT again remained unnoticed. In the present paper, a model is briefly discussed in which Heisenberg and four-spin exchanges are taken into account simultaneously (simultaneous allowance for three- and four-spin interactions raises no difficulties of principle, but the results obtained become unperspicuous). The physical reason for an order-alien disorder PT is the different temperature dependence of the Heisenberg and non-Heisenberg exchanges, as a result of which the high-temperature properties of the magnet may be determined by the first of these and the low-temperature by the second.

These same models allow us to justify a purely magnetic mechanism of phase transitions with change of the type of magnetic order, for example FM-AF. The possibility of a PT between a noncollinear antiferromagnetic structure and collinear structures, because of competition between Heisenberg and non-Heisenberg exchange interactions, was indicated earlier,[4,3] but no analogous investigation for collinear structures was carried out. Yet a purely magnetic mechanism, based on the above-mentioned difference in the temperature dependence of the Heisenberg and non-Heisenberg exchanges, is an important alternative to the generally accepted mechanism of FM-AF phase transition, in which the transition is caused by inversion of the sign of the Heisenberg exchange integral with thermal expansion of the lattice.[6]

For low-temperature PT, when the thermal expansion of the lattice is negligibly small, the purely magnetic mechanism is much more realistic than the Kittel exchange inversion. It may be responsible also for high-temperature PT. The purely magnetic mechanism enables us also to explain the whole series of PT between commensurable magnetic structures that is observed in certain crystals. In particular, we shall reproduce below the series of PT of the first kind between collinear structures that is observed in EuSe: two-sublattice AF-three-sublattice ferrimagnet-four-sublattice AF-PM. The last two magnetic structures, within the framework of the Heisenberg model used by Kittel,[6] would always be unstable.3)

The demonstration of the existence of PT of the order-order and order-alien disorder types is carried out at first for a simplified model, with use of the spin-wave approximation at low temperatures and of high-temperature expansion at high temperatures. The latter provides a possibility of simultaneously demonstrating that three-spin exchange can sharply enhance the singularity of the magnetic susceptibility of a FM at the critical point. Then for the same model, an analysis is carried out in the approximation of the self-consistent field (SCF), which leads to results that are qualitatively the same. This provides a basis for regarding with confidence the qualitative results obtained in the SCF approximation for a more complicated model, which enables us to reproduce the series of PT observed in EuSe. The adequacy of the SCF approximation is essentially due to the fact that the first-order phase transitions that we consider occur sufficiently far from the critical points.

I. GENERAL ANALYSIS

To simplify the treatment presented below, it is supposed that the magnet is made up of equivalent magnetic atoms with spin S, forming a simple cubic lattice. The Hamiltonian of the system is chosen in the form

$$\mathscr{H}=-\frac{I}{2}\Sigma\mathbf{S}_g\mathbf{S}_{g+\Delta}-\frac{R}{2}\Sigma(\mathbf{S}_g\mathbf{S}_{g+\Delta})^2 -\frac{K}{2}\sum_{\Delta'\neq\pm\Delta}(\mathbf{S}_g\mathbf{S}_{g+\Delta})[(\mathbf{S}_{g+\Delta}\mathbf{S}_{g+\Delta'})+(\mathbf{S}_g\mathbf{S}_{g+\Delta+\Delta'})]-H\Sigma S_g^z, \tag{1}$$

where $\mathbf{S}_g$ is the spin operator of atom g, and where the vector Δ enumerates the $z=6$ nearest neighbors of the atom.

The biquadratic term in (1) plays an auxiliary role: it must, in a case of necessity, stabilize collinear structures (AF or FM), for which it is necessary that $R>0$. The three-spin term in (1), besides the obvious requirement that all three atoms must be located as close as possible to one another, satisfies still another requirement, which for our purposes has a fundamental character: it, like the Heisenberg term, changes sign if FM order is replaced by staggered antiferromagnetic. Three-spin terms of the type $(\mathbf{S}_g\mathbf{S}_{g+\Delta})\times(\mathbf{S}_{g+\Delta}\mathbf{S}_{g+\Delta+\Delta'})$ that do not possess this property are not included in the Hamiltonian (1).

Because the Hamiltonian (1) contains no exchange between more distant neighbors, it permits only the two types of collinear structures mentioned above. In the case of the FM structure, the energy per atom E_F in the ground state and the magnon frequencies ω_q^F are given by the expressions

$$E_F=-{}^1/_2(J+\tilde{K})-\tilde{R}/2, \tag{2}$$

$$S\omega_q{}^F=(J+\tilde{K}+2\tilde{R})(1-\gamma_q)+\tilde{K}(1-\lambda_q), \tag{3}$$

where we have adopted the notation

$$J=IS^2z,\quad \tilde{K}=2z(z-2)KS^4,\quad \tilde{R}=zRS^4;$$

$$\gamma_q=z^{-1}\sum_{\Delta}e^{iq\Delta},\quad \lambda_q=[z(z-2)]^{-1}\sum_{\Delta_1\neq\pm\Delta}e^{iq(\Delta+\Delta_1)}.$$

For the staggered AF structure, the corresponding expressions have the form

$$E_A=(J+\tilde{K})/2-\tilde{R}/2, \tag{4}$$

$$S\omega_q^A=\{[-J-2\tilde{K}+\tilde{K}\lambda_q+2\tilde{R}]^2-[-J-\tilde{K}+2\tilde{R}]^2\gamma_q{}^2\}^{1/2}. \tag{5}$$

Having in mind later comparison with experiment, we shall investigate below the case in which the Heisenberg and three-spin exchanges in (2)–(5) have opposite signs, specifically $J>0$ and $\tilde{K}<0$, and the second is stronger than the first ($|\tilde{K}|>J$). With such relations between the parameters, the energy E_A of the AF state is below the energy E_F of the FM state, and the magnon frequencies are determined positively, independently of the value of $\tilde{R} > 0$.

On the other hand, by using the high-temperature expansions one can determine the character of the short-range order at high temperatures. On applying Kubo's formula for the static magnetic susceptibility χ, which expresses it in terms of spin correlators, we get in the limit of classically large spins for $R \to 0$

$$\frac{\chi}{\beta} = \sum_g \langle S_0^z S_g^z \rangle \approx \frac{S^2}{3}\Big\{1+\bar{\beta}\frac{1}{3}\left(1-\frac{k}{3}\right) + \bar{\beta}^2\left[\frac{5}{54}\left(1-\frac{k}{3}\right)^2 - \frac{1}{81}k + \frac{101}{19440}k^2\right]\Big\}, \tag{6}$$
$$\bar{\beta}=J\beta, \quad \beta=1/T, \quad k=3|\tilde{K}|/J,$$

where the first, second, and third terms in the wavy brackets are respectively (except for a factor $S^2/3$) the mean square projection of the spin of an atom, the correlator of the spins of nearest neighbors, and the correlator of the spins of second-nearest neighbors.

As follows from (6), even if the AF state is stable at $T=0$, at high temperatures the correlators for nearest neighbors may turn out to be positive; that is, the short-range order will be FM. The transition from AF long-range to FM short-range order is due to the fact that with rise of temperature, the intensity of the three-spin exchange becomes much weaker. One can explain the particular situation qualitatively thus: the effective exchange integral between atoms 1 and 2 in the presence of atom 3 is given by the sum of the Heisenberg and three-spin terms

$$\mathscr{H}_{12}=-I_{eff}\mathbf{S}_1\mathbf{S}_2, \quad I_{eff}=I+K\overline{(S_3^z)^2},$$

and the value of $\overline{(S_3^z)^2}$ decreases threefold with rise of temperature. The PM Curie temperature, defined as usual by the relation $\chi = 1/T + \Theta/T^2$, is according to (6)

$$\Theta = \lim_{T\to\infty} 2S^{-2}T\langle \mathbf{S}_0\mathbf{S}_\Delta\rangle = \frac{1}{3}J\left(1-\frac{k}{3}\right). \tag{7}$$

The condition under which the crystal is antiferromagnetic at $T=0$ but its PM Curie temperature at high temperatures is positive has the form

$$1<k<3. \tag{8}$$

In principle, a transition from AF long-range to FM short-range order may occur in two ways: 1) By a PT from an AF to a FM state, with a subsequent transition to the PM. This way is already known from Kittel's theory of exchange inversion.[6] 2) By a direct AF-PM phase transition. This possibility has not been noticed earlier.

In order to demonstrate the possibility in principle of a direct AF-PM phase transition with $\Theta > 0$, it is sufficient to estimate the Curie temperature T_C of the FM state and to establish that for certain relations between the parameters, it is low enough so that the free energy $F_A(T_C)$ of the AF state, which is close to E_A of (4), is substantially below the free energy F_F of the FM state, which in the interval from $T=0$ to $T=T_C$ varies from E_F to a value $\sim -T_C$. This is in fact the situation, according to (7), when k is close to 3. In fact, if a FM state existed at all for such k, then for $\Theta \to 0$ its Curie temperature, even if it were not equal to Θ, would also have to approach zero. Thus $F_A(T_C) \ll F_F$; that is, for $k \to 3$ the FM state in fact cannot be realized.

The results obtained above enable us to estimate the value k_C for which a direct AF-PM transition is replaced by a transition via an intermediate FM state. For this purpose, it is necessary to equate the free energies F_A of the antiferromagnet and F_F of the paramagnet at the Curie point T_C. The values of T_C and of $F_P(T_C)$ can be found by using the high-temperature expansions. At not too large k, the variation of T_C with k can be determined from the three-spin series (6). It contains the minimum number of terms necessary in order to find not only T_C but also the critical index γ in the relation $\chi \sim (\beta_C - \beta)^{-\gamma}$, which is valid near T_C. Both the ratio method and the method of Padé approximants lead in this case to the result

$$T_C(k)={}^2/_9Jf(k), \quad \gamma=\Theta/T_C, \quad f(k)=(181k^2-720k+720)/240(3-k). \tag{9}$$

This three-term approximation, at sufficiently small k, insures accuracy sufficient for our purposes: for a Heisenberg FM, the value $T_C^0 = \frac{2}{9}J$ differs by only 7% from the most accurate expression, obtained by Rushbrooke and Wood.[8] The inapplicability of (9) when $k \to 3$ is due to the fact that the second term in (6) becomes small in comparison with the third, whereas the method of high-temperature expansions requires the opposite relation between them.

As follows from (9), the Curie temperature decreases with increase of k faster than does Θ as defined by the expression (7); at $k=1.8$ it is only $0.03T_C^0$. Thus according to (9) and (5), the value of T_C at $T\sim 1-2$ is considerably smaller than the maximum value of $S\omega_q^A$. This provides a possibility of using the spin-wave approximation for calculation of $F_A(T_C)$:

$$F_A=E_A+TN^{-1}\sum_q \ln\{1-\exp(-\omega_q^A/T)\}, \tag{10}$$

where N is the number of elementary cells of the crystal.

For the free energy of the PM state we use the expression

$$F_P(T)=-T[\ln(2S+1)+{}^1/_{72}\beta^2J^2[(1-k/3)^2+{}^1/_{36}k^2]+O(\beta^4)]. \tag{11}$$

The complexity of the problem consists in the fact that the series for F_P in terms of β is asymptotic, and at $\beta=\beta_C$ there is no guarantee that its terms decrease with increase of the power of β. For example, when $k=0.4$ the second term in (11) is 70% of the first when $\beta=\beta_C$ of (9). Nevertheless one can obtain a sufficiently accurate estimate of k_C by using the fact that the first term in (11), in accordance with the variational principle for the free energy, overestimates the value of the latter. Representing the free energy in the form

$$F_P=-T\ln(2S+1)-J\delta, \quad \delta>0,$$

and equating it to the value (10) of F_A at $T=T_C$, we get for $S=\frac{7}{2}$

$$k_C=1.2+1.4\delta, \tag{12}$$

the variation of k_C with S is weakly logarithmic.

In accordance with the properties of asymptotic series, the value of $J\delta$ is of the order of the second term in (11); that is, when $k=0.4, \delta\sim 0.1$. Thus the uncertainty in the value of k_C amounts to ~10%, and its sign is known. The weak sensitivity of k_C to the value of F_P, which at first glance seems paradoxical, is due to the fact that k_C is really expanded with respect to δ not near $k=0$ but near $k=1$, the value of k beginning with which AF ordering is at all possible. It then turns out that for the actual order of magnitude of F_P, always $k_C - 1 \ll 1$. In any cases, it follows from the estimate (12) that the FM phase can be realized only within a small part of the interval (8) of k values. In the rest of it, a direct AF-PM transition must occur, with positive Θ.

The relation (10) and its analog for the FM state can be used directly to demonstrate the possibility of an AF-PM phase transition at small k. For this purpose we note that if $\tilde{R}$ is sufficiently large, then according to (3) and (5) not only AF but also FM magnons are stable (the FM state here corresponds to a relative minimum of the energy). This requires positiveness of the value of $W = J + 3\tilde{K} + 2\tilde{R}$, which is proportional to the reciprocal effective mass of the ferromagnetic magnons. The reason for a transition when $W \ll J$ is the extremely great softness of the FM magnons as compared with the antiferromagnetic; as a result of this, the free energy decreases with rise of temperature considerably faster for the FM than for the AF. As a result, by use of (2)–(5) and (10) we get for the AF-FM transition temperature, if it lies in the spin-wave range, the estimate

$$T_{AF} \sim [(W/S)^{3/2}|J+\tilde{K}|]^{5/2} \ll J/S. \qquad (13)$$

Actually, applicability of (13) requires satisfaction of very strict limitations on the system parameters; but in any case, this result has significance as an existence theorem: in fact, along with the Kittel exchange inversion,[6] there is possible a first-order AF-FM phase transition caused by the non-Heisenberg character of the exchange interaction. The subsequent transition from the FM to the PM state, according to (9), must be of second order.

From formula (9) there follows still another qualitative conclusion, concerning the critical exponent $\gamma = \Theta/T_C$ of ferromagnets with strong AF three-spin interaction, regardless of whether they have a ferromagnetic ($k < 1$) or antiferromagnetic ($k > 1$) ground state. Namely, three-spin exchange increases the critical exponent; for example, for $k = 1.2$ the value of γ is higher by a factor 2.2 than in a Heisenberg magnet. This effect is too significant to be attributed to inaccuracy of formula (9): for a Heisenberg magnet, that formula gives the value $\gamma = 1.5$, which differs by only 12% from the most accurate value obtained for this exponent.[8] Thus three-spin exchange sharply enhances the singularity of the magnetic susceptibility at the Curie point.

If one takes into account only Heisenberg and biquadratic exchange,[2,3] then Θ will be given by formula (7) with $k=0$. From the fact that Θ is independent of R, it follows that in this case the sign of Θ will always be the same as that of J; that is, the character of the short-range order in the PM range is always the same as that of the long-range order in the magnetically ordered range. But as regards the four-spin exchange, it can lead to a PT of the order-alien disorder type if, in its Hamiltonian, three spins belong to one sublattice and the fourth to the other [that is, if the Hamiltonian consists of terms of the type $(\mathbf{S}_{g-\Delta}\mathbf{S}_{g+\Delta})(\mathbf{S}_{g+\Delta}\mathbf{S}_{g+\Delta'})$ with $\Delta' \neq \Delta$]. If, in addition, the four-spin exchange is stronger than the Heisenberg, and if it has the opposite sign, then it is the one that determines the character of the magnetic order at $T=0$. But the character of the short-range order at high temperatures is determined by the Heisenberg exchange ($\Theta = J/3$); that is, in this case it is opposite to the character of the magnetic order at $T=0$.

II. THE SELF-CONSISTENT-FIELD APPROXIMATION

An investigation in the approximation of the SCF is conveniently begun with the model considered in the preceding section; for simplicity, we may set $R=0$ in the Hamiltonian (1). The non-Heisenberg structure of the Hamiltonian (1) leads to a necessity for introducing two SCF.[2,3] One of these, the dipole field d, acts on the projection of the spin; the other, quadratic in $q \sim k$, acts on the square of the projection of the spin. In the SCF approximation, the Hamiltonian (1) is represented in a form that is suitable for investigation either of noncollinear or of collinear structures

$$\mathcal{H} = \mathcal{H}_{\text{SCF}} + \mathcal{H}_1,$$

$$\mathcal{H}_{\text{SCF}} = -s^2(km^2 - {}^1/_2)N\cos 2\theta + (d\cos 2\theta - h\cos\theta)\sum_g x_g + {}^1/_2\, ks^2\cos 2\theta \sum_g x_g^2; \qquad (14)$$

$$s = \overline{|S_g^z|}/S, \quad m^2 = \overline{(S_g^z)^2}/S^2, \quad k = 2(z-2)|K|S^2/I,$$
$$d = s(km^2-1), \quad x_g = S_g^z/S, \quad h = H/zIS^2,$$

where S is the value of the spin of a magnetic atom, and where the bar indicates a temperature average with the Hamiltonian (14). All energies are measured in units of zIS^2. For the z_g axis of atom g, we choose the direction of the moment of the sublattice to which this atom belongs; the y axis is common to all atoms. In the presence of an external field, each of the sublattice moments makes an angle θ with it.

The free energy F_{SCF} corresponding to the Hamiltonian $\mathcal{H}_{\text{SCF}}$ is (per atom)

$$F_{\text{SCF}} = -s^2(km^2 - {}^1/_2)\cos 2\theta - \tau \ln Z, \qquad (15)$$

$$Z = \sum_x \exp\left(-\frac{H_0}{\tau}\right), \quad \tau = \frac{T}{zIS^2},$$
$$H_0 = (d\cos 2\theta - h\cos\theta)x + {}^1/_2 ks^2\cos 2\theta x^2. \qquad (16)$$

Here T is the temperature, $x = \{(-S+n)/S\}$, $n = 1, 2, \ldots, 2S$; the reckoning is from the free energy of the PM state at $h=0$, $-\tau\ln(2S+1)$. The average of the Hamiltonian $\mathcal{H}_1$ calculated by means of the Hamiltonian $\mathcal{H}_{\text{SCF}}$ is zero, so that the value of F_{SCF} can be used directly as an estimate of the free energy F corresponding to the Hamiltonian $\mathcal{H}$.

The stationary values of the variational parameters s, m^2, and θ are found from the condition that the free energy F_{SCF} shall be an extremum with respect to them; this gives

$$s=\sum_{x} x \exp\left[-\frac{H_0(s,m^2,\theta)}{\tau}\right] \Big/ Z(s,m^2,\theta), \tag{17}$$

$$m^2=\sum_{x} x^2 \exp\left[-\frac{H_0(s,m^2,\theta)}{\tau}\right] \Big/ Z(s,m^2,\theta), \tag{18}$$

$$\sin\theta\,(2d\cos\theta-h)=0. \tag{19}$$

As follows from (15), at $T=0$ and $h=0$ the AF ordering is more advantageous than the FM if $k>1$. But with increase of temperature, m^2 drops, and when $k<3$ the dipole field $s(km^2-1)$ above a certain temperature T^* becomes negative, which means absolute instability of the AF state. Thus it must be replaced by the FM or PM state. It is easy to see that in any case the PT must be of first order and must occur below T^*. In fact, if it were of second order, then the field d would have to remain positive at all s; and this is impossible, since m^2 approaches $\frac{1}{3}$ as $s\to 0$ (here and below, we neglect terms $1/2S$ in qualitative discussions, but not in numerical calculation).

A ferromagnetic state is possible if the value of k is not too close to 3, since for stability of it the difference $1-km^2$ must substantially exceed τ as $\tau\to\tau^*=T^*/zIS^2$. The value of m^2, which is less than in the AF phase, must nevertheless in the FM state be significantly larger than its value in the PM state, namely $\frac{1}{3}$. Analysis of Eqs. (17) and (18) shows that the transition from the FM to the PM state must be a PT of second order. This follows from the fact that in the vicinity of the Curie point, the expression for which coincides with (7), the magnetization, on approach of τ to τ_C from the low-temperature side, decreases continuously. In fact,

$$s^2=\frac{15(3-k)}{9+18k-13k^2}(\tau_C-\tau), \tag{20}$$

and the coefficient on the right side of (20) is positive when $1<k<3$ [if it were negative, then the $s(\tau)$ curve at small s would correspond to nonphysical states, for which the free energy was not a minimum but a maximum, and therefore the system would transform discontinuously from a state with finite s to a state with $s=0$, bypassing the states with small s].

Obviously τ_C is higher, the smaller k. If T^* is less than T_C, then on rise of temperature, beginning with $T=0$, there must necessarily occur first an AF-FM transition of first order, and then a FM-PM transition of second order. In fact, the point of transition T_A from the AF state must be below T^* and therefore also below T_C. But below T_C, the FM state is thermodynically more advantageous then the PM. But if T^* exceeds T_C, then, depending on whether the transition point T_A is below or above T_C, there occurs a transition either first to a FM state, or directly to a PM state with FM short-range order (when $T_A>T_C$, ferromagnetic ordering is, so to speak, jumped through).

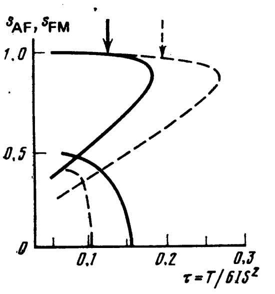

FIG. 1. Results of numerical solution of Eqs. (17) and (18) for the values $k=1.5$ (solid lines) and $k=1.8$ (dotted lines). The upper of the two lines for the same k corresponds to the AF and the lower to the FM state. To the right of the arrow, the AF state is unstable with respect to the PM.

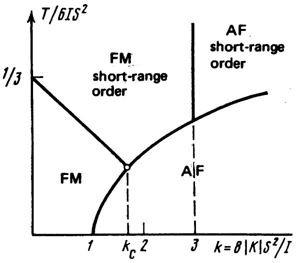

FIG. 2. Qualitative phase diagram in the (T, k) plane for a non-Heisenberg magnet. The circle marks the triple point $\tau_f=\tau_C$; k_C is the value of k corresponding to it.

The results of a numerical solution of equations (17) and (18) for $h=0$ substantiate this qualitative treatment. Figure 1 shows the results of numerical calculations for the cases $k=1.5$ (solid lines) and $k=1.8$ (dotted lines) when $S=7/2$. The upper of the two lines corresponding to a given value of k shows the temperature dependence of the AF order parameter s_{AF}, the lower of the FM order parameter s_{FM}. The free energy F_F of FM ordering is negative at all temperatures $\tau<\tau_C$, whereas the free energy F_A of AF ordering is negative only on the part of the $s_{AF}(\tau)$ curve that lies to the left of the arrow. To the right of the arrow, the AF state is known to be unstable (at the temperature τ_P corresponding to the arrow, the free energies of the AF and PM states become equal). When $k=1.5$ ($\tau_P=0.123<\tau_C$), there first occurs an AF–FM phase transition of first order at $\tau_f=0.12$; then there follows, at $\tau_C=0.153$, a PT of second order to the PM state.

But when $k=1.8$ ($\tau_P=0.198>\tau_C=0.1$), the region of stability of the FM state is absent, and there occurs a PT of first order from the AF state directly to the PM. In the interval between 1.5 and 1.8 there lies a

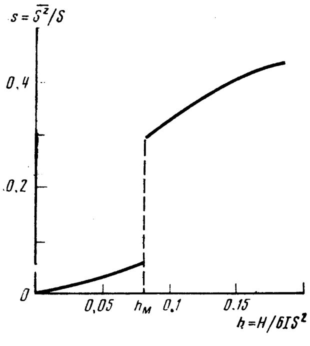

FIG. 3. Metamagnetic phase transition in a non-Heisenberg isotropic magnet (numerical calculation for $k=1.8$ and $\tau=0.19$).

value k_C corresponding to a triple point, $\tau_f = \tau_C$. This estimate agrees with (12), although somewhat above it. In order to show that the PM state is characterized by FM short-range order even for $k > k_C$, when a transition occurs from the AF state directly to the PM, it is sufficient to calculate the PM Curie temperature Θ.

$$\mathcal{H} = -I\sum_{gn} \mathbf{S}_{gn}\mathbf{S}_{g+1,n} - P\sum_{gn\delta} \mathbf{S}_{gn}\mathbf{S}_{gn+\delta} - V\sum_{gn} \mathbf{S}_{gn}\mathbf{S}_{g+2,n} - R\sum_{gn} (\mathbf{S}_{gn}\mathbf{S}_{g+1,n})^2 - K\sum_{gn\delta} [(\mathbf{S}_{gn}\mathbf{S}_{gn+\delta})(\mathbf{S}_{gn+\delta}\mathbf{S}_{g+1,n}) + (\mathbf{S}_{g+1,n}\mathbf{S}_{g+1,n+\delta})(\mathbf{S}_{g+1,n+\delta}\mathbf{S}_{gn})], \tag{21}$$

For Θ one gets an expression coinciding with (7), which is positive when $k < 3$. When $k > 3$, a PT of first order occurs from AF to PM with antiferromagnetic short-range order. Summarizing the results obtained, we can draw a qualitative phase diagram in the (T, k) plane (Fig. 2).

Materials that reveal a PT of first order between AF long-range order and FM short-range order possess still another interesting property: they are isotropic metamagnets. This is indicated by the results of a numerical calculation for the same value $k = 1.8$ as before, at temperature $\tau = 0.19$, which lies below the transition point τ_P (Fig. 3). Up to field $h_M = 0.082$, the magnetization increases continuously with the field because of decrease of the angle 2θ between the moments of the sublattices. But at field h_M there occurs a discontinuous PT from two-sublattice to one-sublattice ordering. Here the magntization increases by about five times.

The model described by the Hamiltonian (1) can be generalized to describe a series of PT between structures with commensurable periods. It is supposed that the magnet can be divided into planes within which the exchange between nearest neighbors (its integral P has a normal value). Only the integral I of Heisenberg exchange between nearest neighbors from neighboring planes is anomalously small; it is therefore necessary to allow also for Heisenberg exchange between atoms from the planes second in distance (its integral is V) and for three-spin exchange, when two spins are nearest neighbors from the same plane but the third belongs to a neighboring plane (its integral is K). Finally, as in (1), we introduce biquadratic exchange between nearest neighbors from neighboring planes, where g is the number of the plane, n is the number of the atom in plane g, and δ enumerates the z_l nearest neighbors to the atom (g, n) from the same plane.

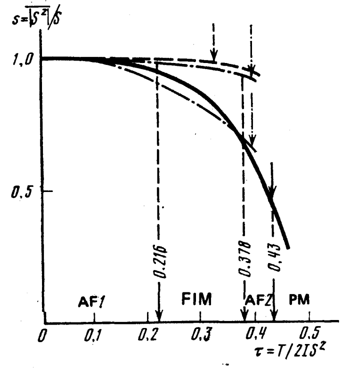

FIG. 4. Results of numerical solution of the SCF equations for the Hamiltonian (21), for the values $k = 2.1$, $v = 0.5$, $p = 0.5$, $r = 0.5$. To the right of the arrow on a curve, the corresponding state is unstable with respect to the paramagnetic (solid curve, state AF2; dotted, AF1; dotted-dashed, FIM).

The various collinear structures that are alone permitted in this model differ in the orientation of the moments of the FM planes. The parameters of (21) are so chosen that the thermodynamically most advantageous structures will be the following: two Heisenberg ferromagnetic (FM) and two-sublattice AF with orientation of the moments of neighboring layers of the type ↑↓ (AF1), and two non-Heisenberg–three-sublattice ferrimagnetic of the type ↑↑↓ (FIM) and four-sublattice AF of the type ↑↑↓↓ (AF2) (all structures collinear). For this purpose, we choose the following signs of the exchange integrals in (21): $I > 0, V < 0, K < 0$.

Depending on the values of the parameters $k = 2z_l|K|S^2/I$ and $v = |V|/I$, any one of the structures AF1, AF2, and FM may prove energywise most advantageous at $T = 0$. In particular, the AF1 state is the ground state when $k > 2v + 1$. The FIM state cannot be the ground state: when $k \neq 2v + 1$, its energy exceeds the energy of at least one of the other states (when $k = 2v + 1$, the energies of the AF1, AF2, and FIM states coincide). The parameter r must be subject to a restriction that insures instability of helicoidal structures when $T = 0$:

$$r > 2v - \tfrac{1}{2}(k-1), \quad r = RS^2/I. \tag{22}$$

Since with rise of temperature the biquadratic exchange decreases to a lesser degree than do the other terms in (21), the inequality (22) insures such instability also at arbitrary temperatures.

Numerical calculations are carried out quite similarly to those made at the beginning of this section. Their results are that the system under consideration possesses a whole series of PT of first order. Thus for $v = 0.5$, $p = 0.5$, $r = 0.5$, and $k = 2.1$ the following sequence of PT of first order is obtained (Fig. 4): at $\tau = 0.216$ a transition AF1-FIM, at $\tau = 0.378$ a transition FIM-AF2, at $\tau = 0.43$ a transition to the PM state. The first two transitions are transitions of the order-order type and occur by the mechanism described in detail in §1. The transition AF2-PM is a transition of the order-alien disorder type. In order to determine the character of the short-range order, it is here necessary only to calculate the correlations of the type $\langle \mathbf{S}_{0n}\mathbf{S}_{1n}\rangle$, since the correlators in the FM plane are known to be positive. We get

$$\langle \mathbf{S}_{0n}\mathbf{S}_{1n}\rangle = S^2\left(1 - \frac{k}{3}\right)\Big/3\tau. \tag{23}$$

Thus the correlator is positive, and the short-range order in the orientation of the spins of neighboring planes is ferromagnetic, if $k < 3$. With other values of the parameters v, p, r, and k one can get other series of PT. Thus for $v = 0.1$, $p = 0.5$, $r = 0$, and $k = 1.3$, we get the following chain of PT of the first kind: AF1-FIM at $\tau = 0.201$, FIM-AF2 at $\tau = 0.205$, AF2-FM at $\tau = 0.2055$. At $\tau = 0.35$ there occurs a PT of second order to the PM state. We note also that similar series of PT can be obtained also for anisotropic crystals, if in the Hamiltonian (21) one introduces, instead of the biquadratic terms, anisotropic ones of the type $(S_g^z)^2$ etc.

III. COMPARISON WITH EXPERIMENT

Series of phase transitions. The best possibility for comparison of the theory developed above with experiment is provided by the isotropic magnet EuSe, which is customarily numbered among the magnetic semiconductors, though undoped EuSe behaves as an insulator. EuSe belongs to the family of monochalcogenides of Eu, all members of which have the NaCl structure. In this family, with increase of the lattice constant there occurs a transition from FM ordering in EuO ($T_C = 67$ K) and EuS ($T_C = 16.3$ K) to AF ordering in EuSe ($T_N = 4.6$ K) and EuTe ($T_N = 9.6$ K). (These data and those given below are collected in a book of one of the authors.[9]) In all these crystals, the magnetic anisotropy is extremely small: in EuSe it is only 100 Oe.

One is struck by the anomalously low ordering temperature in EuSe as compared with the other members of the family. This attests to the weakness of the Heisenberg exchange in EuSe. Taking into account the similarity of properties of the chalcogenides, one can explain the anomalous weakness of the exchange in EuSe by the fact that in EuSe the lattice constant a is close to the value a_0 at which the exchange integral I between neighboring Eu^{++} ions vanishes. How strongly I depends on a in EuSe is indicated by the fact that a pressure of 1 kbar lowers T_N in EuSe by a whole degree.

It is natural to expect that the vanishing of $I(a)$ at the point a_0 is not accompanied by vanishing of the other exchange parameters. Therefore the non-Heisenberg exchange in chalcogenides of Eu should be compared with the Heisenberg at a sufficiently far from a_0. As an estimate of the strength of the latter may be taken T_C in EuO, close to 70 K. If the non-Heisenberg exchange is an order of magnitude weaker than the Heisenberg, then in EuSe it should amount to a few degrees; that is, it is fully able to compete with the Heisenberg. An additional fact that promotes heightening of the role of non-Heisenberg terms in EuSe may be the fact that the forbidden band E_g in it is narrow as compared with classical AF insulators of the type NiO etc.: it is only 1.7 eV. It follows from the Rowland-Bloembergen theory of superexchange that the relative contribution of non-Heisenberg terms is larger, the smaller the forbidden band. In magnetic insulators the non-Heisenberg terms usually amount to 5% of the Heisenberg.

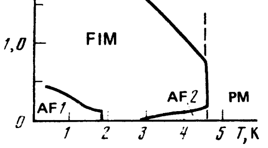

FIG. 5. Experimental phase diagram of EuSe.[9]

While EuO and EuS behave like ideal Heisenberg FM and EuTe like an almost ideal Heisenberg AF, with a magnetic structure of the MnO type, the magnetic properties of EuSe turn out to be incomparably more complicated (Fig. 5). In it, various magnetic structures occur, possessing the common feature that in all of them the spins of atoms belonging to the same (111) plane are parallel to one another, so that these structures differ with respect to the mutual orientation of the moments of the (111) planes. At $T \to 0$, two-sublattice ordering of the MnO type occurs in EuSe, with orientation of the moments of successive planes of the type ↑↓ (AF1). With rise of temperature, there occurs in EuSe a series of PT of first order: AF1 transforms at 1.8 K to a three-sublattice "ferrimagnetic" state of the type ↑↑↓ (a FM phase with admixture of the phase AF1). At 2.8 K there occurs a transition to a four-sublattice state AF2 of the type ↑↑↓↓. Finally, at 4.6 K this state transforms discontinuously to the PM. At fixed temperature, a EuSe crystal in a magnetic field behaves as a metamagnet: with increase of field, both AF1 and AF2 transform first discontinuously to a ferrimagnetic state, and then again discontinuously to a ferromagnetic state.

The model described in §2, for a certain choice of its parameters, reproduces the whole series of PT observed in EuSe. To facilitate the treatment, this model has been somewhat simplified as compared with EuSe: the presence of FM layers in it is caused not by geometric causes but by the character of the exchange interaction within these layers. But it is natural to suppose that the phenomena discussed should not be connected with details of the geometry of the lattice. An indication of this is the fact that the same PT (for example, AF-FM) can be obtained both in the layered-magnet model (§2) and in the isotropic-magnet model (§1). (Leaving aside the question of the reliability of the results of von Boehm and Bak,[10] we note that in their model[10] the FIM structure was found to be unstable.)

The metamagnetic properties of an isotropic non-Heisenberg magnet have also been established on the simplified, in comparison with EuSe, model of §1. Because of the nearest-neighbor approximation used in §1, instead of two successive metamagnetic transitions AF-FIM and FIM-FM a single transition AF-FM was obtained. It may nevertheless be considered that the mechanism treated qualitatively in this paper is suitable for explanation of the metamagnetic properties of EuSe.

Series of PT are observed also in crystals of the type of CeSb, with strong anisotropy; but the structures that occur there are in general more complex than in EuSe. Some of the non-Heisenberg structures, however, for example the three-sublattice FIM, are encountered also in CeSb.[11]

Phase transition between antiferromagnet and paramagnet with ferromagnetic short-range order. Comparison of the experimental data of various authors attests also to the existence in EuSe of the order-alien disorder PT obtained on different models in §§1 and 2. According to Petrich and Kasuya,[5] in EuSe, in contrast to the other Eu chalcogenides, the AF long-range order disappears discontinuously. In the paramagnetic state, Θ is positive in EuSe ($\Theta = 9$ K);[12,13] this indicates FM short-range order. To avoid misunderstanding, we emphasize that in contrast to the anisotropic model of §2, EuSe, despite the presence of FM layers, is an isotropic magnet, and therefore the nature of the short-range order in it can be judged from the sign of Θ. In any Heisenberg AF with ordering of the MnO type, there are FM (111) layers, but their existence is caused by purely geometric factors, since the exchange within layers and between layers is the same for them. Therefore Θ is negative in all of them; an example is EuTe with $\Theta = -6$ K.

Petrich and Kasuya[5] suggested that the positive Θ in EuSe is due to donor defects in whose vicinity FM ordering appears (localized ferrons[9]). Bearing this possibility in mind, we will present additional evidence in favor of the idea that FM short-range order in the PM range is a property of a regular EuSe crystal. First, spectra of the Mössbauer effect show that above the AF-PM transition point, FM short-range order appears.[5] If it were due to localized ferrons, as was supposed by Petrich and Kasuya,[5] it would exist also at all temperatures below T_N.

Second, in the PM range there is observed, on lowering of the temperature, a very strong red shift of the optical absorption edge E_a, which disappears below T_N.[13] 4) A giant red shift of E_a is typical for FM semiconductors: in them it occurs both above and below T_C and is caused by the establishment of FM order, first short-range and then also long-range.[9] At the same time, in isotropic AF semiconductors the red shift is absent both above and below T_N. On the contrary, they display a slight blue shift. In particular, there is no red shift in EuTe, whereas in EuO and EuS it is very strong. The idea that the red shift in EuSe above T_N is due to FM short-range order is supported also by the following fact: a magnetic field, which establishes FM order, intensifies the red shift.[13]

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1) To avoid misunderstanding, it must be emphasized that this effect has nothing in common with positiveness of Θ in layered AF with strong ferromagnetic exchange within the layers. The sign of Θ in them reflects the short-range FM order within the layers. It is of the same type as was the long-range order within the layers below the Néel point.

2) Some of the results of the present paper were presented earlier.[1]

3) In contrast to the paper of Dzyaloshinskiĭ and Kukharenko,[7] where the effect of three-spin exchange on the magnetic structure and on the magnon spectrum was first taken into account, we treat only collinear many-sublattice structures.

4) The variation of E_a with T is shown in Fig. 4.2 of the book by one of the authors.[9] Unfortunately, in Ref. 9 the plot of E_a for T below T_N and for $H = 0$ is inaccurately reproduced: the corresponding sections of the curve in the original[13] are actually practically horizontal.

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