

# Interaction of localized magnetic moments in systems with electron-hole pairing

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(Submitted 20 January 1978)

*Zh. Eksp. Teor. Fiz.* 75, 563-577 (August 1978)

It is shown that the ferromagnetic ordering of the localized magnetic moments of the atoms in substances that are unstable to electron-spectrum restructuring, with formation of a Bose condensate of triplet electric-hole pairs, has a number of interesting singularities. The formation of a condensate of triplet pairs is accompanied by the onset, in the crystal, of a spin-density wave with which the magnetic moments of the atoms become aligned. In other words, the addition to the ordinary indirect Ruderman-Kittel exchange interaction, exchange of triplet electric-hole pairs becomes possible between the atoms of the medium. As a result, different phases can exist in the system, having different interaction mechanisms that lead to magnetic ordering. The article discusses the possibility of using this model to explain the experimentally observed properties of compounds of the  $R_3Al_2$  (where R is a rare-earth element), and semiconducting compounds are of the IV-VI type.

PACS numbers: 75.10.Jm, 75.30.Et

## 1. INTRODUCTION

The free carriers in a metal determine substantially the interaction between the localized magnetic moments that are present in the metal. The indirect exchange interaction introduced by Ruderman and Kittel (the RKKY interaction)<sup>[1]</sup> has made it possible to construct a theory of magnetic structures in rare-earth and transition metals.<sup>[2]</sup> It turns out that the energy spectrum of the conduction electrons, the shape of the corresponding Fermi surface, etc., are important parameters of this theory. It is therefore clear that the change of the spectrum of the particles as a result of some definite interaction can substantially alter the physical picture of formation of magnetic ordering in the system.

We consider below the behavior of localized magnetic moments in substances having a single-electron spectrum with singular properties namely either in semimetals with almost coinciding Fermi surfaces of the electrons and holes,<sup>[3,4]</sup> or in metals with narrow allowed bands, when the condition  $\varepsilon(\mathbf{p}) = -\varepsilon(\mathbf{p} + \mathbf{q})$  is approximately satisfied.<sup>[5]</sup> In all the above cases, at arbitrarily weak interaction between the electrons, the electron system of the crystal is unstable to electron-hole pairing in either the singlet or triplet states, or else when both pair types coexist.<sup>[6]</sup>

The restructuring of the initial spectrum, which is due to formation of electron-hole pairs, can be accompanied by formation of a spin-density wave (SDW) of the carriers even if there are no localized magnetic moments in the crystal.<sup>[4]</sup> This phenomenon is observed, for example, in chromium<sup>[7]</sup> and is connected with the singular form of its Fermi surface, individual sections of which become congruent upon translation by a certain vector  $\mathbf{q}$ , i.e., the condition  $\varepsilon(\mathbf{p}) = -\varepsilon(\mathbf{p} + \mathbf{q})$  referred to above is satisfied. If now a metal that is unstable to CDW formation contains atoms with localized moments, then the latter obviously will align themselves with the CDW. As a result, the magnetic properties of such a

metal should differ from those predicted by the ordinary RKKY model, which does not take into account the interaction between the electrons.

We consider below this situation in detail, using the simple model of an isotropic semimetal with electron and hole Fermi surfaces that coincide in momentum space, and with atoms having localized magnetic moments (for example, each atom has a partially filled  $f$  level). In the calculations we neglect effects connected with overlap of the wave functions of the  $f$  electrons, assuming its contribution to the interaction between the localized moments of the atoms to be small compared with the indirect exchange via the conduction electrons.

It will be shown that besides the indirect Ruderman-Kittel exchange interaction between the atoms of the medium, which was indicated above, exchange of triplet electron-hole pairs is possible. As a result, there can exist in the system various phases that differ in the mechanism whereby the magnetic order is produced.

In the conclusion we discuss the possibility of using this model to explain the experimentally observed properties of compounds of the type  $R_3Al_2$  (where R is a rare-earth element) and semiconducting compounds of the IV-VI type.

## 2. MODEL HAMILTONIAN AND FUNDAMENTAL EQUATIONS

The Hamiltonian of the system in question will be written in the form

$$H = H_0 + H_1, \quad (1)$$

where  $H_0$  is the Hamiltonian of the electron-phonon system of the crystal and  $H_1$  describes the interaction of the carriers with the localized moments.

Just as in Ref. 6, we choose  $H_0$  in the form

$$H_0 = H_{el} + H_{ph} + H_{int}, \quad (2)$$

where

$$H_{el} = \sum_{\mathbf{p}, \alpha} \left( \frac{\mathbf{p}^2}{2m} + \frac{\varepsilon_g}{2} \right) (a_{1\alpha}^+(\mathbf{p}) a_{1\alpha}(\mathbf{p}) - a_{2\alpha}^+(\mathbf{p}) a_{2\alpha}(\mathbf{p})) \quad (3)$$

is the Hamiltonian of the free electrons in the conduction band 1 and in the valence band 2 with isotropic dispersion laws,  $m$  is the effective mass and is assumed to be for simplicity the same for the electrons and holes,  $\varepsilon_g$  is the width of the forbidden band ( $\varepsilon_g < 0$  for semimetals);

$$H_{ph} = \omega_0 (b^+ b + 1/2) \quad (4)$$

is the Hamiltonian of the free phonon mode ( $\omega_0$  is the unrenormalized phonon frequency);

$$H_{int} = \sum_{\mathbf{p}, \mathbf{p}', \mathbf{q}, \alpha, \beta} \{ V_1(\mathbf{q}) a_{1\alpha}^+(\mathbf{p}+\mathbf{q}) a_{2\beta}^+(\mathbf{p}'-\mathbf{q}) a_{2\beta}(\mathbf{p}') a_{1\alpha}(\mathbf{p}) + V_2(\mathbf{q}) [a_{1\alpha}^+(\mathbf{p}+\mathbf{q}) a_{2\beta}^+(\mathbf{p}'-\mathbf{q}) a_{1\beta}(\mathbf{p}') a_{2\alpha}(\mathbf{p}) + a_{1\alpha}^+(\mathbf{p}+\mathbf{q}) a_{1\beta}^+(\mathbf{p}'-\mathbf{q}) a_{2\beta}(\mathbf{p}') a_{2\alpha}(\mathbf{p}) + c.c.] + \sum_{\mathbf{p}, \alpha} g(b+b^*) (a_{1\alpha}^+(\mathbf{p}) a_{2\alpha}(\mathbf{p}) + c.c.) \} \quad (5)$$

is the Hamiltonian of the electron-electron and electron-phonon interactions, in which are retained only the terms responsible for the exciton instability.

In formulas (3)–(5) and hereafter,  $a_{1\alpha}$  and  $a_{2\alpha}$  are the Fermi operators of annihilation of electrons with spin  $\alpha$  in the conduction and in the valence bands, respectively.

The subsequent analysis of the problem will be carried out in the high-density approximation, when the inequality  $na_0^3 \gg 1$  is satisfied ( $n$  is the carrier density, and  $a_0$  is the Bohr radius of the electron). In this case the potential  $V_1(\mathbf{q})$  can be replaced by a constant  $g_1$  which does not depend on the momentum, since it is strongly screened. The potential  $V_2$  is the short-range in accord with its very definition. Therefore the potential  $V_2(\mathbf{q})$  will be replaced by the constant  $g_2$ . We assume furthermore that the constants  $g_1$  and  $g_2$  are real. They can be made real in the case of simple (degenerate in spin only) bands by a gauge transformation.

The interaction of the carriers with the localized moments is written in the form

$$H_1 = \sum_{i,j,\mathbf{p},\mathbf{q},\alpha,\beta} U_{ij}(\mathbf{q}) a_{i\alpha}^+(\mathbf{p}) a_{j\beta}(\mathbf{p}+\mathbf{q}), \quad (6)$$

where

$$U_{ij} = - \int \sum_{\alpha} J_{ij}(\mathbf{r}-\mathbf{r}_\alpha) (\sigma_{\alpha\beta} \mathbf{S}_\alpha) \varphi_{i\mathbf{p}}^*(\mathbf{r}) \varphi_{j,\mathbf{p}+\mathbf{q}}(\mathbf{r}) d\mathbf{r},$$

$\varphi_{i\mathbf{p}}(\mathbf{r})$  are Bloch functions of the  $i$ -th band, normalized to the volume  $v$  of the crystal,  $\mathbf{S}_\alpha$  is the moment of the  $\alpha$ -th atom, and the summation is over all the atoms having localized magnetic moments.

A phase transition in a system of localized moments is accompanied by the appearance of a nonzero mean value  $\mathbf{S} = \langle \mathbf{S}_\alpha \rangle$ . Then, averaging (6) over the atomic moments, we obtain

$$H_1 = - \sum_{i,j,\mathbf{p},\alpha,\beta} J_{ij}(\sigma_{\alpha\beta} \mathbf{S}) a_{i\alpha}^+(\mathbf{p}) a_{j\beta}(\mathbf{p}), \quad (7)$$

where

$$J_{ij} = N \int \varphi_{ij}(\mathbf{r}) \varphi_{i\mathbf{p}}^*(\mathbf{r}) \varphi_{j\mathbf{p}}(\mathbf{r}) d\mathbf{r}.$$

$N$  is the total number of atoms with localized moments in the crystal.

The problem considered by us is conveniently analyzed with the aid of a temperature diagram technique.<sup>[8]</sup> We introduce the temperature Green's functions of the problem

$$G_{ij}(\alpha\beta)(xx') = - \langle T \psi_{i\alpha}(x) \psi_{j\beta}^+(x') \rangle, \quad (8)$$

where  $x = (\mathbf{r}, \tau)$ ,  $\psi_{i\alpha}(x)$  and  $\psi_{i\alpha}^+(x)$  are the annihilation and creation operators of particles with spin  $\alpha$  at the point  $\mathbf{r}$  in the Heisenberg representation.

The system of equations for the Green's functions can be easily obtained in the usual manner.<sup>[8]</sup> However, we shall not write down here these equations in general form, so as not to clutter up the exposition. We consider the case when the relation between the constants  $g$ ,  $g_1$ , and  $g_2$  is such that triplet pairing takes place in the system.<sup>[6]</sup> This case is of interest because the restructuring of the spectrum is accompanied by the onset of SDW, whose period is equal to the lattice period if the extrema of the electron and hole bands coincide in momentum space.<sup>[4]</sup>

The system of equations for the Green's functions whose spin structure is chosen in the form  $G_{\alpha\beta} = G_0 \delta_{\alpha\beta} + G_\pm \sigma_{\alpha\beta}$  takes in the momentum representation the form

$$(i\omega - \varepsilon(\mathbf{p}) \pm I_{11}) G_{11\pm}(\mathbf{p}) \pm (\Delta + I_{12}) G_{21\pm}(\mathbf{p}) = 1, \quad (9)$$

$$(i\omega + \varepsilon(\mathbf{p}) \pm I_{22}) G_{21\pm}(\mathbf{p}) \pm (\Delta + I_{21}) G_{11\pm}(\mathbf{p}) = 0,$$

where

$$G_\pm = G_0 \pm G_\pm, \quad I_{ij} = SJ_{ij}, \quad \mathbf{p} = (\mathbf{p}, \omega).$$

It is assumed that the localized moments of the atoms are directed along the  $z$  axis. The size of the gap in the spectrum is determined by the equation

$$\Delta = g_1 T \sum_{\mathbf{p}} \int G_{21\pm}(\mathbf{p}, \omega) \frac{d^3 p}{(2\pi)^3}, \quad (10)$$

where  $g_\pm = g_1 + g_2$  is the triplet coupling constant.

In the self-consistent-field model, Eqs. (9) and (10) must be supplemented by an equation that determines the average moment of the atoms. Since the moments of the atoms are situated in an effective field produced by magnetized conduction electrons, the value of  $S$  can be obtained as a result of Boltzmann averaging<sup>[9]</sup>:

$$S = \frac{\text{Sp}[\hat{\mathbf{S}} \exp(-E_{int}(\hat{\mathbf{S}})/T)]}{\text{Sp}[\exp(-E_{int}(\hat{\mathbf{S}})/T)]}. \quad (11)$$

The energy  $E_{int}$  can be calculated by averaging, over the state with the SDW, the Hamiltonian  $H_1$  that describes the exchange interaction of the electrons and holes with the atoms:

$$E_{int} = \langle H_1 \rangle = - \text{Sp} \left\{ \sum_{i,j} (\sigma_{\alpha\beta} \mathbf{I}_{ij}) T \sum_{\mathbf{p}} \int G_{ij}(\mathbf{p}, \omega) \frac{d^3 p}{(2\pi)^3} \right\}. \quad (12)$$

As a result of straightforward but rather cumbersome

calculations, we reduce the system of our equations to the following final form:

$$\Delta = \rho g \int d\xi \frac{\Delta + I_b}{4R} \left[ \text{th} \left( \frac{R - I_a}{2T} \right) + \text{th} \left( \frac{R + I_a}{2T} \right) \right], \quad (13)$$

where

$$R = [\xi^2 + (\Delta + I_b)^2]^{1/2}, \quad \rho = m p_F / 2\pi^2, \\ S = L B_L \left( \frac{J_a L s_a + J_b L s_b}{T} \right), \quad (14)$$

and

$$B_L(x) = \frac{2L+1}{2L} \text{cth} \left( \frac{2L+1}{2L} x \right) - \frac{1}{2L} \text{cth} \left( \frac{x}{2L} \right)$$

is the well-known Brillouin function,  $L$  is the localized moment of the atom, and  $\rho$  is the density of states on the Fermi level.

In (13) and (14) we have put  $J_{11} = J_{22} = J_a, J_{12} = J_{21} = J_b$ . The quantities  $s_a$  and  $s_b$  in (14) have the following meaning:  $s_a$  is the polarization of the spins of the unpaired quasiparticles situated over the gap in the restructured spectrum as a result of thermal excitation, while  $s_b$  is the polarization of the spins of the electron-hole pairs. Thus, in triplet exciton dielectric, it is not only the spins of the free carriers that are polarized under the influence of the average field of the moments of the atoms, but also the spins of the electron-hole pairs. This is an important circumstance and determines the singularities of the transition of the system into the magnetically ordered state.

The formulas that describe the dependence of  $s_a$  and  $s_b$  on the character of the restructuring of the initial spectrum and on the value of the average field of the moments of the atoms take the form

$$s_a = \frac{\rho}{2} \int d\xi \left( \text{th} \left( \frac{R + I_a}{2T} \right) - \text{th} \left( \frac{R - I_a}{2T} \right) \right), \quad (15)$$

$$s_b = \frac{\rho}{2} \int d\xi \left\{ \left( \text{th} \left( \frac{R + I_a}{2T} \right) + \text{th} \left( \frac{R - I_a}{2T} \right) \right) \frac{\Delta + I_b}{R} \right\}. \quad (16)$$

### 3. CERTAIN SOLUTIONS OF THE SELF-CONSISTENCY EQUATION

Equations (13)–(16) determine the behavior of the system completely. We consider now the sequence in which the magnetic ordering of the magnetic moments of the atoms takes place. To this end, we calculate the temperature  $T_{cr}$  at which the magnetic transition takes place.

At  $T \lesssim T_{cr}$ , the average magnetization  $S$  is small, and this makes it possible to simplify the equations. Using the expansion of the Brillouin function  $B_L(x) = x(L+1)/3L$  at  $x \ll 1$ , we obtain

$$S = \frac{1}{3} L(L+1) (J_a s_a + J_b s_b) / T. \quad (17)$$

A. We consider the case  $J_a \neq 0, J_b = 0$ , i.e., when the exchange interaction of the moments of the atoms is only via the free electrons. This case practically coincides with the problem considered by Gor'kov and Rusinov<sup>[10]</sup> and by Sarma,<sup>[11]</sup> who investigated the behavior

of paramagnetic impurities in superconductors. In these papers they considered situations when the atoms of the paramagnetic impurities interacting with one another by indirect exchange of electrons over the superconducting gap. Therefore the equations of Refs. 10 and 11 coincide, apart from the notation, with (13)–(15) with  $J_b$  set equal to zero. Formally, the solutions obtained in Refs. 10 and 11 can be applied in the present case. We shall not write out the formulas for the dependences of the gap in the spectrum and of the temperature  $T_c$  of the exciton transition on the "field"  $I_a$  (Ref. 11). We determine only the character of the magnetic phase transitions that are possible in the case  $J_b = 0$ . In weak fields  $I_a \equiv J_a S \ll \Delta$  the integrand in (15) can be expanded in a series. We obtain

$$s_a = 2\rho I_a \int_0^{\infty} \frac{dx}{\text{ch}^2 [x^2 + (\Delta_0/2T)^2]^{1/2}}, \quad (18)$$

where  $\Delta_0$  is the value of the gap in the spectrum in the absence of the field  $I_a$ . The quantity  $s_{a0} = 2\rho I_a$  is the spin moment of the free electrons in a normal semimetal without pairing (the numerical factor 2 is the result of the existence of two bands). The integral in (18)

$$\int_0^{\infty} \frac{dx}{\text{ch}^2 [x^2 + (\Delta_0/2T)^2]^{1/2}} = 1 - \frac{n_d(T)}{n} \quad (19)$$

characterizes the fraction of the unpaired electrons situated above the gap in the restructured spectrum. Substituting the expression for  $s_a$  in (17), we obtain the following expression for the temperature  $T_{cr}$  of the magnetic transition

$$T = T_{cr0} (1 - n_d(T)/n), \quad (20)$$

where  $T_{cr0} = (2/3)\rho J_a^2 L(L+1)$  is the temperature of the ferromagnetic ordering of the moments of the atoms in a normal semimetal.

The solution of (20) is shown graphically in Figure 1. It is seen from this figure that at  $T_{cr0} < T_{c0}$  no solution with  $s \neq 0$  exists at all ( $T_{c0}$  is the temperature at which an excitonic transition is produced in the semimetal in the absence of a field  $I_a$  and an SDW sets in). The physical reason for the absence of ferromagnetic ordering of the moments of the atoms in this case is that at  $T < T_{c0}$  the number of unpaired carriers with the aid of which the indirect interaction is effected decreased rapidly with temperature:  $\sim \exp(-\Delta_0/T)$ .

In the case when  $T_{cr0} > T_{c0}$ , Eq. (2) has two solutions. The first solution,  $T_{cr1} = T_{cr0}$ , corresponds to the Curie point of a normal semimetal. The second,  $T_{cr2}$ , de-

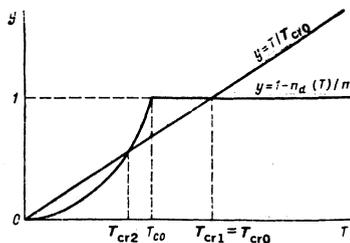


FIG. 1.

creases with increasing interaction constant  $I_a$ . A detailed analysis of an equation similar to (20), carried out in Ref. 10, has shown that the solution  $T_{cr2}$  is unphysical. It indicates that the existence of a nonzero gap  $\Delta \neq 0$  in the spectrum is impossible at  $T_{cr0} > T_{c0}$ .

Thus, in the case  $J_a \neq 0, J_b = 0$  coexistence of ferromagnetic ordering of the moments of the atoms and excitonic pairing of electrons and holes is impossible. Depending on the interaction constants, either a triplet excitonic dielectric phase with the accompanying SDW is realized in the system,<sup>[4]</sup> or else a phase with ferromagnetic ordering of the moments of the atoms. Just as in Ref. 10, it can be shown that the transition from the excitonic state into the ferromagnetic state when the interaction constant  $J_a$  changes is of first order.

B. We consider the case  $J_a = 0, J_b \neq 0$ . It follows from (13) and (16) that a natural connection exists between quantities  $s_b$  and  $\Delta$ :

$$s_b = 2\Delta/g_t. \quad (21)$$

Taking (21) into account, we obtain for  $I_t = J_b S$  with the aid of the formula

$$S = \frac{2L(L+1)}{3T} \frac{\Delta}{g_t} \quad (22)$$

the following expression

$$I_t = \frac{2J_b^2 L(L+1)}{3T} \frac{\Delta}{g_t}. \quad (23)$$

A simple transformation using (23) makes it possible to reduce (13) to the form

$$1 = \rho g_t \int_0^{\tilde{\Delta}} \frac{d\xi}{(\xi^2 + \tilde{\Delta}^2)^{3/2}} \operatorname{th} \frac{(\xi^2 + \tilde{\Delta}^2)^{1/2}}{2T}, \quad (24)$$

where

$$\tilde{\Delta} = \Delta + I_b, \quad \tilde{g}_t = g_t + \frac{2}{3} L(L+1) J_b^2 / T. \quad (25)$$

It must be specially noted that the effective triplet constant  $\tilde{g}_t$  is inversely proportional to the temperature. Therefore, regardless of the value  $J_b$  of the unrenormalized exchange interaction, a semimetal becomes unstable to a transition to a state with SDW at sufficiently low temperature. The solution of an equation of type (24) is well known.<sup>[6]</sup> In particular, at the transition point, i.e., at the temperature  $T_{cr}$ , the quantity  $S$ , and consequently also  $\tilde{\Delta}(T_{cr})$  (see formulas (22) and (23)) vanishes and (24) goes over into (26), from which we determine the transition temperature

$$T_{cr} = \frac{2\tilde{\omega}\gamma}{\pi} \exp \left\{ - \left[ \rho g_t + \frac{2}{3} \frac{\rho L(L+1) J_b^2}{T_{cr}} \right]^{-1} \right\}, \quad (26)$$

where  $\ln \gamma = C$  is the Euler constant.

The solution of (26) can be qualitatively described in the following manner. At a small exchange interaction constant  $J_b \rightarrow 0$  the temperature

$$T_{cr} \rightarrow T_{c0} = \frac{2\tilde{\omega}\gamma}{\pi} \exp \left( - \frac{1}{\rho g_t} \right).$$

This is perfectly natural, for in this case the transition into the phase of the triplet excitonic dielectric is the necessary and sufficient condition for ordering of the moments of the atoms (see formula (22)).

An increase of the exchange interaction constant  $J_b$

leads to an increase of the transition temperature  $T_{cr}$ . In other words, interaction with the magnetic moments of the atoms shifts the point of the transition into the triplet excitonic dielectric phase and shifts the associated ferromagnetic ordering of the moments themselves into the region of higher temperatures, owing to the increase of the effective coupling constant  $\tilde{g}_t$  (25).

To find the dependence of the gap in the spectrum  $\tilde{\Delta}$  and the magnetization  $M$  on the temperature near the point  $T_{cr}$  it suffices to retain in the expansion of the right-hand side of (24) the terms of order  $\tilde{\Delta}^2/T^2$ . As a result of standard calculations, we arrive at the following expression for  $\Delta$ :

$$\Delta = \frac{\pi T_{cr} (8/7 \zeta(3))^{1/2}}{1 + \frac{2}{3} \rho L(L+1) J_b^2 / g_t T_{cr}} \left( 1 - \frac{T}{T_{cr}} \right)^{1/2}. \quad (27)$$

The magnetic moment produced in the sample is obviously equal to  $M = \mu_0 N S$ , and its temperature dependence near  $T_{cr}$  is determined by the relation

$$S = \pi \frac{\frac{2}{3} \rho L(L+1) J_b}{\rho g_t + \frac{2}{3} \rho L(L+1) J_b^2 / T_{cr}} \left( \frac{8}{7 \zeta(3)} \right)^{1/2} \left( 1 - \frac{T}{T_{cr}} \right)^{1/2}, \quad (28)$$

where  $\mu_0$  is the Bohr magneton and  $\zeta(x)$  is the Riemann zeta function.

C. In the case when the constants of the exchange interaction  $J_a \neq 0, J_b \neq 0$ , the derivation of the equation for the temperature of the ferromagnetic ordering of the magnetic moments of the atoms entails likewise no difficulty. Using the smallness of  $S$  near  $T_{cr}$ , we expand the integrands of (13), (15), and (16), retain the terms of first order of smallness in  $S$ , and obtain

$$\begin{aligned} s_a &= 2\rho J_a S (1 - n_d(T)/n), \\ s_b &= 2 \frac{J_b}{g_t} S \left( \frac{1}{\rho g_t \ln(T/T_{c0})} - 1 \right), \\ \Delta &= J_b S \left( \frac{1}{\rho g_t \ln(T/T_{c0})} - 1 \right). \end{aligned} \quad (29)$$

Substituting (29) in (17), we obtain

$$T_{cr} = T_{c0} \left\{ \left( 1 - \frac{n_d(T)}{n} \right) + \frac{J_b^2}{J_a^2} \frac{1}{\rho g_t} \left( \frac{1}{\rho g_t \ln(T_{cr}/T_{c0})} - 1 \right) \right\}. \quad (30)$$

It is easy to verify that if one of the constant (either  $J_a$  or  $J_b$ ) in (30) is set equal to zero, then the result coincides with one of the equations, (20) or (25).

In the general case when  $J_a \neq 0, J_b \neq 0$  the result is determined by the relative values of these two constants. If, for example, the relation between  $J_a$  and  $J_b$  is such that the second term of the right-hand side in (30) is small then, starting with the nonferromagnetic semimetallic phase, where the temperature is decreased, a transition into a ferromagnetic semimetal (FSM) phase will take place at the point  $T_{c0}$  (see (20)); in this phase the magnetic moments of the atoms are ordered as a result of the usual Ruderman-Kittel interaction.<sup>[1]</sup> With further decrease of temperature, generally speaking, a transition from the FSM phase is possible to a ferromagnetic excitonic dielectric (FED) phase, in which the ordering of the magnetic moments of the atoms is due to the SDW which is produced in the triplet excitonic dielectric. Evidence for this is the fact that the effective interaction constant  $\tilde{g}_t$  in (24) increases with decreasing temperature. The point of the transition from the FSM phase into the FED phase is determined by the

equality of the energy gains in both phases.

A calculation of the energy of the state at arbitrary temperature is difficult. We consider therefore the simpler case when  $T=0$ . The varying parameter is then taken to be the constant  $J_a$ , and the remaining interaction constants  $J_b$  and  $g_t$  are assumed fixed. In the calculation of the energy of the ground state we use the well known formula<sup>[8]</sup>

$$\Omega_i - \Omega(0) = \int_0^{\lambda_i} \frac{d\lambda_i}{\lambda_i} \langle H_{int}^i \rangle, \quad (31)$$

where  $\Omega_0$  is the energy of the state without the interaction  $H_{int}^i$  and  $\lambda_i$  is the interaction constant (in our case  $\lambda_i$  runs through the values  $J_a$ ,  $J_b$ , and  $g_t$ ).

Using (12), (15), and (16), we easily find that the energy of the ground state of the FSM state takes the form

$$\delta\Omega_i = -\rho J_a^2 L^2, \quad (32)$$

where  $\rho = m p_F / 2\pi^2$  is the density of states on the Fermi level.

A consistent allowance for the interactions with the constants  $J_b$  and  $g_t$  leads to the following expressions for the energy of the ground state of the FED phase:

1) in the case when the gap in the carrier spectrum is determined only by the matrix element of the interatomic transitions  $J_b$

$$\delta\Omega_2 = -\frac{\rho(J_b L)^2}{2} - \rho(J_b L)^2 \ln \frac{2\bar{\omega}}{J_b L}, \quad J_a < J_b; \quad (33)$$

$$\delta\Omega_2 = -\frac{\rho(J_b L)^2}{2} - \rho(J_b L)^2 \ln \left( \frac{2\bar{\omega}}{J_a L + [(J_a L)^2 - (J_b L)^2]^{1/2}} \right) - \rho(J_b L)^2 \left( 1 - \frac{J_b^2}{J_a^2} \right)^{1/2}, \quad J_a > J_b; \quad (34)$$

2) in the case when the gap in the spectrum of the carriers is determined both by the interband transitions  $J_b$  and by the constant  $g_t$ , we have

$$\delta\Omega_3 = -\frac{\rho \bar{\Delta}^2}{2} - \rho J_b L \bar{\Delta} \ln \frac{2\bar{\omega}}{\bar{\Delta}}, \quad J_a L < \bar{\Delta}, \quad (35)$$

where  $\bar{\Delta} \equiv \Delta + J_b L$  is defined by the expression

$$\bar{\Delta} = \rho g_t \bar{\Delta} \ln \frac{2\bar{\omega}}{\bar{\Delta}} + J_b L; \quad (36)$$

furthermore

$$\delta\Omega_3 = -\frac{\rho \bar{\Delta}^2}{2} - \rho J_b L \bar{\Delta} \ln \left( \frac{2\bar{\omega}}{J_a L + [(J_a L)^2 - \bar{\Delta}^2]^{1/2}} \right) - \rho(J_b L)^2 \left[ 1 - \frac{\bar{\Delta}^2}{(J_a L)^2} \right]^{1/2}, \quad J_a L > \bar{\Delta}, \quad (37)$$

where  $\bar{\Delta} \equiv \Delta + J_b L$  is defined by the expression

$$\bar{\Delta} = \rho g_t \bar{\Delta} \ln \left( \frac{2\bar{\omega}}{J_a L + [(J_a L)^2 - \bar{\Delta}^2]^{1/2}} \right) + J_b L. \quad (38)$$

It is easy to show that in the case when  $g_t = 0$  expressions (35) and (37) coincide respectively with (33) and (34), while in the case when  $J_b = 0$  formulas (35)–(38) yield the well known result<sup>[10]</sup>

$$\delta\Omega_4 = -1/2 \rho \Delta_0^2, \quad \Delta = \Delta_0, \quad J_a L < \Delta, \quad (39)$$

$$\delta\Omega_4 = -1/2 \rho (4\Delta_0 J_a L - \Delta_0^2 - 2(J_a L)^2), \quad (40)$$

$$\Delta = [\Delta_0 (2J_a L - \Delta_0)]^{1/2}, \quad J_a L > \Delta,$$

where  $\Delta_0$  is the gap in the spectrum in the absence of

ferromagnetic ordering.

Figure 2 shows qualitatively the dependence of the energies of the ground states of different phases on the value of the constant  $J_a$ . Curve 1 in this figure corresponds to the FSM phase and, in accordance with (32), characterizes the energy of the ground state of the phase, in which the ferromagnetic ordering of the moments of the atoms is due to the usual RKKY indirect exchange interaction. Lines 2 and 3 correspond to the FED phase, with line 2 corresponding to the relations described by formulas (33) and (34), while line 3 corresponds to (35) and (37). Lines 4 describe the phase of an ordinary excitonic dielectric (ED) (see (39) and (40)), in which the interaction between the localized moments of the atoms is due to indirect RKKY exchange of carriers above the gap in the spectrum.

We note the existence of two branches of the function  $\delta\Omega_{2,3}(J_a)$ . The first of them corresponds to formulas (33) and (35) and describes a physical situation wherein all the carriers are under the gap in the spectrum and the interaction between the moments of the atoms is effected by the SDW, which is produced when electron-hole pairs are produced. This is a so-called "pure" FED phase.

In addition to this pure phase there can exist also a "mixed" FED state, wherein the field  $I_a$  break some of the electron-hole pairs and the interaction of the moments of the atoms with one another is determined both by the remaining electron-hole pairs (SDW) and by the free carriers that appear above the gap (RKKY). This mixed state corresponds to the function  $\delta\Omega_{2,3}(J_a)$  given by formulas (34) and (37). We note that in the mixed ferromagnetic phase, whose energy is described by formula (34), the main contribution to the ordering of the magnetic moments of the atoms at  $J_a \gg J_b$  is made by the RKKY interaction of the electrons above the gap in the spectrum. Therefore at  $J_a \gg J_b$  this phase is close in its properties to the FSM phase.

The shape of the line 3 on Fig. 2 depends on the relation between the interaction constants  $J_b$  and  $g_t$ . It follows from (35) that the point A of the intersection of the two branches of the function  $\delta\Omega_3(J_a)$  shifts when the ratio of the constants changes. Figure 2 corresponds to a relation between  $J_b$  and  $g_t$  such that the following inequality is satisfied

$$\Delta(J_b L) + J_b L < \Delta_0 \sqrt{e}, \quad (41)$$

where the  $\Delta(J_b L)$  dependence is determined by (36).

The point A lies on the parabola 1 when the equation  $\Delta(J_b L) + J_b L = \Delta_0 \sqrt{e}$  is satisfied (see formula (32)), and

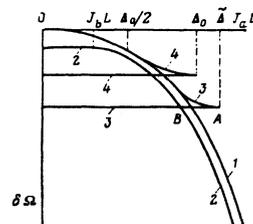


FIG. 2.

goes below the parabola 1 when the opposite of inequality (41) holds.

The sequence of the alternation of the phases with changing  $J_a$  is nevertheless independent of the ratio of the constants  $J_b$  and  $g_t$ , and proceeds in the following manner: At large  $J_a$  the mixed phase described by formula (34) or by line 2 on Fig. 2 is energywise favored. This phase is close in its properties to the FSM phase as mentioned above. With decreasing  $J_a$  a transition into the pure FED phase, described by formulas (35) and (36), takes place at point B of Fig. 2. The phase transition turns out to be of first order. The indicated pure FED phase turns out to be stable down to zero.

#### 4. DISCUSSION OF RESULTS

We have thus shown that, in a system unstable to electron-spectrum restructuring with formation of a condensate of electron-hole pairs, the ferromagnetic ordering of the magnetic moments of the atoms differs substantially from the analogous process in normal metals. The reason is that the produced triplet electron-hole pairs make a substantial contribution to the indirect exchange interaction between the localized moments of the atoms. We call attention to the mutual influence of the localized moments on the temperature of the transition to the triplet ED phase. The additional energy gain due to the ferromagnetic ordering of the magnetic moment of the atoms greatly increases the temperature of the excitonic transition (see formula (26)). An important aspect of the obtained picture of the onset of magnetic ordering in the system is the temperature dependence of the effective interaction constant  $\bar{g}_t$  in Eq. (24) that determines the formation of the SDW and the associated FED phase. Thus, in the discussed model, it becomes possible to observe a sequence of two ferromagnetic transitions. If the ratio of the constants  $J_a$  and  $J_b$  is such that the interaction of the localized magnetic moments with the SDW is small compared with the interaction with the free electrons then, starting with the nonferromagnetic phase of the ordinary semimetal, as the temperature is lowered, a transition to the FSM phase will take place at the point  $T_{cr0}$ , and in the latter phase the interaction between the localized atomic moments is determined by the usual RKKY interaction mechanism.<sup>[1]</sup> This phase remains stable at temperatures  $T > J_b S$ . Further decrease of the temperature when the region  $T \sim J_b S$  is reached leads to a substantial increase of the effective electron-hole interaction constant  $\bar{g}_t$  in the equation, and this in turn causes formation of a triplet gap in the spectrum as well as onset of SDW and of the associated FED phase. Near the phase transition, the magnetization of the sample will then change strongly, as a result of which the dependence of the magnetization on the temperature will take the form of a staircase with two steps (see Fig. 3).

On the other hand, if the ratio of the constants  $J_a$  and  $J_b$  is such that the interaction of the localized moment with the free carriers is much less than the interaction with the SDW, then an FED phase is produced directly in the system when the temperature is lowered, and

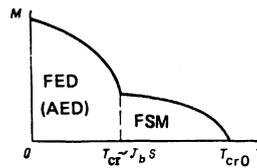


FIG. 3.

this phase remains stable down to zero temperature. The magnetization curve in this case takes the usual form (see Fig. 4).

We note that in the foregoing discussion of the results we had in mind a mixed state of the FED phase, inasmuch as at  $T \neq 0$  there are always unpaired carriers above the gap in the spectrum, and they contribute to the RKKY interaction.

We have considered a simple model of an isotropic semimetal with band extrema that coincide in momentum space, assuming that a magnetic moment is localized at each atom. In this case, the period of the SDW that is produced in the excitonic phase is equal to the lattice period. Therefore the magnetic moments of all the atoms were located at points with identical values of the SDW amplitude. This is precisely why all the magnetic moments became aligned in the same direction and the resultant excitonic phase turned out to be ferromagnetic. It is easy, however, to predict the changes that can occur for a realistic crystal structure. For example, a shift of the band extrema in momentum space by half a period of the reciprocal lattice doubles the SDW period. Therefore the magnetic moments of the neighboring atoms turn out to be at points in which the values of the SDW are shifted in phase by relative to one another. It becomes clear therefore that the alignment of the moments with the SDW in the crystal produces two magnetic sublattices that are rotated by  $180^\circ$  relative to each other. In other words, in this case the produced excitonic phase will be antiferromagnetic. Therefore in Figs. 3 and 4 the excitonic phase is designated as either a ferromagnetic (FED) and as antiferromagnetic (AED) excitonic dielectric. We emphasize that this result does not depend on the signs of the exchange-interaction constants  $J_a$  and  $J_b$  and is determined by the singularities of the band structure of the crystal.

The same pertains to the other aforementioned models that are unstable respect to the electron-hole pairing, particularly to metals with special shapes of Fermi surface, individual sections of which become congruent following translation by a certain vector  $\mathbf{q}$ , i.e., the condition  $\varepsilon(\mathbf{p}) = -\varepsilon(\mathbf{p} + \mathbf{q})$  is satisfied.

The last model enables us to connect the results obtained in the present paper with the data obtained in an experimental investigation of alloys of rare-earth ele-

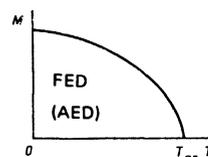


FIG. 4.

ments of the type  $R_3Al_2$ . For example, it is known<sup>[12]</sup> that the compounds  $Er_3Al_2$  and  $Tm_3Al_2$  are antiferromagnetic at all temperatures above the ordering temperature, in accord with the diagram of Fig. 4.

The magnetization curve of the crystal  $Dy_3Al_2$  agrees qualitatively with the curve on Fig. 3. It has been experimentally demonstrated<sup>[13]</sup> that the transition at the point  $T_{cr1}$  is between two ferromagnetic phases that have different degrees of magnetic anisotropy.

In concluding the paper, let us discuss some qualitative aspects of magnetic ordering of magnetic impurities introduced into an intrinsic semiconductor. This can be done conveniently with semiconductors of the IV-VI group as an example, where the ordering has already been observed.<sup>[14]</sup> It is known that semiconductors of the IV-VI group crystallize in a cubic phase with a lattice of the NaCl type which, however, turns out to be unstable in some semiconductors to a transition into a rhombohedral ferroelectric phase at low temperature.<sup>[15]</sup> In this phase, the atoms of element  $A$  are shifted relative to atoms  $B$ , as a result of which spontaneous polarization takes place, and the atoms  $A$  and  $B$  are in a non-central-symmetry environment. The very fact of the structural instability of these compounds is evidence that their electron spectrum has regions with large state density.<sup>[15]</sup> Further, as already noted,<sup>[14]</sup> the introduction of magnetic substitutional ions into the matrix of the crystal produces in these semiconductors a transition into a ferromagnetically ordered phase. Obviously, if account is taken of the exchange interaction of the magnetic ions with the intrinsic electrons of the semiconductor and the inhomogeneity in the distribution of the magnetic impurity is neglected, then we arrive at a problem that is perfectly analogous to that considered above. It must only be taken into account that in place of  $N$  in formulas (7) and those that follow it is necessary to write  $cN$ , where  $c$  is the concentration of the magnetic ions. In addition, it must be remembered that compounds of the IV-VI type are semiconductors already in the initial phase, with a gap width  $\epsilon_g$  of several tenths of an electron volt. The temperature of the ferromagnetic transition in them is  $T_{cr} \ll \epsilon_g$ . Consequently, an intrinsic semiconductor has practically no free carriers at the Curie temperature  $T_{cr}$ . Therefore the temperature  $T_{cr}$  is determined only by the value of the interband exchange constant  $J_b$  and the concentration of the magnetic ions. Recognizing that the effective coupling constant  $\tilde{g}_t$  (25) is inversely proportional to the temperature and that a gap  $\epsilon_g$  exists in the unrenormalized electron spectrum at  $T \ll \epsilon_g$  we obtain an analogy with (24) the following expression for  $T_{cr}$ :

$$T_{cr} = \frac{1/2 \rho L(L+1) J_b^2 c^2}{[\ln(4\bar{\omega}/\epsilon_g)]^{-1} - \rho g}. \quad (42)$$

In the derivation of this formula we took into account the fact that at low temperatures ( $T_{cr} \ll \epsilon_g$ ) the Fermi distribution in a formula of the type (24) can be replaced by a step. We see thus that the temperature of the ferromagnetic transition in a semiconductor doped with magnetic ions is proportional to the square of their concentration and increases with increasing state density

near the end points of the valence band and the conduction band. It is important that the same state density enters in the definition also of the temperature of the structural transformation.<sup>[15]</sup>

We must make here also the following important remark. Throughout this paper we have assumed that the interband exchange interaction is constant. This is not always the actual case. Indeed, the symmetry of  $J_b$  is determined by the symmetry of the matrix element of the Coulomb electron-electron interaction  $V$  in the form

$$J_b \sim \langle \varphi_1(\mathbf{r}) \Phi(\mathbf{r}') | V | \varphi_2(\mathbf{r}') \Phi(\mathbf{r}) \rangle, \quad (43)$$

where  $\Phi(\mathbf{r})$  is the wave function of the unpaired electron, which is bound to the magnetic ion, and  $\varphi_i(\mathbf{r})$  are, as before, the Bloch functions of the electron and the  $i$ -band of the semiconductor. It is seen from (43) that if the functions  $\varphi_1$  and  $\varphi_2$  are transformed in accordance with the representations of different parity with respect to inversion, and the magnetic ion occupies a central-symmetry position, then  $J_b = 0$ . This is precisely the situation realized in IV-VI semiconductors in the high-temperature cubic phase. Consequently, in the absence of excess carriers (intrinsic semiconductor) there should be no ferromagnetic transition via magnetic ions in the IV-VI cubic phase. The situation is entirely different in a structurally distorted ferroelectric phase of these compounds. The point symmetry of the ion now no longer contains an inversion, therefore  $J_b$  (43) is no longer identically equal to zero. It is easy to assume that now  $J_b$  is proportional to the relative displacement  $u$  of the sublattices in the ferroelectric phase, which in the case of a second-order transition depends on the temperature like

$$u \sim (T_s - T)^{1/2}. \quad (44)$$

Therefore, to determine the ferromagnetic Curie temperature  $T_{cr}$  of intrinsic IV-VI semiconductors it is necessary to substitute in formula (30)  $J_b \sim (T_s - T)^{1/2}$ , where  $T_s$  is the temperature of the ferroelectric transition. Thus, for the substances discussed here one should expect the ferromagnetic and the structural transitions in them to be connected, with  $T_s > T_{cr}$ .

To be sure, one can imagine also a different situation. Assume that there is no structural transition at all in the pure IV-VI compound. It is easy to verify, however, that the introduction of magnetic ions into the matrix of such a semiconductor can lead to structural instability, and the structural transformation must of necessity be accompanied by the appearance of ferromagnetic properties (i.e.,  $T_s = T_{cr}$ ).

Indeed, if we examine the expression for the energy gain in the FED phase, we note that the gain is proportional to  $J_b^2$ . On the other hand, in our case the very quantity  $J_b \sim u$ . Therefore a negative contribution appears in the potential energy of the oscillator that determines the frequency of the elastic oscillations of the magnetic ion relative to its central-symmetry position in a cubic crystal, and this contribution is due to the gain in the magnetic energy. Obviously, this will lead to a softening of this oscillation mode, and at a sufficiently low temperature  $T_s$  it will lead also to a struc-

tural transition in which ferromagnetic properties appear in the system.

The authors are grateful to Yu. V. Kopaev for a discussion of the results.

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Translated by J. G. Adashko

## Magnetic phase transition from the antiferromagnetic to the paramagnetic state in NaMnCl<sub>3</sub>

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 (Submitted 26 January 1978)  
 Zh. Eksp. Teor. Fiz. **75**, 577-584 (August 1978)

The magnetic properties of a single crystal of antiferromagnetic NaMnCl<sub>3</sub> have been investigated with a vibrating-sample magnetometer in magnetic fields up to 65 kOe, over the temperature range 2 to 25 K. It is shown that in magnetic fields  $H = 15$  kOe a phase transition of the second kind, from the antiferromagnetic state to the paramagnetic, occurs in NaMnCl<sub>3</sub> at a temperature corresponding to the measurements. The features of this transition that are manifested on the magnetization curve of the single crystal are investigated.

PACS numbers: 75.30.Kz, 75.50.Ec

Sodium manganese chloride, NaMnCl<sub>3</sub>, crystallizes in the hexagonal syngony, space group  $R\bar{3}$ . The parameters of the hexagonal cell at room temperature are:  $a = 6.591$  Å,  $c = 18.627$  Å.<sup>[1]</sup> The structure of NaMnCl consists of alternating layers of Mn<sup>2+</sup> and Na<sup>+</sup> ions separated by layers of Cl<sup>-</sup> ions (Fig. 1). The distance between neighboring Mn<sup>2+</sup> ions located in a single plane is less by a factor 1.63 than the distance between Mn<sup>2+</sup> ions in neighboring planes. The elementary cell of NaMnCl<sub>3</sub> contains two magnetic ions.

It has been discovered<sup>[2,3]</sup> that NaMnCl<sub>3</sub> is antiferromagnetic, with Néel temperature  $T_N = 7.1$  K. Interest in further investigation of this crystal was determined by the possibility of studying a magnetic phase transition produced by application of a magnetic field, and due to destruction of the antiferromagnetic structure at a critical field, since from estimates obtained in Ref. 3 the exchange field is  $H_E \sim 13$  kOe. According to Ref. 3, sodium manganese chloride belongs to the quasi-two-dimensional class of antiferromagnets.

NaMnCl<sub>3</sub> monocrystals for the investigations were grown by B. V. Beznosikov at the L. V. Kirenskiĭ Institute of Physics, Siberian Division, Academy of Sciences, USSR.<sup>2)</sup> X-ray investigations made on the

NaMnCl<sub>3</sub> at room temperature showed agreement of the cell parameters with those given above and absence of paramagnetic impurities, within the limits of accuracy of the method. Investigations of the NaMnCl<sub>3</sub> monocrystals were made with a vibrating-sample magnetometer<sup>[4]</sup> over the magnetic-field range 0 to 65 kOe and the temperature range 2 to 20 K. Temperatures below  $T = 4.2$  K were reached by evacuating helium from a cryostat. The orientation of the crystal axes of the

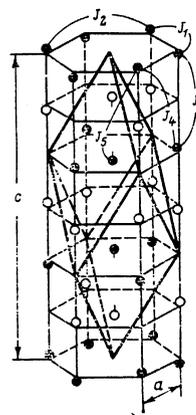


FIG. 1. Elementary cell of NaMnCl<sub>3</sub>. Light points, Na<sup>+</sup>; dark points, Mn<sup>2+</sup>.