

# Anomalous magnetic structures and phase transitions in non-Heisenberg magnetic materials

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This review is primarily devoted to a discussion of isotropic magnetic materials with localized magnetic moments between which the exchange interaction is more complex than in the usual Heisenberg model. They include insulators for which the biquadratic or multispin exchange mechanisms are comparable with the bilinear exchange, conductors which do not satisfy the conditions of validity of the RKKY indirect exchange theory, and the nuclear magnetic material solid helium. Additionally, an analysis is made of high-anisotropy magnetic materials behaving similarly to isotropic non-Heisenberg materials. These anisotropic materials have anomalous properties, compared with the Heisenberg case. Experimental data on these materials and their theoretical interpretation are given. The following topics are discussed: 1) the conditions for a strong non-Heisenberg exchange and non-Heisenberg Hamiltonians; 2) quadrupole ordering and order-proper disorder phase transitions; 3) order-order and order-improper disorder phase transitions; 4) metamagnetism of isotropic materials; 5) normal sequences and "devil's ladders" of phase transitions between commensurate structures; 6) canted antiferromagnetism of high-symmetry crystals which do not obey the condition for the existence of relativistic Dzyaloshinskii-type interactions.

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## INTRODUCTION

This review is devoted mainly to isotropic magnetic materials with localized magnetic moments between which the exchange interaction is more complex than in the usual Heisenberg model. Consequently, the magnetic properties of such materials differ strongly from those expected in the Heisenberg case. They can frequently be described by models in which the biquadratic, three- or four-spin exchange mechanisms are allowed for in addition to the Heisenberg bilinear exchange. However, in the case of conducting non-Heisenberg magnetic materials it is possible to interpret some of their properties without invoking these models.

We shall consider the theory of non-Heisenberg isotropic magnetic materials and analyze in detail the experimental data on some substances which are described satisfactorily by this theory. They include insulators (EuSe, MnO, UO<sub>2</sub>, etc.), metals (GdMg, etc.), and a nuclear magnetic material (solid <sup>3</sup>He). Moreover, a description will be given of such magnetic materials which exhibit a strong magnetic anisotropy but

have properties similar to those of isotropic non-Heisenberg materials, so that one can postulate similar origin of these properties (for example, the behavior of CeSb resembles that of EuSe). For reasons of space we shall consider only some of the anomalous properties of non-Heisenberg magnetic materials which have either been ignored completely by the existing monographs and reviews on magnetism or for which obsolete results have been reported. We shall not deal at all with certain important topics, such as, for example, helical ordering and the problem of phase transitions between commensurate and incommensurate structures.

In speaking of the anomalous properties we must begin by mentioning that in the case of magnetic materials with a very weak magnetic anisotropy and a very simple crystal structure one sometimes encounters complex magnetic structures that do not fit the Heisenberg model. For example, the compound EuSe has the NaCl structure and it exhibits not only the usual two-sublattice ordering, but also collinear four-sublattice antiferromagnetic and three-sublattice ferrimagnetic structures. A similar four-sublattice antiferromag-

netic structure occurs in He (Sec. 4). There are strong arguments for assuming that in the case of  $\text{UO}_2$  the structure is again four-sublattice antiferromagnetic, but the moments of alternate sublattices are oriented at right-angles to one another (Sec. 5).

Reliable experimental data are now available on the existence of a canted antiferromagnetic structure in some intermetallic alloys. Usually the canted (two-sublattice) structures with noncollinear sublattice moments are explained by the nonrelativistic Dzyaloshinskii-Moria interaction, which can occur in crystals with a special symmetry. However, such crystals as  $\text{GdMg}$  with the  $\text{CsCl}$  structure do not have the symmetry necessary for the Dzyaloshinskii-Moria interaction. Nevertheless, the canted antiferromagnetic structure of high-symmetry materials can be explained fully within the framework of the model of an isotropic non-Heisenberg magnetic material as due to competition between the isotropic Heisenberg and non-Heisenberg exchange interactions (Sec. 5).

The model with the biquadratic and bilinear exchange mechanisms predicts the existence of a specific one-sublattice phase which does not exhibit a spontaneous magnetization (quantum quadrupole case, see Sec. 2). However, this phase has not yet been detected experimentally and even its theory is still incomplete.

Order-disorder and order-order phase transitions in non-Heisenberg magnetic materials are also very special. Some time ago attention has been drawn to the fact that the non-Heisenberg exchange may modify a second-order order-disorder phase transition to a first-order transition. It is also known that a magnetic material with a strong volume dependence of the Heisenberg exchange integral can be described in terms of an incompressible non-Heisenberg magnetic material with the biquadratic or multispin exchange (Sec. 1). Therefore, a first-order phase transition in a magnetic material with a compressible lattice represents essentially a special case of a first-order transition in a non-Heisenberg material (Chap. 2). In fact, modification of a second-order phase transition into a first-order transition because of the non-Heisenberg exchange follows from the fluctuation theory of phase transitions in which fluctuations are taken into account by the renormalization group methods more correctly than in the self-consistent field approximation. This theory postulates that for certain types of magnetic ordering an order-disorder phase transition should be of the first order even in the Heisenberg exchange case. Experimental data on first-order phase transitions in several materials are discussed in Sec. 2 in order to determine the extent to which they agree with these two theories.

Many magnetic materials exhibit order-order phase transitions or even whole sequences of these transitions; this is true, for example, of  $\text{EuSe}$ . An exceptionally large number of such phase transitions has been observed in the case of  $\text{CeSb}$  and hence it has been suggested that this compound exhibits a "devil's ladder" of such transitions between structures commensurate with the lattice constant. A devil's ladder is charac-

terized by the fact that some structures are stable only in extremely narrow temperature intervals. Therefore, phase transitions between them are of the first order but occur practically continuously and such a sequence of first-order phase transitions simulates a second-order transition. However, there is an important difference between a second-order phase transition and a devil's ladder of first-order transitions: in the former case there should be no hysteresis, whereas in the latter case it should appear (Sec. 4).

It is quite clear that low-temperature order-order phase transitions, and particularly their sequences including non-Heisenberg structures, cannot be explained by the exchange inversion theory of Kittel based on a change in the sign of the exchange integral as a result of thermal expansion of the lattice. However, allowance for the non-Heisenberg exchange makes it possible to predict the whole sequence of phase transitions observed in  $\text{EuSe}$  (Sec. 4). Moreover, this theory predicts also a new type of order-disorder phase transition (Sec. 3).

It is usual to assume that the short-range order in the paramagnetic phase represents a residue of the long-range order existing below the phase transition point. Since the nature of the short-range order governs the paramagnetic Curie temperature  $\Theta$ , it is self-evident that in the case of ferromagnets the value of  $\Theta$  is positive, whereas for isotropic antiferromagnets it is negative. The theoretical results given in Sec. 3 and an analysis of the experimental data on  $\text{EuSe}$  demonstrate that we have a situation when after the disruption of the antiferromagnetic order in an isotropic crystal the value of  $\Theta$  is positive. Therefore, a phase transition produces a short-range order of a different type than the long-range order before the phase transition. Such phase transitions have been designated as "order-improper disorder," in contrast to the usual transitions in which the nature of the short-range order at temperatures  $T > \Theta$  corresponds to the long-range order below the transition point ("order-proper disorder" phase transitions). In general, order-improper disorder phase transitions are characterized by different vectors of the long- and short-range orders below and above the transition point, respectively, but this is not always manifested by an anomalous sign of  $\Theta$ . This difference between the vectors has been observed experimentally for UAs. The nature of the short-range order in the paramagnetic phase has a considerable influence on many properties of crystals, for example, on the optical and electrical properties.

Both order-order and order-improper disorder phase transitions are due to different temperature dependences of the competing Heisenberg and non-Heisenberg exchange interactions, so that the high-temperature properties may be governed by the former and the low-temperature properties by the latter.

Finally, we must mention another important property of the investigated materials: some of them (for example,  $\text{EuSe}$ ) are isotropic metamagnets (Sec. 4). Usually the metamagnetic properties of materials are explained by a strong anisotropy of the interaction between the

spins and the majority of the known metamagnets can indeed be explained by this model. The existence of isotropic magnetic materials has made it necessary to reconsider whether this concept is universally valid. Metamagnetism of isotropic materials can be explained in a natural manner by the models with the isotropic non-Heisenberg exchange described below (Sec. 3).

## 1. NON-HEISENBERG ISOTROPIC EXCHANGE

For many decades the Heisenberg model has been the basis of the theory of magnetism. However, the number of magnetic materials close to the ideal Heisenberg model is not very large and for the majority of such materials this model describes only the principal properties. In some cases the model is totally inapplicable. In this section we shall discuss the isotropic exchange interaction which does not fit the Heisenberg model. We shall consider separately insulators and metals described by the  $s-d$  (or  $s-f$ ) Vonsovskii model.

### a) Insulators

We shall consider first the exchange interaction between two atoms with arbitrary spins  $S$ , located at a fixed distance from one another. We shall assume that the exchange interaction energy is small compared with the excitation energy of an atom and that the atoms do not have an orbital angular momentum. Since space is isotropic, the Hamiltonian  $H_{12}$  of the exchange interaction can be constructed only as a function of the scalar product of the atomic spin operators  $\mathbf{S}_1$  and  $\mathbf{S}_2$ . This Hamiltonian can be represented in the following form after allowance for the properties of the spin operators:

$$H_{12} = - \sum_{n=0}^{2S} I_n (\mathbf{S}_1 \mathbf{S}_2)^n. \quad (1.1)$$

The summation with respect to  $n$  is limited because the power exponent of the  $i$ -th component  $(S^i)^n$  in the  $n > 2S$  case can be expressed in terms of linear combinations of  $(S^i)^m$  with  $m \leq 2S$ . If  $S > 1/2$ , the Heisenberg Hamiltonian differs from Eq. (1.1) by restriction of the summation with respect to  $n$  to the terms  $n=0$  and 1. This restriction requires special justification.

In the case of crystals we also have to allow for the fact that in addition to the two-spin exchange, there is also the multispin mechanism. In general, the isotropic exchange Hamiltonian is

$$H = - \sum_n \sum_{(i)} J_n (f_1, \dots, f_n) (S_{i_1} S_{i_2}) \dots (S_{i_{2n-1}} S_{i_{2n}}). \quad (1.2)$$

Bogolyubov<sup>1</sup> was the first to draw attention to the existence of the multispin exchange in the course of an analysis of the quasipolar model of metals, but the ideas put forward by him were based essentially on the symmetry properties of the exchange interaction. Attempts have also been made to use the symmetry properties alone in the derivation of the relationships between the coefficients of the two-spin exchange in Eq. (1.1). They were based on the fact that if  $S=1/2$ , then Eq. (1) is identical with the Heisenberg Hamiltonian. Dirac<sup>2</sup> derived originally this Hamiltonian with the aid of the permutation operator  $P_{12}$  of two  $S=1/2$  spins.

This enabled Joseph<sup>3</sup> and Allan and Betts<sup>4</sup> to associate Eq. (1) with the permutation operator of spins of arbitrary magnitude introduced by Schrödinger.<sup>5</sup> This operator determines the ratio of the coefficients in Eq. (1.1) because they all should be of the same order of magnitude (for example, if  $S=1$ , then  $I_0 = -I_1 = -I_2$ ). In fact, there is no reason to regard the exchange energy operator  $H_{12}$  as proportional to the spin permutation operator  $P_{12}$ , although the latter should be given by an expression of the (1.1) type. The proportionality between these two operators in the  $S=1/2$  case is a consequence of the fact that one can form a single scalar  $(\mathbf{S}_1 \cdot \mathbf{S}_2)$  for two spins and this scalar occurs both in  $P_{12}$  and  $H_{12}$ , with the energy of the system being determined to within a constant.

Reliable estimates of the non-Heisenberg exchange integrals can be obtained only from the experimental data. Calculations based on various microscopic models can at best give only the order of magnitude of these integrals. (It should be mentioned that even reliable calculations of the usual exchange integrals for real magnetic materials are not possible on the basis of the available theories. Frequently, even the correct signs of the integrals cannot be deduced, since the  $d$  and  $f$  orbital wave functions are oscillatory. Calculations relating to the exchange of higher orders in respect of the spin are much more complex than those in the Heisenberg case.) Microscopic models can also be used to establish the properties of a crystal that determine the ratio of the energies of the non-Heisenberg and Heisenberg exchange.

In this respect it is useful to analyze the Hubbard model for a simple cubic lattice

$$H = U \sum_{\mathbf{g}} a_{\mathbf{g},\sigma}^* a_{\mathbf{g},\sigma} + B \sum_{\mathbf{g},\sigma} a_{\mathbf{g},\sigma}^* a_{\mathbf{g}+\Delta,\sigma} \quad (1.3)$$

where the number of electrons is equal to the number of atoms in the semiconductor limit  $B \ll U$  ( $\Delta$  is a vector linking an atom  $\mathbf{g}$  with a neighbor and  $\sigma$  is the component of the electron spin). The exchange interaction appears as a result of virtual electron transitions to neighboring atoms. Such transitions are possible if the electron spins at neighboring atoms are antiparallel. Since transitions reduce the degree of localization of electrons and atoms, it follows from the indeterminacy principle that the electron energy decreases. It follows that the energy of an antiferromagnetic state is lower than that of a ferromagnetic state.

The Heisenberg exchange is obtained as a correction to the ground-state energy in the second order with respect to  $B/U$ . The contribution to the energy made by a virtual electron transition from an atom 1 to an atom 2 (i.e.,  $1-2, 2-1$ ) is  $(B^2/U)F_{12}$ . The spin-dependent factor  $F_{12}$  is equal to 0 for parallel spins and to 1 for antiparallel spins. The invariance of the system under spin rotations in space means that  $F_{12}$  can depend only on  $(\mathbf{S}_1 \cdot \mathbf{S}_2)$ . On the other hand, if  $S=1/2$ , any function of  $(\mathbf{S}_1 \cdot \mathbf{S}_2)$  reduces to the linear form. Therefore,  $F_{12}$  is given uniquely by  $F_{12} = 1/4 - (\mathbf{S}_1 \cdot \mathbf{S}_2)$ , i.e., in the main order with respect to  $B/U$  the exchange integral in Eq. (1.2) is  $I_1 = -2B^2/U$ .

The four-spin exchange appears because of cyclic transitions of electrons between four atoms forming a square: 1-2, 3-4, 2-3, 4-1. Such transitions should not affect the original spin configuration. The corresponding correction to the energy is of the fourth order in  $B/U$  and it amounts to  $-2B^4 F_{12} F_{34} / U^3$  (the factor 4 appears because of the permutation of transitions in this cycle). Therefore,  $I_2(1, 2, 3, 4)$  in Eq. (1.2) is  $-8B^4/U^3$ , i.e., we have  $I_2/I_1 = 4B^2/U^2$ . If  $B/U \leq 0.1$ , this ratio does not exceed a few percent, i.e., in the case of systems described well by this simple model the role of the multipin exchange is slight. However, the results obtained within the framework of this model allow us to draw an important qualitative conclusion: since the band gap  $E_g$  is  $U - 12|B|$ , the role of the non-Heisenberg exchange increases on reduction in  $E_g$ . This is supported by calculations based on other models.

The relative role of the non-Heisenberg exchange increases if we go outside the confines of the Hubbard model and allow for the Coulomb repulsion at neighboring atoms. This gives rise to an exchange interaction between electrons at neighboring atoms, tending to establish a ferromagnetic order. Since the contributions to the total exchange integral  $I_1$  made by virtual transitions and by the direct Coulomb interaction are both of the second order with respect to the overlap of the orbits of the neighboring atoms and have opposite signs, it follows that they can largely compensate one another. In the case of the exchange of higher orders in respect of the spin, these two mechanisms need not compensate each other and may even exhibit mutual enhancement.

A similar exchange mechanism occurs in solid  $^3\text{He}$ , which is a nuclear antiferromagnet of spin 1/2, except that now the exchange is due to virtual quantum tunneling of He atoms from one unit cell to another. Four-spin terms in the Hamiltonian are also related to four-atom cyclic transitions and are magnitude-comparable with the Heisenberg terms.<sup>6-9</sup>

Attempts have also been made to estimate the biquadratic terms on the assumption that the exchange interaction between atoms is direct.<sup>10-14</sup> It has been shown in these treatments that when one electron from each atom participates in the exchange, the Heisenberg term  $\sim (\mathbf{S}_1 \cdot \mathbf{S}_2)$  is obtained, whereas for two electrons from each atom the term is biquadratic  $\sim (\mathbf{S}_1 \cdot \mathbf{S}_2)^2$ , etc. Numerical estimates obtained in Ref. 11 for the  $\text{N}_2$  molecule with  $S = 3/2$  indicate that the ratio of the biquadratic and bilinear exchange integrals  $\alpha = I_2/I_1$  of this molecule is very small ( $\sim 0.0025$ ). A more favorable situation occurs in the case of superexchange via non-magnetic atoms: in this case the ratio may amount to a few percent.<sup>15,16</sup> Since the relative contribution of the biquadratic exchange to the magnetic ordering energy is of the order of  $\alpha S^2$ , in the case of large spins it may amount to tens of percent.<sup>15-18</sup>

Kittel<sup>19</sup> was the first to draw attention to the fact that the biquadratic exchange may be a consequence of the lattice deformability. A more rigorous approach shows that the interaction with the lattice gives rise not only

to the biquadratic exchange, but also to the three- and four-spin contributions in those cases when for fixed ion positions the exchange can be regarded as bilinear (see, for example, Ref. 20). Expanding the integrals of the exchange between atoms  $g$  and  $f$ ,  $I(\mathbf{R}_g - \mathbf{R}_f + \mathbf{u}_g - \mathbf{u}_f)$ , in powers of the displacements  $\mathbf{u}_g$  and  $\mathbf{u}_f$  from the equilibrium positions, we obtain the exchange Hamiltonian for a deformable lattice:

$$H = -\frac{1}{2} \sum I_1(gf) (\mathbf{S}_g \mathbf{S}_f) + \hbar \sum \omega_{\mathbf{q}j} b_{\mathbf{q}j}^* b_{\mathbf{q}j} - \frac{1}{2} \sum \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}j} M N}} (b_{\mathbf{q}j} - b_{-\mathbf{q}j}^*) (e^{i\mathbf{q}g} - e^{i\mathbf{q}f}) |I_{1j} \nabla I_1(g, f)| (\mathbf{S}_g \mathbf{S}_f), \quad (1.4)$$

where  $\omega_{\mathbf{q}j}$  and  $\mathbf{l}_{\mathbf{q}j}$  are the frequency and polarization vector of a phonon with a quasimomentum  $\mathbf{q}$  and a polarization  $j$  ( $\mathbf{l}_{\mathbf{q}j} = -\mathbf{l}_{-\mathbf{q}j}$ ),  $M$  is the mass of a unit cell,  $N$  is the number of unit cells, and  $I_1(g, f) \equiv I_1(\mathbf{R}_g - \mathbf{R}_f)$ . If we assume that the spins are classical or if the Curie temperature  $T_C$  is considerably less than the Debye temperature  $\theta_D$ , the terms in Eq. (1.4) linear in respect of the phonon operators  $b^*$  and  $b$  can be removed by canonical transformation of the displacements. Dropping terms of higher orders, we obtain the magnetic part of the Hamiltonian

$$H_M = -\frac{1}{2} \sum I_1(g, f) (\mathbf{S}_g \mathbf{S}_f) - \frac{1}{2} \sum I_2(g_1 f_1 g_2 f_2) (\mathbf{S}_{g_1} \mathbf{S}_{f_1}) (\mathbf{S}_{g_2} \mathbf{S}_{f_2}), \\ I_2(g_1 f_1 g_2 f_2) = \frac{\hbar}{8MN} \sum \omega_{\mathbf{q}} |I_{1j} \nabla I_1(g_1, f_1)| |I_{1j} \nabla I_1(g_2, f_2)| \\ \times [\exp(i\mathbf{q}g_1) - \exp(i\mathbf{q}f_1)] [\exp(-i\mathbf{q}g_2) - \exp(-i\mathbf{q}f_2)]. \quad (1.5)$$

Equation (1.5) yields directly the following estimate for the biquadratic exchange integral:  $I_2(\mathbf{gfgf}) \sim \hbar^2 (M\theta_D)^{-1} (dI_1/da)$ . If we assume that  $M \sim 10^{-22}$  g,  $\theta_D \sim 10^2$  eV,  $dI_1/da \sim (1-3 \text{ eV})/a$  (for  $S \sim 1$ ), and  $a \approx 3 \times 10^{-8}$  cm, we obtain  $I_2(\mathbf{gfgf}) \sim 10^{-3} - 10^{-2}$  eV, the biquadratic term can be quite large for the nearest neighbors with  $|\mathbf{R}_g - \mathbf{R}_f| = a$ .

It is worth considering particularly the case when the orbital angular momentum does not vanish for magnetic atoms but is not frozen by the crystal field. In the case of rare-earth ions the strong spin-orbit interaction combines the orbital and spin angular momenta into the total angular momentum  $J$ . The crystal field splits a  $(2J+1)$ -fold degenerate state with a given value of  $J$  into components. Those which are degenerate correspond to the magnetic state of an ion. For example, an ion of U in  $\text{UO}_2$  is in the  $^3H_4$  state. The lowest state in the crystal field is a triplet. We can describe it conveniently<sup>21</sup> by introducing an effective spin  $\hat{S} = 1$ . States with different values of  $\hat{S}^z$  can be expressed in terms of states  $|J^m\rangle$  with different values of  $J^m$  using the relationships

$$|\hat{S}^z = \pm 1\rangle = \sqrt{\frac{7}{8}} | \pm 3 \rangle - \sqrt{\frac{1}{8}} | \mp 1 \rangle, \\ |\hat{S}^z = 0\rangle = \sqrt{\frac{1}{2}} (| 2 \rangle - | -2 \rangle).$$

The use of these states as the basis in the Anderson super-exchange theory<sup>15,16</sup> yields an effective Hamiltonian of the type

$$\hat{H} = -J_1 (\hat{S}_i \hat{S}_j) - I_2 (\hat{S}_i \hat{S}_j)^2 - I_3 \sum_{i=x,y,z} (\hat{S}_i^x \hat{S}_j^x)^2$$

with  $I_2/I_1 = 0.27$  and  $I_3/I_1 = 0.0024$ . Therefore, in spite of

the strong magnetic anisotropy of a  $\text{UO}_2$  crystal, the effective Hamiltonian  $\tilde{H}$  is practically isotropic and the biquadratic exchange is comparable with the bilinear contribution (apparently, the smallness of  $I_3/I_1$  is accidental).

In the case of transition-metal ions one must first allow for the crystal field and only then for the spin-orbit interaction. This was the method used in Ref. 22 to construct an effective Hamiltonian in the bilinear approximation. The method of Ref. 22 can be generalized to higher approximations in respect of the effective angular momentum.

Finally, we must point out that the problem of the exchange interaction in a system of ions with an orbitally degenerate ground state (Jahn-Teller ions)<sup>167-173</sup> can sometimes be reduced to a Hamiltonian with the non-Heisenberg exchange. In fact, a system of this kind can be described by the Hamiltonian<sup>173</sup>

$$H = -\frac{1}{2} \sum [I_1 (S_{\mathbf{r}} S_{\mathbf{r}+\Delta}) + I_2 (T_{\mathbf{r}} T_{\mathbf{r}+\Delta}) + I_3 (S_{\mathbf{r}} S_{\mathbf{r}+\Delta}) (T_{\mathbf{r}} T_{\mathbf{r}+\Delta})], \quad (1.6)$$

where  $T_{\mathbf{r}}$  are the pseudospin operators describing the occupancy of the orbitals. If the inequality  $|I_1| \gg |I_2|$  is obeyed, we can use the adiabatic approximation and regard the spins as a fast subsystem. Then, the usual method yields the following expression for the Hamiltonian of the slow subsystem (pseudospins)

$$\tilde{H}_n = -\frac{1}{2} \sum I_2 (T_{\mathbf{r}} T_{\mathbf{r}+\Delta}) + E_n (T_{\mathbf{r}} T_{\mathbf{r}+\Delta}),$$

where  $E_n$  is the energy of the spins described by Eq. (1.6) with  $I_2 = 0$  and  $n$  is the index describing their states. In general, the dependence of  $E_n$  on the set of parameters  $(T_{\mathbf{r}} T_{\mathbf{r}+\Delta})$  is nonlinear. Therefore, the Hamiltonian  $\tilde{H}_n$  has the structure of Eq. (1.2). A similar Hamiltonian but now for spins and not for pseudospins is obtained if  $|I_1| \ll |I_2|$ .

The ratio  $I_2/I_1$  was first determined experimentally in an investigation of ESR of  $\text{Mn}^{2+}$  ions in  $\text{MgO}$  containing 1% Mn (Ref. 17). In the case of the  $\text{Mn}^{2+}$  ions which are the nearest neighbors it was found that  $I_2/I_1 \sim 0.05$ . Bearing in mind that  $S = 5/2$ , the exponent of the relative contribution of the biquadratic exchange  $I_2 S^2/I_1$  is now considerable:  $\sim 25\%$ . This is an order of magnitude greater than that expected for the biquadratic exchange resulting from the lattice deformation. A numerical calculation of the superexchange between the  $\text{Mn}^{2+}$  ions in  $\text{MnO}$  gave results<sup>18</sup> which were in an order-of-magnitude agreement with the results of Ref. 17. This made it possible to assume that the anomalous properties of the Mn compounds such as  $\text{MnO}$  can be explained by a considerable difference of the exchange from the Heisenberg form.

The non-Heisenberg exchange has a particularly strong influence on the properties of those materials in which the Heisenberg exchange is for some reason weak. One possible reason for this situation has been mentioned earlier: the contributions due to the various exchange mechanisms balance out. However, even when one particular exchange mechanism predominates, the exchange integral for two atoms can still be small: the oscillatory nature of the  $d$  and  $f$  functions may re-

sult in a change in the sign when the distance  $a$  between the atoms is varied. If the distance is close to that corresponding to  $I(a) = 0$ , the non-Heisenberg exchange becomes important. We can expect that this is exactly the situation in, for example,  $\text{EuSe}$  whose anomalous properties will be discussed in later sections.

Europium selenide belongs to a family of Eu monochalcogenides, all of which have the NaCl structure. As the lattice constant increases in this family, a transition takes place from a ferromagnetic ordering in  $\text{EuO}$  ( $T_C = 67^\circ\text{K}$ ) and  $\text{EuS}$  ( $T_C = 16.3^\circ\text{K}$ ) to an antiferromagnetic ordering in  $\text{EuSe}$  ( $T_N = 4.6^\circ\text{K}$ ) and  $\text{EuTe}$  ( $T_N = 9.6^\circ\text{K}$ ). (These and later data are collected in Ref. 23.) It is important to note that both  $\text{EuO}$  and  $\text{EuS}$  behave as almost ideal Heisenberg ferromagnets, whereas the properties of  $\text{EuTe}$  are close to those of an ideal Heisenberg antiferromagnet with the  $\text{MnO}$  structure.

It is worth noting the anomalously low ordering temperature of  $\text{EuSe}$  compared with the other members of the family: this demonstrates weakness of the Heisenberg exchange in  $\text{EuSe}$ . In view of the similarity of the properties of chalcogenides, the anomalously weak exchange in  $\text{EuSe}$  can be explained by the fact that the lattice constant  $a$  is close to that value  $a_0$  at which the integral  $I_1$  representing the exchange between the neighboring  $\text{Eu}^{2+}$  ions vanishes. The strength of the dependence of  $I_1$  on  $a$  in the case of  $\text{EuSe}$  is indicated by the fact that a pressure of 1 kbar lowers  $T_N$  by a whole degree Kelvin. This substance is easily transformed from an antiferromagnetic to a ferromagnetic state by the application of pressure.

It is natural to expect that the vanishing of  $I_1(a)$  at the point  $a_0$  is not accompanied by the vanishing of the other exchange parameters. Therefore, the non-Heisenberg exchange in Eu chalcogenides should be compared with the Heisenberg exchange at distances  $a$  quite different from  $a_0$ . An estimate of the strength of the latter is given by the value of  $T_C$  which is close to  $70^\circ\text{K}$  for  $\text{EuO}$ . If the non-Heisenberg exchange is an order of magnitude weaker than the Heisenberg interaction, it follows that in the case of  $\text{EuSe}$  it should represent a few degrees Kelvin, i.e., it may fully compete with the Heisenberg contribution. An additional factor tending to increase the importance of the non-Heisenberg terms in the case of  $\text{EuSe}$  is that the band gap is narrow compared with that of "classical" antiferromagnetic insulators, such as  $\text{NiO}$ , etc.:  $E_f$  amounts to just 1.7 eV. The relative contribution of the non-Heisenberg terms increases on reduction in the band gap. In the case of magnetic insulators the non-Heisenberg terms usually represent 5% of the Heisenberg contributions.

It should be noted that the smallness of the exchange integral  $I_1$  for the nearest neighbors makes it necessary to include the integral  $I_{11}$  between the second-nearest neighbors. It is shown in Sec. 4 that allowance for  $I_{11}$  and for the non-Heisenberg exchange between the nearest neighbors is sufficient to explain the main magnetic properties of  $\text{EuSe}$ .

The above theoretical estimate of the relative importance of the biquadratic exchange in  $\text{UO}_2$  seems to be

supported also by the Néel temperature  $T_N = 31^\circ\text{K}$  (Ref. 24), which is low compared with  $T_N$  of a similar compound  $\text{UTe}_2$  ( $78^\circ\text{K}$ —Ref. 25).

## b) Conductors

The number of insulators exhibiting a strong exchange of higher orders in respect of the spin is not very large, whereas the number of conductors with similar properties is much greater. Naturally, in metals containing collective-state electrons the exchange is strongly non-Heisenberg, but in view of the absence of localized magnetic moments the effective magnetic Hamiltonian of the (1.2) type cannot be derived for metals. However, in principle, this Hamiltonian provides a satisfactory description of the properties of conductors in which the conduction electrons ( $s$  electrons) mediate an indirect exchange between the localized  $f$  and  $d$  moments (the  $s$ - $f$  Vonsovskii model<sup>26</sup>). The initial Hamiltonian in the  $s$ - $f$  model is

$$H = \sum E_{k\sigma} a_{k\sigma}^* a_{k\sigma} - \frac{A}{N} \sum (S_g S_{g'}) e^{i(k-k')} a_{k\sigma}^* a_{k'\sigma'}, \quad (1.7)$$

where  $a_{k\sigma}^*$  and  $a_{k\sigma}$  are the  $s$ -electron operators. It is usual to assume that the Fermi energy of electrons  $E_F$  is large compared with  $AS$ . The effective Hamiltonian of the RKKY theory<sup>27-29</sup> is a correction of the second order in respect of  $\kappa = AS/E_F$  to the conduction electron energy and it is expressed in terms of the spin operators. We must bear in mind that in the zeroth order approximation there is no spin polarization of the electrons so that the first-order correction vanishes. It is quite clear that in the second order the spins  $S_k$  occur in the form of a bilinear term in the magnetic Hamiltonian, i.e., the RKKY Hamiltonian should have the same structure as the Heisenberg expression.

Attempts have been made to obtain terms of higher orders in respect of the spins  $S_k$  as successive approximations of perturbation theory with respect to  $AS/E_F$ , but this approach has yielded diverging expressions.<sup>30-32</sup> The reason for this becomes clear when we consider the results reported in Refs. 33 and 34: the energy of the system under consideration is nonanalytic in respect of  $AS/E_F$  and the nonanalyticity increases on increase of deviation of the Fermi surface from the spherical form. Singular terms  $\sim \ln \kappa$  may play a definite role when the magnetic structure period is close to the extremal radius of the Fermi surface.<sup>33</sup> For example, in the case of a one-dimensional chain with a simple cosinusoidal dispersion law for the conduction electrons, whose number is equal to the number of atoms, a rigorous calculation of the energy of an antiferromagnetic state within the framework of the model of Eq. (1.7) has the effect that the main term is  $\sim \kappa^2 \ln \kappa$  and not  $\kappa^2$ , which should be obtained from the RKKY theory.<sup>23</sup> In the three-dimensional isotropic case the main term is indeed  $\sim \kappa^2$  and this justifies application of the RKKY theory. However, the correction to this term is  $\sim \kappa^4 \ln \kappa$  and it is nonanalytic in respect of  $\kappa$ .

It therefore follows that the non-Heisenberg exchange should be described by the Hamiltonian (1.2) with an infinitely large number of terms. Additional complications in its structure may appear because of the scat-

tering of the conduction electrons by magnons and phonons, giving rise to smearing of the Fermi surface. In the RKKY approximation this implies truncation of the long-range part of the exchange (attention to the temperature dependence of the RKKY interaction was first drawn in Ref. 35).

The situation is even more complex when instead of the strong inequality  $E_F \gg AS$ , we find that only the inequality  $W \gg AS$  is obeyed, where  $W$  is the conduction band width. The latter corresponds to degenerate magnetic semiconductors of the  $\text{EuO}$  type and to metals with relatively few electrons per atom. In this case the results of the RKKY theory are valid only if there is no magnetization in a crystal. This theory cannot be applied in the case of a finite average magnetization or in the case of slow spatial variation of the direction of local magnetization.<sup>23</sup> For example, if  $E_F < AS$  and the ordering is ferromagnetic, the electron gas is completely spin-polarized, i.e., the magnetic ordering energy is proportional to  $A$  and not to  $A^2$ , as in the RKKY theory. However, the antiferromagnetic ordering energy and the paramagnetic Curie temperature are described by the same expressions as in the RKKY theory.

In principle, even in this case we can construct an equivalent magnetic Hamiltonian but its structure is extremely complex and its coefficients should depend on the temperature and field. In order to obtain some idea on its structure we shall consider the simpler case of indirect exchange mediated by a single donor electron between localized spins in a magnetic semiconductor.<sup>32</sup> Clearly, the moment of this conduction electron is aligned parallel or antiparallel to the total moment  $M$  of a group of  $n$  atoms in the vicinity of a defect (these are the atoms at which the probability of finding the conduction electron in question is highest) and the energy of its  $s$ - $f$  exchange is  $\pm AM/2n$ . The transition from this case to the magnetic Hamiltonian is performed by replacing  $M$  with the operator  $\sqrt{\hat{M}^2}$ , where  $\hat{M} = \sum S_k$  is the moment operator of this group of atoms. A rigorous derivation yields the following expression for the magnetic Hamiltonian:

$$H = -\frac{A}{2n} \left( \frac{1}{2} \pm \sqrt{M^2 \pm \frac{1}{4}} \right) + H_2, \quad (1.8)$$

where  $H_2$  contains expressions proportional to  $A^2$  and having the structure of the RKKY Hamiltonian.

It is clear from Eq. (1.8) that in this special case of indirect exchange via spin-polarized electrons the multispin terms appear already in the first order of  $A$  as a result of expansion of the square-root operator in terms of  $(S_k \cdot S_l)$ :

$$\sqrt{M^2 + \frac{1}{4}} \approx \sqrt{R} \left( 1 + \frac{Q}{2R} - \frac{Q^2}{8R^2} + \dots \right), \quad (1.9)$$

$$R = nS(S+1) + \frac{1}{4}, \quad Q = \sum_{l \neq g} (S_g S_l),$$

and in the case of strongly magnetized states it is necessary to sum the whole series, i.e., we have to allow for the multispin interaction in which all  $n$  spins participate (a more general expression is obtained also in Ref. 36 without assuming that an electron is equally likely to appear at all  $n$  atoms).

Finally, when not even the inequality  $W \gg AS$  is satisfied, the magnetic properties of such systems can be investigated only in the limit  $W \ll AS$  (Refs. 37, 38, and 23). The limit  $T \rightarrow 0$  is meaningful only for semiconductors and not for metals. In semiconductors the  $s$  electrons of magnetic cations are transferred to neighboring anions and complete their external shells. For example, in the case of NiO two  $s$  electrons are transferred from Ni to the neighboring oxygen atom. The indirect exchange between the  $Ni^{2+}$  ions is via holes which appear as a result of doping of a crystal with impurities. The appearance of a hole at an  $Ni^{2+}$  ion corresponds to its transfer to the  $Ni^{3+}$  state. A hole energy band appears as a result of hole transitions from one Ni ion to another. Clearly, this band should consist of atomic  $d$ -type small-radius orbitals, and, moreover, the distance between magnetic ions in semiconductors is greater than in metals, because they are separated by nonmagnetic ions. Therefore, this band is relatively narrow ( $W \lesssim 1$  eV, whereas the value of  $AS$  which is now the exchange integral within the  $d$  shell of the atoms can represent a few electron volts).

In the case of metals the  $s$  electrons are in the collective state and their energy band is fairly wide. Therefore, the condition  $W \ll AS$  is in this case nonrealistic. However, the condition  $W \sim AS$  may be satisfied by metals. The conditions for this to happen are particularly favorable in the case of metallic alloys: the equal probability of finding the conduction electrons at atoms of different components of an alloy reduces the conduction band width (some metal alloys even behave as insulators). In the case of metal alloys one can expect particularly strong deviations of the properties from the Heisenberg type. By way of example, we can quote here ferromagnetism of PuP. In this compound the conduction electrons are strongly spin-polarized, in contrast to metals characterized by  $W \gg AS$ ; neutron-diffraction investigations show that the magnetic moment of these electrons reaches  $0.35\mu_B$  per electron.<sup>39</sup>

In contrast to an insulator, in the case of metals the non-Heisenberg exchange may be important even if the ordering temperature is not low. In view of the extreme difficulty and sometimes impossibility of constructing the effective Hamiltonian for magnetic conducting materials exhibiting the non-Heisenberg exchange, we can analyze these materials only in two ways: 1) by deriving whenever possible reliable results directly from the Hamiltonian (1.7); 2) by applying the Hamiltonian (1.2) with a finite number of terms by way of a model representation.

## 2. QUADRUPOLE ORDERING AND ORDER-PROPER DISORDER PHASE TRANSITIONS

In this section we shall consider the quadrupole ordering and the influence of the biquadratic and multi-spin exchange mechanisms on order-disorder phase transitions. The term "proper disorder" means that after the disappearance of the long-range order in a crystal the remaining short-range order is of the same type as the long-range order that has just disappeared. Therefore, the short-range order can be regarded as

the trace residue of the long-range order. As usual, the long-range order parameter is

$$\eta_{LO}(\mathbf{q}) = \frac{1}{N S^2} \sum_{\mathbf{g}} \langle S_0 S_{\mathbf{g}} \rangle \exp(-i\mathbf{q}\mathbf{g}), \quad (2.1)$$

where  $\mathbf{q}$  is the wave vector of the corresponding magnetic structure and  $\langle S_0 S_{\mathbf{g}} \rangle$  is the correlation function of the spins 0 and  $\mathbf{g}$ .

The required information on the short-range order in the paramagnetic range can be obtained from the susceptibility  $\chi(\mathbf{q}, T)$  which is related to the spin correlation functions by the Kubo formula:

$$\chi(\mathbf{q}, T) = \frac{1}{3T} \sum_{\mathbf{g}} \langle S_0 S_{\mathbf{g}} \rangle \exp(-i\mathbf{q}\mathbf{g}). \quad (2.2)$$

To within the normalization factor, the short-range order parameter is

$$\eta_{SO}(\mathbf{q}) = T\chi(\mathbf{q}, T) - \lim_{T \rightarrow \infty} [T\chi(\mathbf{q}, T)],$$

which—according to Eq. (2.2)—has the same structure as  $\eta_{LO}$  in Eq. (2.1) but it is not asymptotically small in the paramagnetic range. We then obtain that value of the short-range order vector  $\mathbf{q}$  for which  $\eta_{SO}(\mathbf{q})$  and  $\chi(\mathbf{q})$  are maximal.

A less accurate characteristic of the short-range order is the paramagnetic Curie temperature  $\Theta$ . It follows from Eq. (2.2) that in the case of a simple cubic lattice considered in the nearest-neighbor approximation the expression for this temperature is

$$\Theta = \frac{2}{S(S+1)} \lim_{T \rightarrow \infty} [T \langle S_0 S_1 \rangle]. \quad (2.2')$$

If the Hamiltonian includes the biquadratic terms  $\sim (S_1 S_2)^2$ , then in the case of positive sign of the biquadratic exchange integral  $I_2(1, 2, 1, 2) \equiv K$ , this exchange tends to ensure a parallel or antiparallel orientation of spins 1 and 2. In the classical spin case the biquadratic exchange energy is the same for the parallel and antiparallel spin orientations. It follows that the biquadratic exchange performs in a sense the function of the easy-axis magnetic anisotropy except that the easy axis is no longer associated with any crystallographic direction and can have any orientation in space.

We shall assume that  $K$  is the largest parameter of the system. Then, if  $T \ll K$ , the loss of the long-range order of the spin directions may result in their disorientation. However, some degree of order is retained because they still remain collinear with one another [ordering in respect of  $(S^x)^2$  rather than in respect of  $S^x$ ]. This is known as the quadrupole ordering. If  $K < 0$ , the spins of the neighboring atoms should be orthogonal to one another. This state can be called orthogonal quadrupole.

We can introduce the quadrupole order parameter<sup>40, 41</sup>

$$q = \langle (S^x)^2 \rangle - \frac{S(S+1)}{3} \quad (2.3)$$

in addition to the dipole order parameter, which can conveniently be the average magnetization  $m = \langle S^x \rangle \equiv S \sqrt{\eta_{LO}(0)}$  in the ferromagnetic case and the sublattice magnetization in the case of antiferromagnets. (One

can also introduce the order parameters for higher multiple ordering,<sup>41</sup> but we shall not consider them in the present review.) The quadrupole ordering is characterized by the fact that the parameter  $q$  differs from zero, but  $m=0$  (in the ferromagnetic state both  $m$  and  $q$  differ from zero). Under certain conditions the quadrupole-ordering state may be the ground state.<sup>42, 43</sup>

The problem of the ordering of spins in the case of an arbitrary isotropic exchange can be solved only for a one-dimensional chain of classical spins,<sup>44</sup> when the spin correlation functions can be obtained at finite temperatures. (A one-dimensional chain with the biquadratic exchange was also investigated in Ref. 45.)

We shall now report the results obtained by various authors in the analysis of the Hamiltonians with the biquadratic exchange

$$H = -\frac{1}{2} \sum I (g-f) (S_g S_f) - \frac{1}{2} \sum K (g-f) (S_g S_f)^2 \quad (2.4)$$

and with the four-spin exchange

$$H = -\frac{1}{2} \sum I (g-f) (S_g S_f) - \frac{1}{2} \sum K (gfhk) (S_g S_f) (S_h S_k). \quad (2.5)$$

All the indices in Eq. (2.5) are assumed to be different.

### a) Quadrupole states

Clearly, for certain ratios of their parameters the Hamiltonians of Eqs. (2.4) and (2.5) describe the usual ferromagnetic and antiferromagnetic states. The energies of these states and the magnon spectrum are given in Refs. 42 and 46 for the Hamiltonian of Eq. (2.5). These parameters may describe also magnetic structures of the non-Heisenberg type, for example canted antiferromagnets (Sec. 5). However, it is found that the permissible ground states in the case of the Hamiltonian of Eq. (2.4) include those in which the dipole ordering does not occur at all but the quadrupole ordering does. These states cannot be derived in the classical spin limit, i.e., their existence is a definite quantum effect.<sup>42, 43</sup>

The origin of these states can be found by considering the Hamiltonian of Eq. (2.4) in the nearest-neighbor approximation and assuming that  $I > 0$  and  $K > 0$ . In the classical spin case ( $S \rightarrow \infty$ ) the biquadratic exchange energy is not affected by a change from the ferromagnetic to the antiferromagnetic ordering. However, in the case of finite spins this energy decreases. In fact, if we consider two atoms, their total spin  $S_t$  is  $2S$  for the parallel orientation and 0 for the antiparallel case. Squaring  $S_t = S_1 + S_2$  and expressing  $(S_1 \cdot S_2)$  in terms of  $S_t^2$  and  $S_1^2, S_2^2$ , we find that  $(S_1 \cdot S_2)^2$  is equal to  $S^4$  in the ferromagnetic case and to  $S^2(S+1)^2$  for antiferromagnets. This treatment cannot be applied automatically to a crystal in which each atom interacts not with just one but with the  $z$  nearest neighbors. However, it shows that the quantum quadrupole structure may appear because of the competition between the bilinear and biquadratic exchange mechanisms that tend to establish opposite types of structure: for  $K=0$  the ordering should be ferromagnetic whereas for  $I=0$  it should be antiferromagnetic.

The calculation reported in Ref. 42 was carried out for  $S=1$ . In a quadrupole state we have  $m=0$ . Therefore, the vacuum state is selected to be such that  $S_t^z = 0$  applies to all the atoms. Operators representing deviation of the spin from the value  $S_t^z = 0$  are introduced and these operators are of two types. The operators  $b_{t_1}^*$  and  $b_{t_1}$  describe transitions between the states  $\delta(S_t^z - 1)$  and  $\delta(S_t^z)$  with the spin components 1 and 0, respectively:  $b_{t_1}^* \delta(S_t^z) = \delta(S_t^z - 1)$ ,  $b_{t_1} \delta(S_t^z - 1) = \delta(S_t^z)$ . The operators  $b_{t_2}^*$  and  $b_{t_2}$  describe transitions between the states with  $S^z = 0$  and  $S^z = -1$ :  $b_{t_2}^* \delta(S_t^z) = \delta(S_t^z + 1)$ , and  $b_{t_2} \delta(S_t^z + 1) = \delta(S_t^z)$ . These operators are related to the spins by

$$S_t^z = \sqrt{2} (b_{t_1}^* + b_{t_2}), \quad S_t^- = \sqrt{2} (b_{t_1} + b_{t_2}^*), \quad (2.6)$$

$$S_t^+ = b_{t_1}^* b_{t_1} - b_{t_2}^* b_{t_2}.$$

Fairly complex commutation relationships apply between the operators  $b_{t_1}^*$  and  $b_{t_1}$ . If we ignore the kinematic interaction between spins, the operators can be regarded as of the Bose type. Substituting Eq. (2.6) into Eq. (2.4) and diagonalizing in the usual way the magnon Hamiltonian, it is found<sup>42</sup> that the energy of the ground state and the magnon spectrum are described by the following expressions:

$$E_Q = -KNz \left[ 1 + \frac{1}{2z} \left( 1 - \frac{I}{K} \right)^2 \right],$$

$$\omega_k = K^2 z^2 (1 - \gamma_k) \left( 1 + \gamma_k - \frac{2I}{K} \gamma_k \right), \quad \gamma_k = \frac{1}{z} \sum_{\Delta} e^{i k \Delta}. \quad (2.7)$$

Comparison of  $E_Q$  given by the first expression in Eq. (2.7) with the energies of the ferromagnetic and antiferromagnetic states shows that if  $K > I > 0$ , then the energy  $E_Q$  is lower. The stability of the quadrupole state for this relationship between  $I$  and  $K$  indicates that the magnon frequencies of Eq. (2.7) are real. If  $I=0$ , the energy  $E_Q$  and the frequencies  $\omega_k$  are identical with those given by the corresponding expressions for antiferromagnets, whereas for  $I=K$  they reduce to those for ferromagnets. Therefore, the quadrupole ordering is intermediate between antiferromagnetism and ferromagnetism. However, it neither shows partial magnetization nor two lattices. The first conclusion follows from the fact that according to Eq. (2.7) at low values of  $k$  we have  $\omega_k \propto k$ , whereas the phenomenological theory predicts that for any crystal with a spontaneous magnetization we should have  $\omega_k \propto k^2$ . The second conclusion follows from the inequality  $\omega(\pi/a, \pi/a, \pi/a) \neq 0$ .

It is natural to expect the development of the ferromagnetic and antiferromagnetic short-range order at the points  $I=K$  and  $I=0$ , respectively, representing the limits of the quadrupole phase. Evidence is given in Ref. 42 in support of the conclusion that the quantum quadrupole ordering may occur also for  $S \geq 2$  although the actual conditions are much more stringent.

If  $K < 0$  and  $S=1$ , more complex structures are expected: a canted antiferromagnetic structure (Sec. 5) and an orthogonal quadrupole structure.<sup>43</sup> The latter is characterized by the fact that the quantization axes of the nearest-neighbor spins are orthogonal, but for each atom the average value of  $S^z$  considered in a local coordinate system vanishes with the accuracy to within the zero-point vibrations. A calculation demonstrating



this behavior represents a generalization of that described above. An orthogonal quadrupole state may be realized if in addition to the inequality  $K < I < 0$  in Eq. (2.4) for the exchange constants of the nearest neighbors, the inequality  $0 < I_2 < K_2$  is also satisfied for the constants of the second-nearest neighbors. If this is not true, then we can expect canted antiferromagnetic ordering.

Other types of quadrupole ordering are considered in Ref. 47 on the assumption that the law governing changes in the directions of the quantization axes in space is more complex. A calculation carried out by a variational method confirms in particular the results of Refs. 42 and 43. The spectrum of coupled magnon states in a ferromagnet with the Hamiltonian of Eq. (2.4) subject to the conditions  $I > 0$  and  $K > 0$  is considered in Ref. 166. It is shown there that if  $K > I$ , the ground ferromagnetic state is unstable in the presence of such elementary excitations. This can be understood in the light of the results given in Ref. 42.

In addition to the quantum quadrupole states discussed above, we can expect also quadrupole states of statistical origin. In the limit  $T \rightarrow 0$  they are less likely than dipole ferromagnetic or antiferromagnetic states, but they may appear at finite temperatures because their entropy is higher than that of the dipole states. In contrast to the quantum states, such statistical quadrupole states are possible also in the limit  $S \rightarrow \infty$ . In the case of these statistical states all the spins are parallel or antiparallel to one another. Therefore, the parameter  $q$  of Eq. (2.3) is then positive, whereas for a one-sublattice quantum state it is negative. The quantum states are truly ordered, whereas the statistical states are only partly ordered. Phase transitions transform quadrupole structures into dipole configurations or they destroy them altogether.

## b) Phase transitions

The main results on phase transitions considered within the framework of the model represented by Eqs. (2.4) and (2.5) have been obtained mainly in the molecular field approximation and by the method of high-temperature expansions. The first attempt to consider a Hamiltonian with the biquadratic exchange was made in Ref. 48. However, the self-consistent field variant used there was incorrect: separation of  $\langle (S_1^x S_2^x)^2 \rangle$  into  $\langle (S_1^x)^2 \rangle \langle (S_2^x)^2 \rangle$  was clearly wrong. A correct analysis of the problem was carried out in Refs. 42 and 49–51 allowing for the biquadratic exchange and also in Ref. 52 allowing for the four-spin exchange. For example, in the latter case the molecular field  $\mathcal{B}$  acting on a ferromagnetic spin subject to Eq. (2.5) is found from an equation which is cubic in respect of the Brillouin function  $B_S(x)$  (Ref. 52):

$$\begin{aligned} \mathcal{B} &= SJ B_S \left( \frac{S\mathcal{B}}{T} \right) + 2S^3 R B_S \left( \frac{S\mathcal{B}}{T} \right), \\ J &= \sum_{\Gamma} I(\mathbf{g}, \Gamma), \quad R = \sum_{\Gamma \mathbf{hk}} K(\mathbf{g}\Gamma \mathbf{hk}). \end{aligned} \quad (2.8)$$

An analysis of Eq. (2.8) demonstrates that the nature of the ferromagnetic–paramagnetic transition depends on the ratio  $\lambda = J/2S^2R$ . If  $\lambda > \lambda_S$ , where  $\lambda_S$  varies from 3

for  $S = 1/2$  to 1.66 for  $S \rightarrow \infty$ , the transition is of the second order, in the opposite case it is of the first order. Therefore, the multispin exchange gives rise to an abrupt ferromagnetic–paramagnetic phase transition. Similar results are reported also in Ref. 52 for antiferromagnets.

One should stress an important feature which applies not only to the results of Ref. 52 but also to the results of many other papers cited in the present review. The self-consistent field method which exaggerates the role of fluctuations cannot be accurate in the vicinity of a second-order phase transition. Moreover, some authors are of the opinion that this method can even give qualitatively wrong results predicting, for some magnetic structures, a continuous instead of an abrupt transition obtained from the fluctuation theory (see the following subsection). However, if the self-consistent field method predicts that a phase transition is abrupt, then this qualitative result can be regarded as reliable: a more correct allowance for fluctuations can only enhance the discontinuity at the phase transition. It should be noted that the fluctuation theory of phase transitions predicts second-order transitions for ferromagnets.

Analyses of the biquadratic exchange reported in Refs. 42 and 49–51 are made using not only the conventional self-consistent field acting on  $S_i^x$  (“dipole” field), but also a “quadrupole” field acting on  $(S_i^x)^2$ . Then, the Hamiltonian (2.4) for a ferromagnet can be represented in the form

$$\begin{aligned} H &= H_0 + H_1, \\ H_0 &= -Jm \sum S_i^z - Qq \sum (S_i^z)^2, \\ J &= z \left( I - \frac{K}{2} \right), \quad Q = \frac{3}{2} zK, \end{aligned} \quad (2.9)$$

where  $z$  is the number of nearest neighbors. The order parameters  $m$  and  $q$  in Eq. (2.3) act as variational quantities. They can be found by minimizing the model energy of the system  $F_M$  with respect to these parameters:

$$\begin{aligned} F &\leq F_M = F_0 + \langle H_1 \rangle_0, \\ F_0 &= -NT \ln Z, \quad Z = \sum_{\{s_i\}} \exp \frac{JmL + QqL^2}{T}, \end{aligned}$$

where the symbol  $\langle \dots \rangle_0$  denotes the thermal average with the Hamiltonian  $H_0$ .

We shall now consider the case of ferromagnetic ordering with  $J > 0$  and  $Q > 0$ . At low values of  $\kappa = Q/J$  the biquadratic exchange does not alter the nature of the phase transition, but simply lowers  $T_C$ . This lowering of the Curie point is due to the tendency of the biquadratic exchange to establish antiferromagnetic ordering. A ferromagnetic–paramagnetic phase transition is transformed from continuous to abrupt for  $\kappa = \kappa_1(S)$  ranging from 1.5 for  $S = 1$  to  $1.25S^{-2}$  for  $S \rightarrow \infty$  (Refs. 42 and 49–51); a similar result was obtained by a different method in Refs. 53 and 54. The range of existence of a first-order ferromagnetic–paramagnetic phase transition has an upper limit of  $\kappa = \kappa_2(S) \sim (3-4)S^{-2}$  (Ref. 42). A further increase in  $\kappa$  results in a considerable difference in the behavior of magnetic materials with  $S = 1$  and  $S > 1$ . The special nature of the

case  $S=1$  is due to the fact that this is the limiting value of the spin from which the biquadratic exchange becomes possible.

If  $S > 1$  and  $\kappa$  is not very much greater than  $\kappa_2$ , an increase in temperature results in a first-order phase transition from a ferromagnetic to a statistical quadrupole state with  $m=0$  but  $q > 0$ . Then, a first-order transition from the quadrupole to a paramagnetic state takes place. Its abruptness is a consequence of the symmetry properties of the system<sup>50</sup>: the parameter  $q$  transforms in accordance with the representation  $D_2$  of the complete group of rotations because a quadrupole is a tensor. A symmetric cube of this representation contains a unit representation.<sup>55</sup>

Finally, if  $\kappa > \kappa_3$ , where  $\kappa_3/\kappa_2$  varies from 1.74 for  $S=2$  to 1.91 for  $S \rightarrow \infty$ , a phase transition from a ferromagnetic to a statistical quadrupole state becomes of the second order (but a transition from a quadrupole to a paramagnetic state is still of the first order),<sup>42</sup> as shown in Fig. 1. Physically, this change in the nature of the phase transition from the first to the second order can be explained by the fact that in the limit  $K/I \rightarrow \infty$  the system becomes an analog of an Ising material. However, in the Ising model an order-disorder phase transition is always of the second order.

If  $S=1$  and the exchange mechanism is isotropic biquadratic, a phase transition from a ferromagnetic to a statistical quadrupole state is impossible, contrary to the conclusion reached in Ref. 40. The real situation is as follows<sup>42, 49, 51</sup>: if  $\kappa < \kappa_2 = 3$ , the ground state is ferromagnetic. When temperature is increased, a paramagnetic state is reached by a second-order phase transition if  $\kappa < \kappa_1 = 1.5$  and by a first-order transition if  $\kappa_1 < \kappa < \kappa_2 = 3$ . If  $\kappa > 3$  (i.e., if  $K > 1$ ), then the self-consistent field approximation predicts, in full agreement with the results of the spin-wave approximation,<sup>42</sup> that a ferromagnetic state is unstable even in the limit  $T \rightarrow 0$ . Cooling gives rise to a phase transition from a paramagnetic state to a state with  $m=0$  and  $q < 0$ , i.e., to a quantum quadrupole state (Fig. 2). It is possible that more rigorous calculations would reveal also a quantum quadrupole state in the phase diagrams of magnetic materials with  $S=2, 3, \dots$

An attempt to construct a phase diagram for the  $K < 0$  case is made in Ref. 51 but it is not fully justified because of lack of allowance for the possibility of canted antiferromagnetic ordering. The properties of mag-

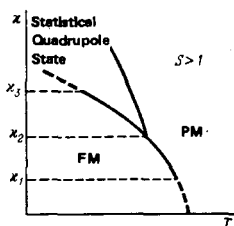


FIG. 1. Phase diagram of a ferromagnet with biquadratic exchange in the  $S > 1$  case. The continuous curves correspond to first-order transitions and the dashed curves correspond to second-order transitions.

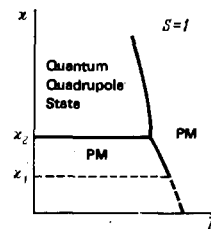


FIG. 2. Phase diagram of a ferromagnet with biquadratic exchange in the case when  $S=1$ . The notation is the same as in Fig. 1.

netic materials with a strongly anisotropic exchange are also analyzed in Refs. 49, 51, and 56–59 in the self-consistent field approximation.

The properties of the systems described by the Hamiltonians (2.4) and (2.5) have also been studied by other methods but they are usually less reliable than the self-consistent field approximation. This applies to the constant coupling method<sup>53, 54</sup> in which a change in the nature of the ferromagnetic-paramagnetic phase transition is observed on enhancement of the biquadratic exchange, but a quadrupole phase is not obtained. Decoupling of higher Green's functions in different variants of the Green's function method is used in Refs. 60–66 but the correctness of this procedure is difficult to establish in the absence of a small parameter.

The sign of the paramagnetic Curie temperature  $\Theta$  for systems exhibiting an order-disorder phase transition of the first order is important from the conceptual point of view. A direct calculation carried out using Eq. (2.2') shows that

$$\Theta = \Theta_0 \left(1 - \frac{K}{2I}\right), \quad \Theta_0 = 2IS(S+1). \quad (2.10)$$

Since the relative strength of the biquadratic exchange is governed by  $KS^2/I$ , it follows from Eq. (2.10) that in the limit of the classical spin when  $S \rightarrow \infty$  and  $K \rightarrow 0$ , and for comparable values of  $I$  and  $KS^2$  the biquadratic exchange does not influence the paramagnetic Curie temperature of a magnetic material. The expression (2.10) agrees with the results of Refs. 67–69. If  $S=1$ , this expression reduces to that for  $T_c$  obtained in Ref. 50. It should be stressed that in contrast to  $T_c$ , the value of  $\Theta$  retains its meaning even in the case when a second-order phase transition changes to a first-order transition or ferromagnetic ordering is altogether impossible.

It follows from Eq. (2.10) that throughout the range of stability of paramagnetic ordering the paramagnetic Curie temperature is positive and the function  $\chi(q)$  of Eq. (2.2) is maximal when  $q=0$ . Therefore, irrespective of whether a ferromagnetic-paramagnetic phase transition is of the first or second order, it should be classified as an order-proper disorder phase transition. If  $S=1$ , the positive nature of  $\Theta$  in the range  $I < K < 2I$  demonstrates the existence of a short-range ferromagnetic order in a quantum quadrupole phase, whereas the negative sign of this temperature in the  $K > 2I$  case is evidence of a short-range antiferromagnetic order.

Attempts have been made to investigate the properties

of magnetic materials with the biquadratic exchange by the method of high-temperature expansions.<sup>3,4,70,71</sup> This approach can give important information on second-order phase transitions but in systems with the biquadratic exchange they frequently reduce to first-order transitions and, therefore, the usual formulation of the problems—determination of the critical point and critical indices—is now meaningful only for some values of  $K/I$ . Moreover, the corresponding series have not been always analyzed correctly. For example, three terms of the series for  $\chi$  and  $T_C$  are calculated in Ref. 3 from the condition  $\chi^{-1} = 0$ , i.e., the critical index of  $\chi$  is automatically assumed to be 1. However, even when an analysis is self-consistent the presence of biquadratic terms gives rise to serious mathematical difficulties which prevent obtaining reliable conclusions from the calculations. Therefore, work on high-temperature expansions has not resulted in significant progress in studies of non-Heisenberg magnetic materials.

A new feature (compared with the Heisenberg case) has been a study of the quadrupole susceptibility  $\chi_Q$  investigated for  $S = 1$  and defined as the change in the quadrupole moment in a virtual quadrupole field applied to a system.<sup>70,71</sup>

### c) Experimental results

We must begin by noting the absence of reliable experimental data that would confirm the existence of quadrupole phases. It was suggested in Ref. 72 that they appear in rare-earth pnictides with the NaCl structure. The existence of the second phase transition several degrees higher than the magnetic ordering point is typical of these compounds. For example, DySb exhibits an abrupt tetragonal distortion of the lattice at  $T^* = 11.5^\circ\text{K}$  and then at  $T_N = 9.5^\circ\text{K}$  an antiferromagnetic order is established (Ref. 73).<sup>1)</sup> In the case of CeSb, whose unique properties below  $T_N = 16^\circ\text{K}$  will be discussed in Sec. 4, the value of  $T^*$  is  $19.5^\circ\text{K}$ . According to Ref. 72, the lattice distortion may be due to the appearance of a quadrupole order. However, the absence of such distortion in the lattice of GdSb, where the  $\text{Gd}^{3+}$  ions (in contrast to  $\text{Dy}^{3+}$  and  $\text{Ce}^{3+}$ ) have no orbital momentum, suggests that the cooperative Jahn-Teller effect is observed in DySb and CeSb. We have mentioned above also the suggestions of the existence of a quadrupole phase transition in  $\text{DyVO}_4$  (Ref. 51). It is possible that the quadrupole phase transition and the cooperative Jahn-Teller effect, although not necessarily equivalent, always seem to occur together.

Order-disorder phase transitions of the first order are observed quite frequently in magnetic materials (see, for example, Ref. 26) and the problem is to determine their true origin. Frequently, a first-order phase transition is explained by a finite compressibility of the lattice.<sup>74-76</sup> As shown in Sec. 1, this mechanism is essentially equivalent to the special case of

the biquadratic and multispin exchange mechanisms, so that no special analysis is needed. A real alternative to the non-Heisenberg mechanism of first-order phase transitions discussed in Sec. 1 is the fluctuation mechanism.<sup>77-80</sup> According to Refs. 77-80, the Landau-Ginzburg-Wilson Hamiltonian of some magnetic structures does not have a fixed point, which is interpreted as the transformation of a first-order into a second-order phase transition because of the growth of critical fluctuations. However, it has recently been suggested<sup>80</sup> that the absence of a fixed point need not be manifested by an abruptness of a phase transition: other singularities are also possible. This conclusion has been drawn from an analysis of the experimental data on antiferromagnetic  $\text{NdSn}_3$  whose order parameter varies continuously at the phase transition but the residue of the short-range order can be detected well above  $T_N$ .

The conclusion that the absence of a fixed point does not always result in a first-order transition is in agreement with the continuity of the phase transitions in CeSe and CeTe established in Ref. 162. This can be also explained<sup>81</sup> by assuming that the fixed point is almost stable in the case of cubic crystals. The experimental results reported below demonstrate that, in some cases when there is no fixed point and a first-order phase transition is observed experimentally, this transition can be explained not only by fluctuations but also by a non-Heisenberg mechanism.

In fact, according to Refs. 77-80 a first-order phase transition should be exhibited by antiferromagnets with ordering of the MnO type. However, so far the only material in which this has been found in MnO itself<sup>81,82</sup> and weakening of the magnetic scattering of neutrons is accompanied by weakening of the nuclear scattering, indicating major changes in the lattice state.<sup>82</sup> The theory of Refs. 77-80 is in good agreement with the fact that a weak uniaxial stress applied to a MnO crystal makes its phase transition continuous.<sup>83</sup> However, other antiferromagnets with the MnO symmetry do not exhibit a first-order phase transition. Therefore, we cannot exclude the possibility that the first-order phase transition in MnO is at least partly due to a strong biquadratic exchange between the Mn ions whose existence has been proved in Ref. 17 (see Sec. 1). This is supported by the first-order phase transition observed in  $\text{MnS}_2$  which is a material of such symmetry that the first-order phase transition cannot be due to critical fluctuations.<sup>84</sup>

Another example is  $\text{UO}_2$  in which the postulated four sublattice antiferromagnetic structure (Sec. 5) should, according to Refs. 77-80, result in a first-order phase transition. On the other hand, it was shown in Ref. 85 and confirmed by an investigation of the magnon spectrum in Ref. 86 that this structure is possible only in the case of a strong non-Heisenberg exchange. Its existence is supported also by calculations<sup>21</sup> (Sec. 1), so that once again we have some doubt about the origin of the first-order phase transition. The situation is complicated further by possible displacements of the oxygen ions at the phase transition occurring without a change in the crystal volume.<sup>87,88</sup> This displacement

<sup>1)</sup> According to G. A. and K. A. Gehring,<sup>167</sup> the compound DySb undergoes not two but one phase transition.

can also give rise to a first-order phase transition. Finally, we must bear also in mind the possibility<sup>89</sup> that  $\text{UO}_2$  is a singlet magnetic material with a low-lying triplet (it is assumed in Ref. 21 that, conversely, the triplet is below the singlet). According to Ref. 89, the Heisenberg exchange splits a triplet so that its lower component is below a singlet. Therefore, a magnetic triplet state is then preferred for energy reasons to a nonmagnetic singlet state. However, as the temperature is increased the sublattice magnetization decreases and the lower component of the triplet rises above the singlet. This gives rise to a first-order phase transition to a nonmagnetic state.

The theory of Ref. 52 predicting a first-order phase transition for magnetic materials with the four-spin interaction of the (2.5) type is in good agreement with the results on  $^3\text{He}$ , in which the biquadratic or three-spin exchange are impossible because the nuclear spin is  $1/2$ . It is interesting to note that according to the data of Sec. 4, an order-disorder phase transition of the first order has been observed for many materials with structures that cannot be described by the Heisenberg model ( $^3\text{He}$ ,  $\text{EuSe}$ ,  $\text{CeSb}$ ,  $\text{CeBi}$ ,  $\text{UAs}$ , etc.) indicating a connection between the abrupt nature of a phase transition and the non-Heisenberg exchange. At least some of these materials (for example,  $\text{UAs}$ ) exhibit an order-improper disorder phase transition.

### 3. ORDER-ORDER AND ORDER-IMPROPER DISORDER PHASE TRANSITIONS AND METAMAGNETISM. GENERAL ANALYSIS

This and the subsequent two sections are devoted to various aspects of order-order phase transitions. The present section will deal with the general aspects of this phenomenon and also with order-improper disorder phase transitions which appear instead of order-order phase transitions if the temperature is sufficiently high.

A phase transition accompanied by a change in the magnetic order occurs in very many materials (see, for example, Ref. 26). The simplest phase transition of this kind is from an antiferromagnetic to a ferromagnetic state. It was explained by Kittel on the basis of the exchange inversion concept according to which the thermal expansion of the lattice alters the sign of the exchange integral.<sup>19</sup> This explanation, if valid at all, applies to a very limited class of magnetic materials with high-temperature phase transitions. In fact, the linear expansion coefficient  $\alpha = d \ln a / dT$  of metals is  $\sim (1-2) \times 10^{-5} \text{ }^\circ\text{K}^{-1}$ , whereas for ionic crystals it is  $\sim (1-5) \times 10^{-5} \text{ }^\circ\text{K}^{-1}$ . However, typical values of  $\lambda = d \ln I / d \ln a$  are  $\sim 5-6$ , which is true, for example, of  $\text{EuO}$  and  $\text{EuS}$  (Ref. 90). Record values of this quantity, amounting to  $\sim 50-100$ , are exhibited by  $\text{DyGd}$  alloys, which therefore have a giant magnetostriction.<sup>91</sup> Even if we consider the highest values of  $\alpha$ , in the case of ionic crystals such inversion of the sign of the exchange integral can occur only at  $T_i \sim 10^3-10^4 \text{ }^\circ\text{K}$ . For the record value of  $\lambda = 100$  this inversion can occur at  $T_i \sim 10^2-10^3 \text{ }^\circ\text{K}$ , but so far such values of  $\lambda$  and of giant magnetostriction have not yet been observed for other

materials exhibiting order-order phase transitions. Moreover, in many of these materials this phase transition occurs at very low temperatures, for example, in the case of  $\text{EuSe}$  there is a whole series of phase transitions at temperatures below  $4.6 \text{ }^\circ\text{K}$  (Sec. 4). Therefore, it is clear that purely magnetic mechanisms of order-order phase transitions are more realistic and these are not related to the thermal expansion of the lattice. An example of such a mechanism in the case of phase transitions from canted to collinear structures is given in Ref. 92: the evidence is a complex temperature dependence of the magnetic anisotropy which is very strong in the case of rare-earth metals.

Isotropic systems with an exchange mechanism which is very different from the Heisenberg type may exhibit order-order phase transitions because of the difference between the temperature dependences of the Heisenberg and non-Heisenberg exchange. Consequently, the high-temperature properties may be governed by the former and the low-temperature properties by the latter. For example, in the case of the four-spin exchange of Eq. (2.5), when the inequality  $K_{-} > 0$  is obeyed, a crystal may be ferromagnetic in the ground state if the effective exchange integral is  $I_{-} + 2K_{-}S^2 \equiv \bar{I}(0) > 0$  and antiferromagnetic for the opposite sign<sup>52</sup>; here,

$$I_{-} = \sum_{\mathbf{g}} I(\mathbf{f}-\mathbf{g}), \quad K_{-} = \sum_{\mathbf{g}, \mathbf{h}, \mathbf{k}} K(\mathbf{f}, \mathbf{g}, \mathbf{h}, \mathbf{k}), \quad K_{+} = \sum_{\mathbf{g}, \mathbf{h}, \mathbf{k}} K(\mathbf{f}, \mathbf{g}, \mathbf{h}, \mathbf{k}). \quad (3.1)$$

In the expression for  $I_{-}$  the summation is over atoms  $\mathbf{g}$  from the sublattice other than that containing an atom  $\mathbf{f}$ , and in the expressions for  $K_{-}$  and  $K_{+}$  the  $\mathbf{f}$  and  $\mathbf{g}$  atoms belong to different sublattices, whereas the  $\mathbf{h}$  and  $\mathbf{k}$  atoms belong to the different and the same sublattices, respectively.

At finite temperatures the spin  $S$  in the expression for  $\bar{I}$  is replaced by its average value  $S(T)$ . We shall assume that  $|I_{-}| < 2S^2|K_{-}|$  and that  $I_{-}$  and  $K_{-}$  have the opposite signs. Then, when temperature is increased the quantity  $\bar{I}(T) = I_{-} + 2K_{-}S^2(T)$  should experience reversal of its sign, i.e., an antiferromagnetic-ferromagnetic phase transition should take place.

This "non-Heisenberg" phase transition mechanism was first investigated in detail using the model with the Heisenberg and three-spin exchange  $\sim (S_1 S_2)(S_2 S_3)$  (Refs. 93 and 94) and a model with the four-spin exchange.<sup>174</sup> Moreover, this mechanism makes it possible to explain low-temperature phase transitions and it has that advantage over the exchange inversion theory of Kittel that it can explain a phase transition between complex structures which are impossible in the Heisenberg model (Secs. 4 and 5).

The possibility of occurrence of an antiferromagnetic-ferromagnetic phase transition is proved in Refs. 93, 94, and 174, together with the possibility of a phase transition from an antiferromagnetic state directly to a paramagnetic state characterized by a short-range ferromagnetic order (the definition of the short-range order is given in Sec. 2). As a generalization of this result Nagaev and Kovalenko introduced in Refs. 93, 94, and 174 the concept of an order-improper disorder

phase transition applicable not only to magnetic but also to other materials. Its origin in the case of non-Heisenberg magnetic materials can be explained physically as follows: for certain ratios of the parameters of the bilinear and three- or four-spin exchange the temperature of an antiferromagnetic-ferromagnetic transition becomes so high that a long-range ferromagnetic order cannot exist at this temperature and only the short-range ferromagnetic order remains.

It is usual to assume as self-evident that heating of an isotropic antiferromagnet results in a transition to a paramagnetic state with a negative paramagnetic Curie temperature  $\Theta$ , whereas heating of a ferromagnet produces a transition to a state with a positive  $\Theta$ . According to Eq. (2.2') the sign of  $\Theta$  is the same as that of binary correlation functions of the neighboring atoms describing the short-range magnetic order. Therefore, the negative sign means that the destruction of the long-range antiferromagnetic order still leaves a residue of the short-range antiferromagnetic order, whereas the positive sign of  $\Theta$  implies that the remaining short-range order is ferromagnetic. Similarly, in other cases when order-disorder phase transitions are discussed, it is understood that above the transition point the short-range order is of the same type as the long-range order below the transition point (this is known as proper disorder; see Sec. 2).

The existence of order-improper disorder phase transitions makes it necessary to review these conclusions. For example, if such a transition occurs in an isotropic antiferromagnet, its paramagnetic Curie temperature may not be negative but positive;<sup>2)</sup> in the case of a ferromagnet it may be negative. In general, an order-improper disorder phase transition is characterized by noncoincidence of the long- and short-range order vectors [see Eq. (2.1)] below and above the transition point, respectively. It does not always result in an anomaly of the sign of  $\Theta$ , for example, in the case of UAs. Such phase transitions are necessarily of the first order, whereas order-proper disorder phase transitions may be of the first or second order.

The question of the nature of the short-range order above the point of disappearance of the long-range order is very important since many properties of crystals are not determined by the long-range order but by the short-range one. One example has already been given: it is the paramagnetic susceptibility of strong magnetic materials. Other properties which are governed by the short-range order include the electrical and optical. In particular, the position of the optical absorption edge of magnetic semiconductors and insulators depends very strongly on the short-range order.

<sup>2)</sup> To avoid misunderstanding, it must be stressed that this effect has nothing in common with the positive nature of  $\Theta$  in the case of layer antiferromagnets characterized by a strong ferromagnetic exchange within the layers. In the latter case the sign of  $\Theta$  reflects the short-range ferromagnetic order inside the layers. It is also of the type that ensures a long-range order within the layers below the Néel point.

## Nearest-neighbor approximation

We shall consider an antiferromagnet in which only the interaction between the nearest neighbors is important. We shall show that we can have an order-improper disorder transition in this case and that the short-range order vector  $\mathbf{q}_{SO}$  above  $T_N$  has the components (0, 0, 0), whereas the long-range order vector  $\mathbf{q}_{LO}$  below  $T_N$  is  $(\pi/a, \pi/a, \pi/a)$  (order-commensurate disorder transition). According to the results given in Sec. 4, if allowance is made also for the interaction of the second-nearest neighbors, the vector  $\mathbf{q}_{SO}$  may have an arbitrary value (order-incommensurate disorder phase transition). We shall use the nearest-neighbor approximation to show that metamagnetism may appear in isotropic antiferromagnets.

We shall assume that a magnetic material consists of equivalent magnetic atoms with the spin  $S$  forming a simple cubic lattice with the constant  $a$ . The Hamiltonian of the system is selected in the form ( $\mathcal{H}$  is the magnetic field)

$$H = -\mathcal{H} \sum S_k^z - \frac{I}{2} \sum (S_k S_{k+\Delta}) - \frac{K}{2} \sum_{\Delta' \neq \pm \Delta} (S_k S_{k+\Delta}) [(S_{k+\Delta} S_{k+\Delta'}) + (S_k S_{k+\Delta+\Delta'})]. \quad (3.2)$$

The three-spin term in Eq. (3.2) must satisfy not only the self-evident requirement that all the three atoms should be as close to one another as possible, but also another requirement which is of fundamental importance in our case: like the Heisenberg term, its sign changes when ferromagnetic order becomes modified to chessboard antiferromagnetic. The three-spin terms of the  $(S_k S_{k+\Delta}) \times (S_{k+\Delta} S_{k+\Delta'})$  type which do not have this property are not included in the Hamiltonian (3.2). We shall consider the case when the Heisenberg and three-spin exchange in Eq. (3.2) have opposite signs with  $I > 0$  and  $K < 0$ , and the latter exchange is stronger than the former. For these relationships between the parameters the energy of an anti-ferromagnetic state  $E_{AF}$  is less than the energy of a ferromagnetic state  $E_{FM}$ .

High-temperature expansions allow us to determine the nature of the short-range order at high temperatures. Applying the Kubo formula (2.2), we find that in the limit of classically large spins

$$\tilde{\beta}^{-1} \chi \approx \frac{S^2}{3} \left\{ 1 + \frac{\tilde{\beta}}{3} \left( 1 - \frac{k}{3} \right) + \tilde{\beta}^2 \left[ \frac{5}{24} \left( 1 - \frac{k}{3} \right)^2 - \frac{k}{81} + \frac{101 k^2}{19440} \right] \right\}, \quad (3.3)$$

$$\tilde{\beta} = \frac{J}{T}, \quad k = \frac{1}{J} \tilde{k}, \quad J = zIS^2, \quad \tilde{K} = 2z(z-2)KS^4.$$

It follows from Eqs. (3.3) and (2.2) that even at  $T=0$  an antiferromagnetic state is stable and at high temperatures the correlation functions for the nearest neighbors may be positive, i.e., the short-range order is ferromagnetic. The paramagnetic Curie temperature (2.2') deduced from Eq. (3.3) is

$$\Theta = \frac{J}{3} \left( 1 - \frac{k}{3} \right). \quad (3.4)$$

The condition for a crystal to be antiferromagnetic at  $T=0$  and for its paramagnetic Curie temperature to be

positive at high temperatures is  $1 < k < 3$ . For comparison, we should mention that in the case of the four-spin exchange the value of  $\Theta$  is governed only by the Heisenberg part of the Hamiltonian (2.5) and in a similar situation when  $I_{-} > 0$  and  $K_{-} < 0$  the value of  $\Theta$  is always positive.

In principle, the transition from the antiferromagnetic long-range order to the ferromagnetic short-range order can occur in two ways: 1) by a phase transition from an antiferromagnetic to a ferromagnetic state followed by a transition to a paramagnetic state; 2) by a direct antiferromagnetic-paramagnetic state.

The fact that, in principle, a direct antiferromagnetic-paramagnetic phase transition with  $\Theta > 0$  is possible can be demonstrated simply by estimating the Curie temperature of a ferromagnetic state and showing that for certain relationships between the parameters it is so low that the free energy of the antiferromagnetic state  $F_{AF}(T_C)$  is close to  $E_{AF}$  and much lower than the free energy of the ferromagnetic state  $F_{FM}$ , which varies between  $T = 0$  and  $T = T_C$  from  $E_{FM}$  to a value  $\sim (-T_C)$ . According to Eq. (3.4), this is also true for values of  $k$  close to 3. In fact, if a ferromagnetic state does exist at all for such values of  $k$  that  $\Theta \sim 0$ , then its Curie temperature even if not equal to  $\Theta$  should also approach zero. Therefore, we have  $F_{AF}(T_C) \ll F_{FM}$ , i.e., when  $k \sim 3$  a ferromagnetic state cannot indeed form.

In those cases when a second-order ferromagnetic-paramagnetic phase transition takes place, we can use the expansion of Eq. (3.3) and the method of ratios or of the Padé approximants<sup>95</sup> to find the critical index  $\gamma[\chi \propto (T - T_C)^{-\gamma}]$ . It is found that the three-spin exchange increases  $\gamma$ . For example, if  $k = 1.2$ , the value of  $\gamma$  is 2.2 times greater than for a Heisenberg ferromagnet.

More detailed information on the properties of such a system can be obtained using the self-consistent field approximation and introducing, as in Eq. (2.9), the dipole and quadrupole fields. The general relationships can be deduced from Fig. 3, which shows the results of numerical calculations for the cases  $k = 1.5$  (continuous curves) and  $k = 1.8$  (dashed curves) in the  $S = 7/2$  case. The upper of the two lines corresponding to a given value of  $k$  represents the temperature dependence of the antiferromagnetic order parameter  $S_{AF}$ , whereas the lower curve represents the same dependence for the ferromagnetic order parameter  $S_{FM}$  ( $\tau = T/zIS^2$ ). The free energy of the ferromagnetic order  $F_{FM}$  is negative at all temperatures,  $\tau < \tau_C$ , whereas the free energy

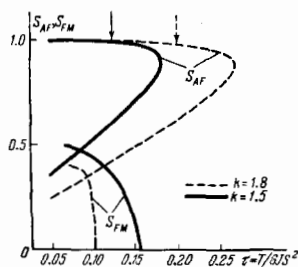


FIG. 3. Temperature dependences of the order parameters of a magnetic material with three-spin exchange.<sup>95</sup>

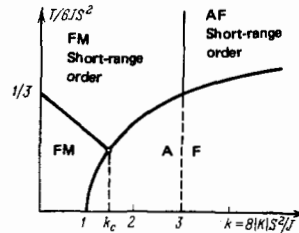


FIG. 4. Qualitative phase diagram of a magnetic material with three-spin exchange.

of the antiferromagnetic order  $F_{AF}$  is negative only in that part of the  $S_{AM}(\tau)$  curve which lies to the left of the arrow. To the right of the arrow the antiferromagnetic state is known to be unstable (at a temperature  $\tau_p$  corresponding to the arrow the free energies of the antiferromagnetic and paramagnetic states become equal). For  $k = 1.5$  ( $\tau_p = 0.123 < \tau_C$ ), a first-order antiferromagnetic-ferromagnetic phase transition occurs first for  $\tau_f = 0.12$  and then when  $\tau_C = 0.153$  a second-order transition takes place to the paramagnetic state.

However, if  $k = 1.8$  ( $\tau_p = 0.198 > \tau_C = 0.1$ ), there is no stability region of the ferromagnetic state and the first-order phase transition takes place directly from the antiferromagnetic to the paramagnetic state. In the interval between 1.5 and 1.8 there is a value of  $k_C$  corresponding to the triple point:  $\tau_f = \tau_C$ . In order to show that the ferromagnetic state is characterized by a short-range ferromagnetic order also in the  $k > k_C$  case, when a transition from the antiferromagnetic to the paramagnetic states takes place, it is sufficient to calculate the paramagnetic Curie temperature  $\Theta$ . In the case of  $\Theta$  we obtain an expression which is identical with Eq. (3.4) and positive if  $k < 3$ . If  $k > 3$ , a first-order antiferromagnetic-paramagnetic phase transition takes place and it results in an antiferromagnetic short-range order. We can summarize these results by plotting a qualitative  $k$ - $\tau$  phase diagram (Fig. 4).

Materials exhibiting a first-order phase transition from an antiferromagnetic long-range order to a ferromagnetic short-range order have another interesting property: they are isotropic metamagnets. This is indicated by the results of numerical calculations for the same value  $k = 1.8$  as before but at a temperature  $\tau = 0.19$ , which lies below the transition point (Fig. 5). Right up to a field  $\mathcal{H}_M = 0.082IzS^2$  the magnetization increases continuously with the field because of a reduction in the angle  $2\varphi$  between the sublattice moments. However, in the field  $\mathcal{H}_M$  there is an abrupt phase tran-

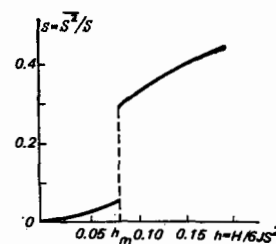


FIG. 5. Magnetization of an isotropic metamagnet with three-spin exchange plotted as a function of the field.

sition from the two-sublattice to the one-sublattice order. At the same time the magnetization increases approximately fivefold.

Expressions for the susceptibility  $\chi$  of an antiferromagnet with the four-spin and biquadratic exchanges are obtained in Refs. 52 and 43. It follows from them that an increase in the field should make  $\chi$  larger and at some value of the field the susceptibility should be its critical value the two-sublattice structure changes abruptly to the one-sublattice form, i.e., a metamagnetic transition takes place. In the biquadratic exchange case the condition for this to happen at  $T = 0$  is found from the relationship

$$\chi \sim [6I + 2(2 + 3 \cos \varphi)(2S - 1)^2 K]^{-1}$$

with  $I < 0$  and  $K > 0$ ;  $\varphi$  is the angle between the field and the sublattice moment. These results are interesting because they are in conflict with the generally accepted idea that metamagnets are materials with a very strong magnetic anisotropy. It should be pointed out that if a ferromagnet undergoes a first-order transition to a paramagnetic state, the magnetic field above the transition point may cause its magnetization to rise abruptly.<sup>52</sup> Isotropic metamagnetism is possible also in the model with the double Heisenberg Hamiltonian describing Jahn-Teller systems.<sup>170</sup>

An example of an isotropic metamagnet is EuSe (Sec. 4). Its magnetic properties are more complex than those derived on the basis of the model used in Sec. 4 (the existence of two critical fields with two magnetization jumps instead of one is demonstrated above). However, the important fact is that allowance for the non-Heisenberg exchange is sufficient to explain the metamagnetism of isotropic materials.

#### 4. COLLINEAR MULTISUBLATTICE STRUCTURES. SEQUENCES AND DEVIL'S LADDERS OF PHASE TRANSITIONS

##### a) Sequences of order-order and order-improper disorder phase transitions (experimental results)

Experimental results show that many magnetic materials with a very simple crystal structure (of the NaCl or CsCl type) have at the same time very complex and unusual magnetic properties: their magnetic structures cannot be explained by the Heisenberg model and when temperature or an external magnetic field is varied, they undergo phase transitions or sequences of transitions between various commensurate structures. Such anomalous properties are exhibited not only by crystals with a strong magnetic anisotropy but also by crystals with a very weak anisotropy. In this respect the magnetic semi-conductor EuSe with the NaCl structure is characteristic. The  $\text{Eu}^{2+}$  ions in this compound do not have an orbital angular momentum and the anisotropy field is only 100 Oe (Ref. 90).

Magnetic ordering of EuSe has been investigated<sup>96-109</sup> using various experimental methods, including neutron diffraction and NMR. The results are summarized by the phase diagram in Fig. 6: all the magnetic struc-

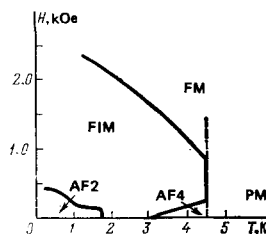


FIG. 6. Phase diagram of EuSe (Ref. 97).

tures occurring in EuSe can be represented by a set of ferromagnetic (111) planes whose angular momenta are parallel or antiparallel to one another.

If the field is  $\mathcal{H} = 0$ , the transition from the paramagnetic to the antiferromagnetic state at the Néel point  $4.6^\circ\text{K}$  produces an unusual structure: the ferromagnetic planes form four equivalent sublattices with the  $(+ + - -)$  order. Cooling to  $2.8^\circ\text{K}$  alters this order abruptly to a "ferrimagnetic" (FIM) state with a finite but unsaturated magnetic moment. This state is assumed to consist of two phases: one phase is the usual two-sublattice antiferromagnetic of the MnO type, i.e.,  $(+ -)$ , whereas the other phase is a magnetized three-sublattice ferrimagnet  $(+ + -)$ . The phases are present in the ratio 5:13. Therefore, the resultant moment per each  $\text{Eu}^{2+}$  ion is not  $7 \mu_B$  but only  $1.68 \mu_B$ . The results of magnetic and dilatometric investigations<sup>103</sup> indicate that at  $1.8^\circ\text{K}$  there is a phase transition to a completely antiferromagnetic state with ordering different from  $(+ + - -)$ . According to the neutron-diffraction data,<sup>99</sup> the ferrimagnetic  $(+ + -)$  state coexists near the transition point at  $1.9^\circ\text{K}$  with the antiferromagnetic  $(+ -)$  state and it is that state that should occur below the transition point. Additional confirmation that below  $1.8^\circ\text{K}$  the antiferromagnetic order is of the MnO type is reported in Ref. 107: cooling below  $1.8^\circ\text{K}$  makes the Faraday rotation spectra of EuSe of the same type as those of EuTe, which has the magnetic structure of MnO.

In the range of stability of the antiferromagnetic states a weak magnetic field transforms a crystal first to the ferrimagnetic and then to the ferromagnetic state. A study of the Mössbauer effect<sup>96</sup> has shown that the order-disorder phase transition at  $4.6^\circ\text{K}$  is of the first order, in agreement with the experimental NMR data.<sup>106</sup>

It should be pointed out that the phase diagram of Fig. 6 may oversimplify the behavior of EuSe in magnetic fields. According to Ref. 108, the temperature derivatives of the anisotropy constants exhibit anomalies below  $T_N$  in a field 4 kOe and these anomalies are not compatible with a complete ferromagnetic ordering. At  $1.3^\circ\text{K}$  the magnetization does not reach saturation even in a field  $\mathcal{H} = 19$  kOe (Ref. 108). According to Ref. 106, if the field or temperature is varied cyclically, magnetic phase transitions exhibit a hysteresis. There is some intermediate phase between the ferrimagnetic and ferromagnetic states.

Data from an unpublished thesis<sup>104</sup> which do not agree fully with the phase diagram of Fig. 6 are quoted in Refs. 110 and 111. However, we must bear in mind

that these data were obtained for samples containing 1–5% Sn, i.e., for crystals which were strongly defective. It is known that defects have a very strong influence on the properties of EuSe. For example, the presence of defects may destroy completely the magnetic polymorphism of EuSe crystals.<sup>112</sup> Therefore, the results quoted in Refs. 110 and 111 are not sufficiently reliable to regard them as applicable to pure EuSe.

A comparison of the experimental results reported by different authors shows that EuSe exhibits an order-improper disorder phase transition. In fact, according to Ref. 96, the long-range magnetic order in EuSe disappears abruptly, in contrast to other Eu chalcogenides. In the paramagnetic state the value of  $\Theta$  of EuSe is positive ( $\Theta = 9^\circ\text{K}$  according to Refs. 90 and 97), whereas for the isomorphous antiferromagnet EuTe this temperature is negative. It is suggested in Ref. 96 that the positive paramagnetic Curie temperature of  $\Theta$  of EuSe is due to donor defects near which the indirect exchange via a donor electron gives rise to a ferromagnetic order (localized ferrons whose existence is demonstrated in Ref. 175). Bearing in mind this possibility, we shall quote additional evidence in support of the conclusion that the ferromagnetic short-range order in the paramagnetic temperature range is not due to defects but is an intrinsic property of the perfect EuSe crystal. Firstly, the Mössbauer spectra show that above the antiferromagnetic-paramagnetic transition point there is a ferromagnetic short-range order.<sup>98</sup> If this order had been associated with localized ferrons, as assumed in Ref. 96, it would have existed at all temperatures below  $T_N$ .

Secondly, in the paramagnetic region the result of cooling is a very strong red shift of the optical absorption edge  $E_g$  which disappears below  $T_N$  (Fig. 7 taken from Ref. 97). A giant red shift of  $E_g$  is typical of ferromagnetic semiconductors: it occurs both above and below  $T_C$  and it is due to the establishment of a ferromagnetic order, first of the short-range type and then of the long-range form.<sup>23</sup> On the other hand, in the case of isotropic antiferromagnetic semiconductors there is no red shift above or below  $T_N$ . Such antiferromagnets exhibit a weak blue shift. In particular, the red shift is not exhibited by the antiferromagnet EuTe, whereas the ferromagnets EuO and EuS are characterized by a very strong red shift. The attribution of the red shift of EuSe above  $T_N$  to the ferromagnetic short-range order is supported also by the following

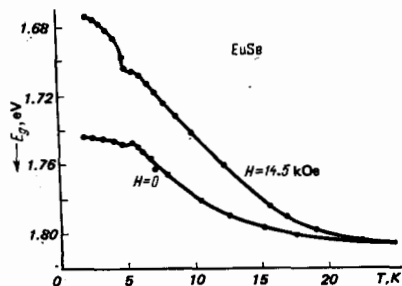


FIG. 7. Temperature dependences of the optical absorption edge ( $E_g$ ) of EuSe (Ref. 97).

observation: a magnetic field which establishes the ferromagnetic order enhances the red shift (Fig. 7). These data are insufficient to find the short-range order vector  $q_{SO}$  above  $T_N$ : it is not necessarily equal to  $(0, 0, 0)$  because even for an arbitrary  $q_{SO}$  there is some degree of local ferromagnetic order in a distance equal to the correlation length. However, the disappearance of the red shift below  $T_N$  can apparently be explained only by the difference between the long-range order vector  $q_{LO}$  from  $q_{SO}$ , i.e., by an order-improper disorder phase transition. It would be desirable to resolve this question by neutron diffraction.

A collinear four-sublattice antiferromagnetic structure apparently occurs also in another isotropic magnet which is solid  $^3\text{He}$  with the bcc structure. The results of an investigation of nuclear antiferromagnetic resonance<sup>113</sup> are in agreement with an antiferromagnetic order representing ferromagnetic  $(111)$  planes whose moments are arranged in the sequence  $(+ + - -)$ , but these resonance data do not exclude the possibility of even more exotic structures. At  $T_N = 0.002^\circ\text{K}$  a first-order phase transition takes place from an antiferromagnetic to a paramagnetic state. Helium also exhibits phase transitions in a magnetic field whose nature is not yet clear.<sup>114, 115</sup>

Many-sublattice collinear structures are observed also in some metals. For example, in the case of CeBi with the NaCl structure a two-sublattice antiferromagnetic structure of the  $(+ -)$  type with ferromagnetic  $(001)$  layers is established below  $25.2^\circ\text{K}$  and at  $12.5^\circ\text{K}$  this structure changes abruptly to a four-sublattice sequence of the  $(+ + - -)$  type.<sup>116</sup>

Antiferromagnet UAs isostructural with CeBi is particularly interesting; its Néel point  $T_N$  occurs at  $123.5^\circ\text{K}$ . At  $63.5^\circ\text{K}$  it undergoes another transition from a high-temperature two-sublattice antiferromagnetic order to a low-temperature four-sublattice configuration.<sup>117-119</sup> The most important point is that UAs is the first material for which the existence of an order-improper disorder phase transition has been established reliably. In fact, as  $T_N$  is approached from the high-temperature side, the intensity of diffuse scattering of neutrons corresponding to the short-range order vector  $q_{SO} = (2\pi/a)(0; 0; 0, 7)$  first rises. However, below  $T_N$  such a modulated state is not observed but there is an abrupt transition to an antiferromagnetic order with the long-range order parameter  $q_{LO} = (2\pi/a)(0; 0; 1)$ , which is evident from Fig. 8 showing the

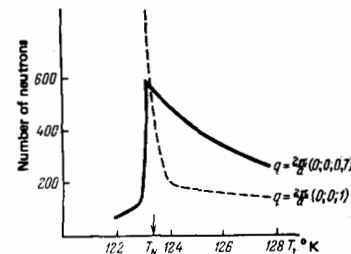


FIG. 8. Temperature dependence of the number of neutrons scattered by UAs (Ref. 120).



temperature dependence of the neutron scattering intensity for the above values of  $q_{SO}$  and  $q_{LO}$  (Ref. 120). According to Refs. 163 and 164 the value of  $\Theta$  for UAs is positive, exactly as for antiferromagnets UP and USb, in which below  $T_N$  only the two-sublattice structure is observed. However, the very large difference between the values of  $\Theta$  obtained in these two investigations suggests that the positive sign of  $\Theta$  is at least partly due to crystal defects. It may also be due to a strong anisotropy of the exchange interaction because of which the exchange between atoms in the (0, 0, 1) planes is ferromagnetic.<sup>165</sup> In any case, in view of the moderately large difference between  $q_{SO}$  and  $q_{LO}$  it is unlikely that the sign of  $\Theta$  for UAs is related to an order-improper disorder phase transition.

The most complex properties among materials of this type are exhibited by CeSb, which is isomorphous with CeBi. Of the numerous investigations of this material we shall mention the latest neutron-diffraction studies. It is reported in Ref. 121 that below  $T_N = 16.2^\circ\text{K}$  there are three magnetic structures. A much greater number of structures is reported in Ref. 122. All these structures are composed of four blocks of ferromagnetic planes with spins parallel to the [001] axis and to spin-free paramagnetic planes (the exact magnetic structure is unknown):  $F_+ \equiv (++)$ ,  $D_+ \equiv (+0-)$  and  $F_-$ ,  $D_-$ , whose moments are directed opposite to those of  $F_+$  and  $D_+$ . The number of planes  $N$  in a unit cell varies in an irregular manner depending on temperature:  $D_+$  has  $N = 3$  at  $16.1-15.9^\circ\text{K}$ ;  $F_+ D_+ D_+ F_+$  has  $N = 13$  at  $15.9-15.3^\circ\text{K}$ ;  $F_+ D_+ F_+$  has  $N = 7$  at  $13.7-11.3^\circ\text{K}$ ;  $F_+ D_+ F_+ F_+ D_+ F_+ F_+$  has  $N = 18$  at  $13.7-11.0^\circ\text{K}$ ;  $F_+ F_+ F_+ D_+ F_+$  has  $N = 11$  at  $11.0-8.9^\circ\text{K}$ . Below  $8.9^\circ\text{K}$  and at least down to  $2.2^\circ\text{K}$  we have the same  $F_+ F_+$  structure with  $N = 4$  as for the other materials discussed in the present section. Thus, CeSb exhibits—like EuSe—a sequence of phase transitions between commensurate structures.

The phase transition at  $T_N$  and all the other first-order phase transitions exhibit a strong hysteresis. The application of a magnetic field transforms paramagnetic planes to a magnetized state. According to Ref. 123, an increase in the field first induces a transition to a ferrimagnetic state of the  $(+-)$  type, whereas in still stronger fields ( $\sim 40$  kOe) there is a transition to a ferromagnetic state [according to Ref. 121, in weak magnetic fields we can also have a ferrimagnetic state of the  $(+-+-+-)$  type]. Partly ordered layers are observed in the field also at temperatures  $T > T_N$ , but this effect is strongly anisotropic.<sup>123</sup> It has been suggested that near  $T_N$  there is a triple point in sufficiently strong fields, but neutron investigations reported in Ref. 124 have failed to reveal it.

### b) Theory of normal sequences of phase transitions

The first attempt to explain the special magnetic ordering of EuSe was made in Refs. 110 and 111. It was assumed that the spins in the (111) planes are coupled by a strong ferromagnetic interaction. The coupling between the individual planes is weak, because the exchange integral  $I_1$  of an atom with its nearest

neighbor in the nearest plane is almost equal (and opposite in sign) to the integral  $I_2$  of the exchange of an atom with its nearest neighbor in the second-nearest plane. Therefore, the interplanar coupling is governed by the dipole-dipole interaction which stabilizes, in a narrow range of the values of  $I_2 \approx -I_1$ , structures of the antiferromagnet-2 $(+-)$ , ferrimagnet  $(+-)$ , and antiferromagnet-4  $(+-+-)$  type. However, it does not ensure a first-order phase transition between them and to the paramagnetic state.<sup>110</sup> A first-order phase transition is obtained in Ref. 111 when an allowance is made for the fact that a change in the type of order alters the distance between the ferromagnetic layers: in the  $(++)$  configuration it is less than for  $(+-)$ . In fact, only the sublattice magnetization  $\sigma$  was calculated as a function of  $T$  for a structure of the  $(+-+-)$  type using the self-consistent field approximation. In view of the deformability of the lattice the expression for the self-consistent field should contain not only the term  $\sim \sigma$  but also the term  $\sim \sigma^3$ , as in the case of the four-spin interaction [see Eq. (2.8)]. However, it is clear from Eq. (1.5) that the dependence of the exchange integral on the distance between atoms gives rise also to the biquadratic and three-spin terms, i.e., an unjustified replacement of averages of the  $\langle (S_1 S_2)^2 \rangle$  type with those of the  $\langle (S_1^z)^2 \rangle \langle (S_2^z)^2 \rangle$  type is made in Ref. 111. For the parameters employed in Ref. 111 it is not possible to predict an order-disorder phase transition of the first order.

We shall describe a model which makes it possible to reproduce the phase transitions observed in EuSe (Refs. 94 and 125). It is assumed that a magnetic material with  $S \gg 1$  can be divided into planes in which the exchange between atoms is ferromagnetic and that it is sufficient to allow only for the Heisenberg exchange between the nearest neighbors (the integral  $P$  has its normal value). Only the integral of the Heisenberg exchange  $I$  between the nearest neighbors in adjacent planes is anomalously small so that we have to allow also for the Heisenberg exchange of atoms in the second-nearest planes (its integral is denoted by  $V$ ) and for the three-spin exchange when two spins are the nearest neighbors in the same plane and the third belongs to the neighboring plane (it is denoted by the integral  $K$ ). Finally, we introduce the biquadratic exchange between nearest neighbors in adjacent planes, which ensures stability of collinear structures. The complete Hamiltonian of the model is

$$H = -I \sum (S_{gn} S_{g+1, n}) - P \sum (S_{gn} S_{gn+\delta}) - V \sum (S_{gn} S_{g+2, n}) \\ - R \sum (S_{gn} S_{g+1, n})^2 - K \sum [(S_{gn} S_{gn+\delta}) (S_{gn+\delta} S_{g+1, n}) \\ + (S_{g+1, n} S_{g+1, n+\delta}) (S_{g+1, n+\delta} S_{gn})], \quad (4.1)$$

where  $g$  is the number of a plane and  $n$  is the number of an atom in a plane  $g$ ;  $\delta$  labels  $z$ , nearest neighbors of an atoms ( $g, n$ ) in the same plane.

Different collinear structures, which are the only ones admitted by this model, differ in respect of orientations of the moments of the ferromagnetic planes. The parameters in the Hamiltonian (4.1) are selected so that the following structures are preferred for thermodynamic reasons: two Heisenberg structures (one ferromagnet and the other antiferromagnet-2) and

two non-Heisenberg structures (one ferromagnet and the other antiferromagnet-2) and two non-Heisenberg structures (ferrimagnet and antiferromagnet-4). This is done by selecting the following signs of the exchange integrals in Eq. (4.1):  $I > 0, R > 0, V < 0, K < 0$ . This model simplifies somewhat the situation in real EuSe in which the ferromagnetic planes exist for geometric reasons.

Depending on the values of the parameters  $k \approx 2z_1 |K| S^2 / I$  and  $v \approx |V| / I$  at  $T = 0$  we may find that one of the following structures: antiferromagnet-2, antiferromagnet-4, or ferromagnet is preferred for thermodynamic reasons. In particular, antiferromagnet-2 is the ground state for  $k > 2v + 1$ , whereas the ferrimagnetic state cannot be found: if  $k \neq 2v + 1$  its energy exceeds the energy of at least one of the other states (for  $k = 2v + 1$  the energy of the antiferromagnet-2, antiferromagnet-4, and ferrimagnet states are all equal).

Phase transitions between structures are due to, as in Sec. 3, the temperature dependence of the effective integral of the exchange between the nearest neighbors  $\bar{J}$ , which allows for the bilinear and three-spin mechanisms; when the temperature rises, the ratio between  $\bar{J}(\tau)$  and  $V$  and, even the sign of  $\bar{J}(\tau)$ , all change ( $\tau = T / I$ ).

The calculations are made in the self-consistent field approximation in exactly the same way as described in Secs. 2 and 3. The results of these calculations are as follows: the system in question can exhibit a whole sequence of first-order phase transitions. For example, if  $p \approx Pz_1 / I = 0.5$ ,  $r \approx RS^2 / I = 0.5$ ,  $v = 0.5$ , and  $k = 2.1$ , the following sequence of first-order transitions is obtained for EuSe (Fig. 7): at the temperature  $\tau = 0.216$ , there is a transition from the antiferromagnet-2 to the ferrimagnetic state; at  $\tau = 0.378$ , there is a transition from the ferrimagnetic state to the antiferromagnet-4; at  $\tau = 0.43$  the transition is to the paramagnetic state. The first two transitions are of the order-order type and they occur in accordance with the mechanism described in detail in Sec. 3. We shall show that the transition from the antiferromagnet-4 to the paramagnetic state is of the order-improper disorder type. The nature of the short-range order can be determined by calculating only the correlation functions of the  $\langle S_{0n} S_{0m} \rangle$  type, because the correlation functions in a ferromagnetic plane are known to be positive (it is worth recalling that the model is somewhat simplified compared with the situation in an isotropic crystal of EuSe). Using Eq. (4.1) and the definition of the short-range order vector  $\mathbf{q}_{SO}$  given after Eq. (2.2), we obtain the expression  $\mathbf{q}_{SO} = (Q, 0, 0)$  for this vector, where  $Q = 0$  for  $1 - (k/3) > 4v$  or

$$Q = \cos^{-1} \frac{1 - (k/3)}{4v} \quad (4.2)$$

when the sign of this inequality is reversed. Below  $T_N$  we have  $\mathbf{q}_{LO} = (\pi/2, 0, 0)$ , i.e., the long- and short-range order vectors below and above the transition point, respectively, are different and are generally incommensurate. Thus, the model corresponding to Eq. (4.1) allows us to predict not only the whole sequence of order-order phase transitions in EuSe but also to de-

scribe correctly the nature of the order-disorder phase transition. We recall that a similar but simpler model used in Sec. 3 accounts qualitatively for the metamagnetism of isotropic EuSe, i.e., allowance for the non-Heisenberg exchange makes it possible to explain practically all the anomalous properties of EuSe.

For other values of the parameters  $v$ ,  $p$ ,  $r$ , and  $k$  we can obtain also a different sequence of phase transitions. For example, for  $v = 0.1$ ,  $p = 0.5$ ,  $r = 0.4$ , and  $k = 1.3$ , we obtain the following sequence of first-order phase transitions: antiferromagnet-2 to ferrimagnet at  $\tau = 0.201$ ; ferrimagnet to antiferromagnet-4 at  $\tau = 0.205$ ; antiferromagnet-4 to ferromagnet at  $\tau = 0.2055$ . At  $\tau = 0.35$  a second-order phase transition takes place to the paramagnetic state. Similar sequences of phase transitions can be predicted also for anisotropic crystals if the biquadratic terms in Eq. (4.1) are replaced with anisotropic terms of the  $(S_m^z)^2$  type, etc. We can set the parameters so that the ferrimagnetic phase is generally unstable and only antiferromagnet-2-antiferromagnet-4 phase transitions occur, as in UAs or CeBi.

Next, instead of the three-spin exchange we can allow for the four-spin exchange in Eq. (4.1) and this gives qualitatively similar results to those obtained in the three-spin case, but it can also be applied to describe the properties of magnetic materials with  $S = 1/2$ . This is exactly the approach used in Ref. 126: the Hamiltonian with the Heisenberg and four-spin exchange mechanisms is used to demonstrate the stability of the antiferromagnet-4 state and its abrupt transition to the paramagnetic state. A similar result (a first-order antiferromagnetic-paramagnetic phase transition) was obtained earlier in Ref. 52.

### c) Theory of devil's ladders of phase transitions

The above model provides a fully satisfactory description of a sequence of phase transitions if their number is not too large (normal sequences). However, the large number of experimentally detected phase transitions in CeSb, which suggests that an increase in the resolution would reveal even more transitions, has led the authors of Refs. 127 and 128 to the idea that CeSb possibly exhibits a "devil's ladder" of phase transitions.

The theory of a devil's ladder originates from the theory of discontinuous quantities (fractals).<sup>129</sup> It deals with Cantor's discontinuum obtained as follows. In the first stage the central one-third  $[1/3, 2/3]$  is taken from a segment  $[0, 1]$ . The process is repeated and the central third ( $[1/9, 2/9]$  from  $[0, 1/3]$  and  $[7/9, 8/9]$  from  $[2/3, 1]$ ) is taken from the remaining segments, and this goes on *ad infinitum*. A devil's ladder describes a quantity  $M(x)$  which is a mass concentrated in an interval  $[0, x]$  on condition that in the regions removed from the interval  $[0, 1]$  there is no mass (these regions are represented by the horizontal parts of the steps). A characteristic feature of a devil's ladder is an alternation of steps of a great variety of lengths from  $1/3$  to infinitesimally narrow, and the lengths of

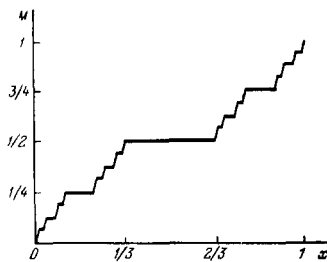


FIG. 9.

the steps vary nonmonotonically, even at first sight quite randomly (Fig. 9).

The concept of a devil's ladder of phase transitions was first introduced in Ref. 130 in considering these transitions on the basis of a one-dimensional model due to Frenkel and Kontorova; they occur at  $T=0$  when pressure is varied. Although in a devil's ladder of phase transitions the discontinuities of the order parameter may be so small that a phase transition appears as practically continuous, in contrast to a second-order transition, hysteresis should be observed. The question of stability of a devil's ladder of phase transitions in the presence of thermal and quantum fluctuations has not yet been resolved. In contrast to Ref. 130, a convincing proof of the existence of devil's ladders in magnetic materials is not given in Refs. 127 and 128, but only arguments and results of numerical calculations confirming this hypothesis are provided. The analysis is based on the Ising Hamiltonian with the interaction between the first- and second-nearest neighbors; the calculation is carried out in the self-consistent field approximation. It is assumed<sup>128</sup> that a magnetic material consists of ferromagnetic layers of atoms with the spin  $1/2$ , and an allowance is made for the exchange between the nearest and second-nearest ferromagnetic layers, exactly as in the isotropic model of EuSe discussed above; it is assumed that  $I_1 > 0$  and  $I_2 < 0$ . If the magnetic structure near the critical point  $T_C$  can be represented by a sinusoidal wave with the wave vector  $q = (2\pi/a)(0, 0, q)$ , then the structure formed below  $T_C$  should have such a value of  $q_C$  that the paramagnetic susceptibility  $\chi(q)$  first diverges at  $q = q_C$  as  $T_C$  is approached from the high-temperature side, i.e.,

$$2\pi q_C = \cos^{-1} \left( -\frac{I_2}{4I_1} \right). \quad (4.3)$$

On the other hand, the exact state of the system is known at  $T=0$ . If  $-2I_2 > I_1$ , this is the antiferromagnet-4 corresponding to  $q_0 = 1/4$ . The question arises how does the dependence  $q(T)$  behave in this case. This can be answered by representing a crystal as a set of periodically repeated groups of  $N$  layers in each of which the average spin has its own value. The actual distribution of spins in the layers is found by an iteration procedure in which the initial stage is either a sinusoidal structure or a self-consistent solution at the adjacent temperature. The free energy  $F(N)$  for a given value of  $N$  is minimal when self-consistency is achieved. At each temperature that value of  $N$  is selected for which  $F(N)$  obtained as above is minimal.

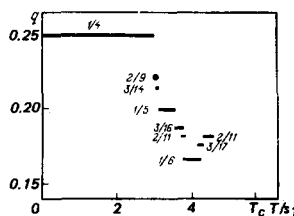


FIG. 10. Temperature dependence of the structure vector of an Ising magnetic material.<sup>128</sup>

Figure 10 shows the dependence  $q(T)$  obtained in this way for the case when  $-I_2/I_1 = 0.6$ . More than 95% of the phase diagram is occupied by simple commensurate values  $q = 1/4, 1/5, \text{ and } 1/6$ . However, other wave vectors are also stable although this is true only in very narrow temperature intervals  $\Delta T$ :  $q = 2/9$  and  $q = 3/14$  are stable in an interval  $\Delta T = 0.0004T_C$  and  $q = (3/16)$  in an interval  $\Delta T = 0.03T_C$ . We can see that some rational values of  $q$  are unstable at all temperatures. This is characteristic of a devil's ladder but it does not agree with a continuous variation of  $q(T)$ . It is worth noting that  $q(T)$  is nonmonotonic. A similar approach in the geometry corresponding to CeSb with  $S = 5/2$ , as that for Ce, makes it possible to obtain for certain parameters the sequence  $N = 4, 11, 8, 7, \text{ and } 3$  in the same order as found for CeSb (Ref. 127). However, in addition to those quoted above, there are several other stable values of  $N$ , although they occur in very narrow intervals.

In order to understand the nature of the commensurate phases at relatively high temperatures, the Ginzburg-Landau functional  $F_{GL}$  is obtained in Ref. 128 for the special case when  $q$  is close to  $1/4$ . It is assumed that the order parameter depends on the coordinate in accordance with the law  $S_{\pm 1/4}(z) = A \exp\{\pm \Phi(z)\}$ , so that  $F_{GL}$  should be minimized with respect to the phase  $\Phi(z)$ . The Lagrange equation for  $\Phi(z)$  is simply the well-known sine-Gordon equation. Its soliton-type solution describes a domain wall separating two almost commensurate phases. Cooling results in such a value of this quantity that the creation of solitons reduces the free energy of the system. In terms of solitons the commensurate phases with a narrow range of existence  $\Delta T$  can be interpreted as phases in which solitons form a superlattice. For example, the phase with  $q = 4/17$  is formed by including one domain wall in each four periods of the structure with  $q = 1/4$ .

The question arises to what extent the results of the theory of Refs. 127 and 128 are dependent on the use of the Ising model. Within the framework of the usual Heisenberg model we can neither obtain a devil's ladder of phase transitions nor even order-order transitions. In fact, it follows from the condition for the energy minimum of a Heisenberg magnetic material with the same values of  $I_1$  and  $I_2$  as in Eq. (4.3) that at  $T=0$  a helical (canted) structure should appear in this material and its vector  $q$  should be identical with  $q_C$  of Eq. (4.3). On the other hand, the considerations leading to the expression for  $q_C$  near  $T_C$  for Ising magnetic material apply equally to a Heisenberg material.

Therefore, cooling does not alter the canted structure period in a Heisenberg magnetic material.

The position may be quite different in the case of a strong non-Heisenberg exchange. In particular, if the magnetic Hamiltonian is dominated by the biquadratic terms ensuring collinearity of the structure, we may expect the results of Refs. 127 and 128 to be applicable also to an isotropic system. However, if the biquadratic terms are comparable with the others, the situation requires further study.

One should point out that a numerical calculation carried out in the molecular field approximation does not of itself guarantee that a devil's ladder does occur even in the Ising model. It is quite likely that the difference between the free energies of successive phases becomes less than the accuracy of this approximation and, therefore, it is not possible to draw a definite conclusion whether a phase transition does indeed occur between such phases. The same model as in Ref. 128 is used in Ref. 131 to obtain results that do not confirm the existence of a devil's ladder of phase transitions. The self-consistent field approximation is also used there but in a different variant: the free energy is assumed to be a sum of the bilinear magnetization function of the sublattices and of a function which is quadratic in respect of the magnetization of each of them separately. An analysis of this expression shows that the interaction between solitons does not have to be negative, in contrast to what was achieved in Ref. 128. This circumstance converts a devil's ladder of phase transitions into a sequence of well-defined first-order transitions. However, such expressions for the free energy are normally used only in the vicinity of  $T_C$  and, as shown in Ref. 131, their application far from  $T_C$  requires justification.

A numerical calculation of  $q(T)$  was carried out in Ref. 132 using a similar model and the Monte Carlo method. It was found there that  $q(T)$  corresponding to  $I_2/I_1 = -0.6$  varies rapidly in the range  $(0.8-0.9)T_C$  but the accuracy of the calculations was insufficient to determine whether a devil's ladder of phase transitions does appear. The same authors considered analytically the problem in Ref. 133 using the method of low-temperature expansions with the aim of accounting for the magnetic structure of erbium.

## 5. CANTED ANTIFERROMAGNETISM OF HIGH-SYMMETRY CRYSTALS

### a) Experimental results

In this section we shall consider mainly canted antiferromagnetic ordering when the moments  $M_1$  and  $M_2$  of two magnetic sublattices of an antiferromagnet are not directed opposite to one another but at a certain angle  $2\varphi \neq \pi$ . Consequently, the system has a spontaneous magnetic moment  $M = M_1 + M_2$  directed at right-angles to the antiferromagnetic vector  $L = M_1 - M_2$  (Fig. 11). Such ordering was first observed in insulator crystals, such as  $MnCO_3$ ,  $CoCO_3$ ,  $NiF_2$ ,  $\alpha-Fe_2O_3$ , etc. (see Refs. 176 and 26). As shown in Ref. 134, this canted configuration is a consequence of the special

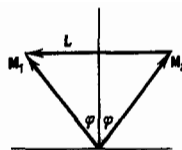


FIG. 11. Canted antiferromagnetic structure.

symmetry of these crystals admitting, in their thermodynamic potential, invariants of the type  $L_i M_j$  or terms of higher order in  $L$  but linear in  $M$ . These invariants are of relativistic origin and this accounts for the smallness of the moments of such crystals. High-symmetry crystals, for example those in which all the magnetic sites belong to the same Bravais sublattice or a magnetic unit cell is obtained by  $n$ -fold repetition of a chemical unit cell ( $n \geq 2$ ), should be collinear antiferromagnets according to the Dzyaloshinskii theory.<sup>134</sup>

However, experimental investigations of magnetic ordering in conducting crystals have led to the impression that canted antiferromagnetism is also possible in these materials and that the conditions for its appearance are not related to the crystal symmetry. The idea was first put forward in Ref. 135 before the studies<sup>134</sup> of the magnetic properties of the semi-conductor  $LaMnO_3$  doped with Ca, Sr, or excess oxygen. The undoped compound behaved as an antiferromagnet with the Néel point at  $T_N \gg 100^\circ K$ , but a magnetic moment appeared on increase in the degree of doping and initially this moment was much less than the saturation value. At the same time the neutron scattering spectra acquired at  $4.2^\circ K$  not only the reflections corresponding to the antiferromagnetic order but also reflections representing the ferromagnetic order.

The authors of Ref. 135 did not conclude that this is always due to canted antiferromagnetism because some of their results (behavior of the reflections in a magnetic field discussed below) did not agree with this hypothesis. As an alternative, they suggested the existence of a mixture of the ferromagnetic and antiferromagnetic phases. This hypothesis is in agreement with the experimental results, but the authors could not see why homogeneous crystals should consist of two phases. It is now known that such a situation is possible in the case of heavily doped magnetic semiconductors.<sup>23</sup> It is usual to assume the results of Ref. 135 as a proof of the existence of canted antiferromagnetism in doped  $LaMnO_3$ . Although this is incorrect, the error has been found useful because it has stimulated the development of a theory of canted antiferromagnetic ordering different from Ref. 134, as well as experimental investigations of other magnetic semiconductors in the search for canted antiferromagnetic ordering.

Extensive experimental data currently available on magnetic materials demonstrate the existence of canted antiferromagnetic ordering, even although this is impossible to predict by the theory of Ref. 134. The most convincing proof of the existence of canted antiferromagnetic ordering is available for the intermetallic compound  $GdMg$  (Ref. 136). This material has an extremely simple crystal structure of the CsCl type and

an analysis of its magnetic properties is simplified by the fact that the  $Gd^{3+}$  ions from which it is composed do not have an orbital angular momentum. Therefore, its magnetic anisotropy is weak. The interest in GdMg has resulted from its spontaneous magnetization<sup>137</sup>: the material becomes ordered at 110°K but the magnetization per Gd atom at 4.2°K is only  $4.54 \mu_B$ , i.e., it is considerably less than the magnetic moment of the  $Gd^{3+}$  ions amounting to  $7 \mu_B$ . In an external magnetic field the moment rises but does not reach the saturation value even for 150 kOe. Since Gd absorbs strongly thermal neutrons, the reflection spectra of hot neutrons of the  $\lambda \approx 0.5 \text{ \AA}$  wavelength were investigated in Ref. 136.

At 130°K only the coherent nuclear scattering was observed and it corresponded to the CsCl-type structure. At 12°K the scattering lines become enhanced and at the same time new  $(h, k, 1/2)$  reflections were observed. This is compatible with the existence of the ferromagnetic and antiferromagnetic contributions to the scattering with moments per atom of Gd amounting to  $\mu_{FM} = 4.9 \pm 0.3 \mu_B$  and  $\mu_{AF} = 5.1 \pm 0.3 \mu_B$ , respectively. The directions of the antiferromagnetic components are perpendicular to the vector  $q = (0, 0, 1/2)$ . The values of  $\mu_{AF}$  and  $\mu_{FM}$  indicate that the vectors  $M$  and  $L$  are mutually perpendicular in any single-phase system: in the opposite case the moment per Gd atom should be greater than for free  $Gd^{3+}$ . In other words, if the system consists of a single phase, the ordering should be of the canted antiferromagnetic type.

However, there is still another possibility to which attention was drawn in a similar situation already in Ref. 135: the superposition of the antiferromagnetic and ferromagnetic reflections may be due to a non-coherent mixture of the antiferromagnetic and ferromagnetic phases. A method was suggested in Ref. 135 for distinguishing a single-phase system from a two-phase one by the behavior of reflections in a weak field  $\mathcal{H}$  applied parallel to the neutron scattering vector  $k$ . The intensities of the ferromagnetic and antiferromagnetic scattering lines are proportional to  $[1 - (kM)^2 k^{-2} M^{-2}]$  and  $[1 - (kL)^2 k^{-2} L^{-2}]$ , respectively. In the case of two phases the field  $\mathcal{H}$  is less than the field for the spin flipping of the antiferromagnetic sublattices and it af-

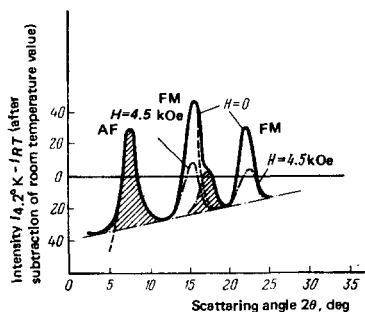


FIG. 12. Angular dependences of the intensity of neutron scattering in  $LaMnO_3$  with 18%  $Mn^{4+}$  at 4.2°K. The sample of  $LaMnO_3$  was homogeneous in the x-ray sense; it consisted of ferromagnetic (72%) and antiferromagnetic (28%) phases. The shaded peaks are antiferromagnetic and the unshaded are the ferromagnetic contributions; the chain curve is the spectrum recorded in a field of 4.5 kOe (Ref. 135).

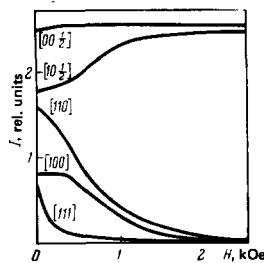


FIG. 13. Magnetic-field dependences of the intensity of the scattering of neutrons in GdMg (Ref. 136).

fects only the vector  $M$  weakening the ferromagnetic scattering. The antiferromagnetic scattering should remain unchanged. In the case of single-phase ordering the vectors  $M$  and  $L$  are related to one another and, therefore, a change in the ferromagnetic scattering involves also a change in the antiferromagnetic scattering.

It is clear from Fig. 12 that in the case of  $LaMnO_3$  a field of 4.5 kOe reduces strongly the intensity of the ferromagnetic reflections with practically no influence on the antiferromagnetic reflections.<sup>135</sup> Hence, it is clear that the material consists of two phases. Figure 13 shows the dependences of the intensities of the various reflections of GdMg on the field when the latter is directed along the scattering vector. The ferromagnetic reflection  $[111]$  disappears already in fields of  $\sim 400$  Oe. This is due to the fact that  $[111]$  is the easy-magnetization axis and that a domain with  $M \parallel k$  grows in a field at the expense of the other seven domains. The intensity of the  $[100]$  reflection decreases only as a result of reorientation of the magnetic vector which occurs when the field  $\mathcal{H}$  reaches the anisotropy value  $\mathcal{H}_A$ , which is found from Fig. 12 to be 2 kOe. As far as the antiferromagnetic reflections are concerned, the  $[1, 0, 1/2]$  reflection becomes enhanced in a field reaching saturation for  $\mathcal{H}_A$ , as expected in the case when the rotation of the vector  $M$  results in rotation of the perpendicular vector  $L$ . The fact that the intensity of the  $[0, 0, 1/2]$  line is independent of  $\mathcal{H}$  is a consequence of the fact that  $L$  is perpendicular to this direction with  $\mathcal{H} = 0$ .

The value of the moment of the canted antiferromagnetic state is even higher than in the materials where the canted antiferromagnetism is due to the relativistic interactions. On increase in temperature, the angle between the sublattice moments decreases and at 85°K a phase transition from the canted antiferromagnetic to the ferromagnetic state takes place.

Apparently canted antiferromagnetic ordering occurs in  $TbMg$  which has the same structure as CsCl (Refs. 137 and 138). However, its magnetic properties are much more complex<sup>137, 138</sup> than those of GdMg, because the  $Tb^{3+}$  ions have an orbital angular momentum. In particular, the magnetization in a field of 4.2°K reveals a hysteresis, because the magnetization depends on whether the cooling treatment was carried out in or out of the field.<sup>138</sup> Neutron-diffraction investigations have revealed the coexistence of the antiferromagnetic and ferromagnetic reflections with  $\mu_{FM} = 4.5 \mu_B$  and  $\mu_{AF}$

$= 5.1 \mu_B$ , both of which disappear simultaneously at  $81^\circ\text{K}$  (Ref. 138). However, it was found to be impossible to carry out such an investigation in a field described above and this was due to the strong anisotropy field.

There is also convincing evidence that a canted antiferromagnetic structure appears when a ferromagnet  $\text{FePd}_3$  is alloyed to an antiferromagnet  $\text{FePt}_3$  (Ref. 139). Alloys of this kind have the  $\text{Cu}_3\text{Au}$  structure with Pd and Pt distributed at random between the Cu sites. For some compositions, for example  $\text{FePd}_{1.6}\text{Pt}_{1.4}$ , the ferromagnetic and antiferromagnetic reflections are superimposed in the neutron scattering spectra. The ferromagnetic reflections appear below  $270^\circ\text{K}$  and  $\mu_{FM}$  rises to  $140^\circ\text{K}$ , where it reaches  $1.7 \mu_B$ , and further cooling to  $4.2^\circ\text{K}$  decreases it to  $1.2 \mu_B$  (Fig. 14). At  $140^\circ\text{K}$  the antiferromagnetic reflections  $(1/2, 1/2, 0)$ ,  $(1/2, 1/2, 1)$ , and  $(3/2, 1/2, 0)$  appear simultaneously and their relative intensities correspond to those of the antiferromagnetic ordering in pure  $\text{FePt}_3$  [the moments of Fe in (110) layers are parallel to one another and the overall moments of neighboring layers are antiparallel]. At  $4.2^\circ\text{K}$ , we have  $\mu_{AF} = 2.7 \mu_B$ . Since among all the atoms only Fe has a nonzero spin and its moment cannot exceed  $3 \mu_B$ , the above values of  $\mu_{AF}$  and  $\mu_{FM}$  indicate that in the single-phase state the vectors  $\mathbf{M}$  and  $\mathbf{L}$  are mutually orthogonal. Results in many respects similar to those given in Ref. 139 were also obtained by neutron-diffraction investigation<sup>140</sup> of alloys formed by ferromagnetic MnSb with antiferromagnetic CrSb, and by ferromagnetic CrTe with antiferromagnetic CrSb.

These results obtained for alloys of ferromagnetic and antiferromagnetic metals are unexpected on the basis of the current ideas: according to these ideas, such alloys should have the properties of spin glasses.

One might also assume that the alloys are mictomagnetic, i.e., that spatial fluctuations of the distributions of the Pd and Pt atoms (or Mn and Cr atoms) produce predominantly ferromagnetic and also predominantly antiferromagnetic regions. This is not true of  $\text{FePd}_{1.6}\text{Pt}_{1.4}$  as indicated by the observation that at  $140^\circ\text{K}$  the antiferromagnetic reflections split off from the ferromagnetic reflections so that the intensity of the latter decreases as a result of further cooling. This can only be explained by assuming that at  $140^\circ\text{K}$  a phase transition takes place from the ferromagnetic to the canted antiferromagnetic state accompanied by rotation of the sublattice moments relative to one another. Had the crystal consisted of separate ferro-

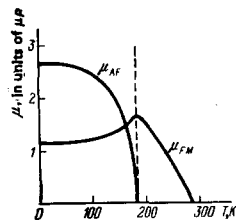


FIG. 14. Temperature dependences of the ferromagnetic and antiferromagnetic components of the moment of the Fe atoms ( $\mu_{FM}$  and  $\mu_{AF}$ ) in  $\text{FePd}_{1.6}\text{Pt}_{1.4}$  (Ref. 139).

magnetic and antiferromagnetic regions, its magnetization would have increased monotonically as a result of cooling. Moreover, it is unlikely that for some ratios of the concentrations of Pt and Pd and after certain treatments of the alloys they could behave as spin glasses.

An even more complex canted antiferromagnetic structure is the one not with two but with four sublattices with a combined net zero magnetic moment, as observed in  $\text{FeGe}_2$  with the tetragonal lattice and with  $T_N = 286^\circ\text{K}$  (Refs. 141 and 142). This compound was investigated not only by neutron diffraction but also using the Mössbauer effect, which made it possible to determine very accurately the directions of the moments. The magnetic structure of  $\text{FeGe}_2$  can be described as consisting of antiferromagnetic (001) planes with the antiferromagnetic vectors lying in these planes. The angle between these vectors in the neighboring planes at  $243^\circ\text{K}$  is  $71^\circ$  (Fig. 15); this structure is represented also in Fig. 10, except that the moments  $M_1$  and  $M_2$  of the two sublattices should be replaced with the antiferromagnetic vectors in the neighboring planes.

It is interesting to note the similarity of the structure of  $\text{FeGe}_2$  to one of the structures proposed for the insulator  $\text{UO}_2$  having the fluorite structure.<sup>143</sup> It also consists of four sublattices with noncollinear moments, the sum of which is zero. In the case of  $\text{UO}_2$  the moments lie in the (001) ferromagnetic planes. Atoms in each such plane split into two sublattices, whose moments are directed at an angle relative to one another (i.e., each such plane is a noncollinear antiferromagnet). The moments of the neighboring planes are directed opposite to one another. However, the results of neutron-diffraction investigations are not yet sufficiently reliable to reject the alternative explanation postulating a collinear antiferromagnetic structure which in the presence of domains gives the same spectra.<sup>143,144</sup> It is possible that a study of the Mössbauer spectrum of  $\text{UO}_2$  would help to resolve this question.

## b) Theory

P. G. de Gennes<sup>145</sup> assumed that  $\text{LaMnO}_3$  does indeed have a canted antiferromagnetic structure<sup>135</sup> and he attempted to develop a theory of such structures in degenerate antiferromagnetic semiconductors on the basis of the  $s-d$  model. He began by postulating that introduction of carriers into a Heisenberg antiferromagnet has a tendency to establish an antiferromagnetic order. A theory of the indirect RKKY exchange does not predict a canted antiferromagnetic structure because the conduction electrons only change the co-

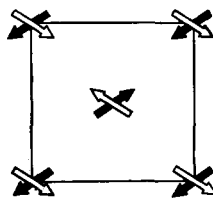


FIG. 15. Magnetic structure of  $\text{FeGe}_2$  (Refs. 141 and 142).

efficients of the Heisenberg Hamiltonian but not its form. This Hamiltonian does not admit at all a two-sublattice canted antiferromagnetic structure. Therefore, de Gennes considered the case when the width  $W$  of an energy band of charge carriers (in this case holes) is small compared with the energy  $AS$  of the  $s$ - $d$  exchange irrespective of the spin configuration. In this situation the RKKY theory is known to be invalid because the Fermi energy of carriers  $E_F$  is low compared with  $AS$ . The carrier energy in the  $W \ll AS$  case was described by de Gennes by postulating that the effective integral  $B(\varphi)$  of a transition of a hole from one atom to another depends on the angle  $2\varphi$  between the spins of the atoms and varies as  $B \cos\varphi$ , where  $B$  is the true integral of the transition. This last expression represents simply the energy of two equivalent atoms between which an electron is moving ("double exchange") in the case when  $|B| \ll AS$  and the atomic spin approaches the limit  $S \rightarrow \infty$  (Ref. 146). Bearing in mind that the antiferromagnetic order in  $\text{LaMnO}_3$  is of the layer type, we find that the part of the energy of the crystal which depends on the angle between the sublattices  $2\varphi$  can be written in the form

$$E(\varphi) = -NIS^2 \cos 2\varphi - 2|B|n \cos \varphi, \quad (5.1)$$

where  $N$  and  $n$  are the concentration of the magnetic atoms and the density of carriers, respectively;  $I$  is the integral of the exchange between the nearest magnetic atoms belonging to different layers. All the carriers in Eq. (5.1) should be attributed to the lowest energy in accordance with the condition  $n \ll N$ . Minimization of Eq. (5.1) with respect to  $\varphi$  leads to the conclusion that a canted antiferromagnetic structure may occur irrespective of how small is the value of  $n$ . The moment should rise linearly with  $n$  until the ferromagnetic order is established at  $n = n_R$ .

A more rigorous analysis of this problem of a quantum mechanical description of the  $d$  spins<sup>147, 148</sup> showed that canted antiferromagnetic ordering becomes energetically preferred to collinear ordering only beginning from a certain limiting value  $n_L$ . If the magnetic atoms form a simple cubic lattice and the antiferromagnetic order is of the chessboard type, then  $n_L$  is described by the following expression:

$$\frac{n_L}{N} = \left(\frac{\pi}{3}\right)^4 \left[ 2 \left| \frac{I}{B} \right| (2S+1)^{3/2} \right] \quad (5.2)$$

and a similar result should apply also to a layer antiferromagnet. Although, according to Eq. (5.2), for a given value of  $T_N \propto IS^2$  the limiting carrier density  $n_L$  decreases on increase in the spin as  $S^{-3/2}$ , for realistic values of the parameters it may amount to  $10^{19}$ - $10^{20}$   $\text{cm}^{-3}$ . These are, in fact, typical carrier densities in degenerate semiconductors and it follows from Eq. (5.2) that the doping of antiferromagnetic semiconductors need not give rise to a canted antiferromagnetic ordering. According to Refs. 147 and 148, if such an ordering does appear at all, the dependence of the moment  $M = S \cos\varphi$  on  $n$  is generally nonlinear.

An attempt to generalize the analysis to finite temperatures was made in Ref. 145 but the results obtained should be treated with great caution even in the limit  $S$

$\rightarrow \infty$  because the expression for the carrier energy occurring in Eq. (5.1) ceases to be valid at temperatures  $T \neq 0$  (Ref. 23).

It is also possible to show that, in a certain range of carrier densities, canted antiferromagnetic ordering is preferred to antiferromagnetic or ferromagnetic for energy reasons also in the opposite case of degenerate semiconductors with wide energy bands characterized by  $W \gg AS$  (Ref. 148). Because of the relative smallness of  $n$ , the inequality  $E_F \gg AS$  is again disobeyed. For this reason the indirect exchange between localized  $d$  moments cannot be described by the Heisenberg Hamiltonian (this result was obtained again in Ref. 149, where the temperature dependence of canted antiferromagnetic ordering is also considered). The tendency for the conduction electrons to establish a ferromagnetic order in this case is due to the fact that because of the  $s$ - $d$  exchange the energy of an electron with a spin  $\sigma$  is increased by  $AS\sigma \cos\varphi$ , i.e., spontaneous Zeeman splitting of the conduction band takes place and the bottom of the lowest subband is lowered by an amount which increases as the moment of a crystal increases.

Minimization of the energy of a crystal shows that if  $W \gg AS$ , the magnetization in a canted antiferromagnetic state can be found by equating to zero the effective exchange integral  $\tilde{J}$ , which allows both for the direct antiferromagnetic exchange and also for the indirect ferromagnetic exchange via the conduction electrons.<sup>148</sup> The solution exists for  $AS < E_F(n_L)$  beginning from the threshold carrier density  $n_L$ :

$$\frac{n_L}{N} = \left[ 32 \frac{(3\pi^2)^{2/3} |I|}{m^* a^3 A^2} \right]^3 \equiv \frac{32 |I| E_F(n_L)}{A^2}, \quad (5.3)$$

where  $m^*$  is the effective mass of an electron. On the high density side the limiting value  $n_R$  obtained for the case  $E_F(n_R) < AS$  is given by the expression

$$\frac{n_R}{N} = \frac{3AS}{4E_F(n_L)}, \quad E_F(n) = \frac{(3\pi^2 n)^{2/3}}{2m^*}. \quad (5.4)$$

According to Eq. (5.4) the carrier density range  $[n_L, n_R]$  in which a canted antiferromagnetic order is preferred for energy reasons to antiferromagnetic and ferromagnetic orders increases in width on reduction in  $E_F(n_L)/AS$ , i.e., the width of this interval increases on increase in the deviation of the indirect exchange from the Heisenberg form.

However, the results reported in Refs. 147-149 do not guarantee the stability of a canted antiferromagnetic structure. It has been shown later<sup>150</sup> that if  $W \gg AS > E_F$ , then magnon frequencies for canted antiferromagnetic ordering are positive only in the carrier density interval  $n_L < n < 4n_L$ . Outside this interval the frequencies of short-wavelength magnons are imaginary. Since under typical conditions ( $AS \sim 0.5$  eV,  $E_F \gg 0.01$  eV), the carrier density  $n_R$  of Eq. (5.4) may be one or two orders of magnitude higher than  $n_L$ , we can expect stability of canted antiferromagnetic ordering only in a much narrower range of carrier densities than that predicted by Eqs. (5.3) and (5.4). However, even when the magnon frequencies are positive, it does not automatically follow that canted antiferromagnetic ordering is stable: it may be unstable in the presence of fluc-

tuations of the electron density, i.e., when a transition takes place from a spatially homogeneous state to one which is inhomogeneous. The reason for this transition is that a local increase in the electron density enhances the local magnetization in the region of a fluctuation and this in turn lowers the bottom of the conduction band and favors the growth of fluctuations. This is prevented by the increase in the Fermi and electrostatic energies in the inhomogeneous state. The conditions for stability of a homogeneous canted antiferromagnetic state in the presence of relatively small density fluctuations are given in Ref. 23.

However, a typical situation is the one in which a degenerate antiferromagnetic semiconductor is in a homogeneous state even if it is stable in the presence of relatively small density fluctuations but unstable in the presence of large fluctuations. As a result of this instability a homogeneous crystal splits into alternate ferromagnetic and antiferromagnetic regions and carriers are concentrated in the former. At lower carrier densities the ferromagnetic regions are spheres of radius  $\sim 20\text{--}50 \text{ \AA}$  inside an antiferromagnetic matrix, but these regions are not in contact with one another. Carriers are locked within these regions in the form of drops, and the crystal remains in an insulating state. A homogeneous state can be induced by the application of a magnetic field which makes the whole crystal ferromagnetic or by increasing the temperature which makes it completely paramagnetic. This destroys the tendency for electrons to become localized in isolated regions so that the crystal becomes conducting. As  $n$  increases, the ferromagnetic regions grow in size and when they come in contact with one another, the whole crystal becomes conducting at all temperatures.<sup>151, 152, 23</sup>

The above inhomogeneous antiferromagnetic-ferromagnetic state of a crystal corresponds exactly to the observations made on  $\text{LaMnO}_3$  (Ref. 135). This conclusion is confirmed by an analysis of the measured conductivity<sup>153</sup> of samples with a dopant concentration in the range corresponding to the superposition of the antiferromagnetic and ferromagnetic reflections. A sample with 10% Sr, i.e., with the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  ratio  $\sim 0.1$ , is indeed conducting and behaves as a degenerate semiconductor at 300 °K. However, cooling causes the conductivity to decrease exponentially and already in the region of 100 °K when magnetic ordering appears, the conductivity is less than  $10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ , i.e., it is the same as for a nondegenerate semiconductor. Consequently, in the limit  $T \rightarrow 0$  we have  $n \ll n_L$ . Therefore, the theory of Refs. 147–149 is clearly inapplicable. If we assume the existence of a mixture of antiferromagnetic and ferromagnetic phases, then—judging by the results of Ref. 135—the ferromagnetic part of a sample with this concentration of  $\text{Mn}^{4+}$  represents the smaller proportion of the crystal and its transition to an insulating state is in agreement with the theory of Refs. 151 and 152. This theory is also supported by the observation that a sample with 20%  $\text{Mn}^{3+}$ , much of it ferromagnetic, behaves as a degenerate semiconductor also at low temperatures.<sup>153</sup>

Some authors (for example, Umehara and Kasuya<sup>149</sup>)

have suggested that canted antiferromagnetic ordering occurs in the degenerate antiferromagnetic semiconductor  $\text{EuTe}$  which exhibits an unsaturated ferromagnetism according to Refs. 154 and 155. The fact that this material is indeed in a mixed ferromagnetic-antiferromagnetic state is supported by the behavior of the conductivity of those samples which exhibited unsaturated ferromagnetism. For example, cooling of one sample from 77 to 4 °K decreased the conductivity by two orders of magnitude but the field of 84 kOe inducing a homogeneous ferromagnetic state restored the conductivity.<sup>154</sup> The temperature and field had an even greater influence on doped  $\text{EuSe}$  which is also in a two-phase ferromagnetic-antiferromagnetic state.<sup>112</sup>

In contrast to degenerate semiconductors, homogeneous metals cannot go over to an inhomogeneous ferromagnetic-antiferromagnetic state because the Fermi and Coulomb interaction energies are high and because, in contrast to semiconductors, the latter energy does not decrease due to the permittivity of the medium (in contrast to semiconductors). Therefore, even in those cases when it is not possible to carry out such comprehensive experimental investigations as in Ref. 136, one can conclude with a very high degree of probability that the superposition of the antiferromagnetic and ferromagnetic neutron-diffraction reflections indicates the presence of a single-phase intermediate antiferromagnetic-ferromagnetic state of a metal if it is crystallographically homogeneous. However, we cannot *a priori* say that the magnetic vector is always perpendicular to the antiferromagnetic vector. In principle, we can expect structures also in which  $\mathbf{M} \parallel \mathbf{L}$ , whereas in the case of strongly anisotropic crystals one can, of course, have other variants.

Important information on the properties of canted antiferromagnetic ordering can be obtained by a model approach utilizing the simplest non-Heisenberg Hamiltonians: Eqs. (2.4) or (2.5) (Refs. 52 and 43). Subsequently, similar results have been obtained by a number of authors (see, for example, Refs. 156–158). A very similar approach is used in Ref. 159, where an attempt is also made to relate the phenomenological coefficients in the expression for the free energy with the properties of the collective-state electrons. In Ref. 142 the method of Refs. 52 and 43 was generalized to the case of four-sublattice ordering in  $\text{FeGe}_2$ .

The simplest case of the four-spin Hamiltonian is discussed in Ref. 52. If we assume that the lattice is simple cubic and the ordering is of the chessboard type, we find from Eq. (2.5) that, in addition to the condition of extremality of the collinear structure energy  $\sin\varphi = 0$ , we also have to satisfy the condition of extremality of the energy of a canted antiferromagnetic structure  $E_{\text{NCAF}}$  [in the notation of Eq. (3.1)]:

$$\cos 2\varphi = -\frac{I_{-} + 2S^2 K_{+-}}{2S^2 K_{--}}. \quad (5.5)$$

The energy  $E_{\text{NCAF}}$  is minimal if the inequality  $K_{--} < 0$  is obeyed. In order to determine whether a canted antiferromagnet is stable, we have to find its magnon spectrum. In the range of small quasimomenta the magnon spectrum is of the same type as for a ferromagnet,



whereas near the point  $\Pi = (\pi/a, \pi/a, \pi/a)$  it is of the same type as in an antiferromagnet. If the ferromagnetic coupling between the atoms in the same sublattice is sufficiently strong, the magnon frequencies are found to be positive.

The temperature dependence of the magnetic ordering has been investigated in the self-consistent field approximation. In this approximation the spin in Eq. (5.5) should be modified by replacing it by its average value  $S(T)$ . Since the denominator of Eq. (5.5) decreases when temperature is increased, it follows that at some temperature a canted antiferromagnetic structure is transformed by a second-order phase transition to a ferromagnetic or an antiferromagnetic state. However, we may find that an increase in the temperature  $T$  results in violation of the condition of stability of a canted antiferromagnetic state formulated in Ref. 52. Then, a first-order phase transition should take place to one of the collinear states or to a paramagnetic state. If the quantities  $I_-$  and  $K_+$  have opposite signs and if  $|I_-| < 2S^2|K_+|$ , a whole sequence of phase transitions may take place. On increase in temperature  $T$  the quantity  $I_- + 2S^2(T)K_+$  changes its sign. In a certain range of temperatures  $T$  the condition (5.5) for the existence of a canted antiferromagnetic structure becomes satisfied and on further increase in  $T$  the structure becomes again collinear and of the type opposite to that observed at low temperatures (i.e., a sequence of phase transitions takes place from a ferromagnetic, to a canted antiferromagnetic, to an antiferromagnetic, and to a paramagnetic state or from an antiferromagnetic, to a canted antiferromagnetic, to a ferromagnetic, and to a paramagnetic state).

In the case of the Hamiltonian with the biquadratic exchange given by Eq. (2.4), we can expect in addition to the above also a possibility for a continuous phase transition from a canted antiferromagnetic to a statistical quadrupole orthogonal state (see Sec. 2). The experiments reported above revealed so far only continuous transitions from a canted antiferromagnetic to a collinear state.

The susceptibility  $\chi$  in a canted antiferromagnetic state was calculated in Refs. 52 and 42. This susceptibility depends strongly on the field and decrease as the field rises. The initial susceptibility for  $2\varphi$  tending to  $\pi$  diverges as  $\cos^{-2}\varphi$ .

One should stress the difference between the mechanisms of canted antiferromagnetic ordering considered here for an isotropic crystal and the Dzyaloshinskii mechanism associated with the magnetic anisotropy. According to Ref. 134, even an infinitesimally small addition of the required symmetry to the Heisenberg Hamiltonian is sufficient to give rise to a spontaneous moment. However, the effect discussed in the present review has a threshold: a magnetic moment appears only if the non-Heisenberg exchange is of sufficient strength. In the case of models with indirect exchange via carriers this would be manifested by the presence of the limiting density  $n_L$  (Refs. 147 and 148). In the model with the four-spin exchange the condition  $\cos 2\varphi \leq 1$  imposes restrictions on the smallest possible value

of the quantity  $|K_-|$  in Eq. (5.5) and exactly the same applies to the biquadratic exchange.

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