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Re-entrant electronic phase separation in magnetic semiconductors and materials exhibiting colossal magnetoresistance

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Abstract. The electronic phase separation in doped antiferromagnetic semiconductors and materials exhibiting colossal magnetoresistance, with the charge-carrier density n close to the density n_u at which the entire crystal becomes ferromagnetic, is investigated theoretically. The case of wide s bands and that of double exchange are investigated. At $n < n_u$ a first-order phase transition from the phase-separated state to the ferromagnetic state should take place on increase of the temperature. At $n > n_u$ a re-entrant phase separation is possible when, with increasing temperature, first, the first-order phase transition from the ferromagnetic state to the phase-separated state takes place and, then, the latter melts.

1. Introduction

Electronic phase separation, predicted theoretically for degenerate magnetic semiconductors by one of the present authors in 1972 [1, 2], is now firmly established (see the review article [3]). For degenerate antiferromagnetic semiconductors, the reason for the phase separation occurring is as follows [1–4]. The energy of the charge carriers is minimal when the ferromagnetic ordering sets in. For this reason, they tend to establish it in an initially antiferromagnetic crystal. But, if the density of charge carriers is insufficient for establishing the ferromagnetic ordering throughout the entire crystal, they may concentrate in a certain portion of the crystal and make it ferromagnetic. The rest of the crystal remains insulating and antiferromagnetic. As the ionized donors are frozen and cannot diffuse at actual temperatures, this constitutes simultaneous charge separation in the crystal, when, for example, the ferromagnetic portion is charged by the excess conduction electrons negatively and the antiferromagnetic portion is charged by ionized donors positively. On increase in the density n , the size of the ferromagnetic portion increases until the entire crystal becomes ferromagnetic at a certain density n_u .

In the case considered, the phase-separated state is the ground state of the crystal. In this respect it differs basically from the well known phase separation at the temperature of the first-order phase transition. On increase in temperature, the phase separation disappears, and the state of the crystal becomes uniform as a result of a first-order or second-order phase transition [5]. But the investigations in [5] were carried out for densities far below n_u . So, a study of the phase diagram close to n_u is worth carrying out.

In what follows, it will be shown that at $n < n_u$ a phase-separated state can be abruptly replaced by a uniform ferromagnetic state, on increase in temperature.

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Even more interesting is the case in which the electron density in an antiferromagnetic crystal is so high that the ground state is ferromagnetic. It will be shown here that an increase in temperature can cause phase separation with formation of a highly conductive ferromagnetic phase and an insulating antiferromagnetic phase. On further increase in temperature, the phase-separated state disappears again, so phase separation manifests itself as a re-entrant phenomenon.

The present treatment supplements the theory from [1–5] in yet another respect. Colossal-magnetoresistance materials are believed to be, in essence, heavily doped antiferromagnetic semiconductors with double exchange. For this reason the treatment of [1–5] carried out for wide-band materials is generalized here to the case of narrow-band materials, to which double exchange corresponds.

Now the experimental situation will be discussed briefly. In addition to the degenerate antiferromagnetic semiconductors EuSe and EuTe, HTSC have recently been observed to exhibit phase separation (see [3]). The problem of the electronic phase separation is highly relevant for colossal-magnetoresistance materials, too. In the pioneering investigation [6] it was established by means of neutron studies that $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ displays ferromagnetic–antiferromagnetic phase separation in the ground state, though the nature of this separation was not established, and it was not shown that it is just electronic and not chemical. NMR investigations [7] show that in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ferromagnetic and antiferromagnetic phases exist below the Curie point. The authors of [7], on the basis of the theory from [1, 2], explain this fact by electronic phase separation.

Quite recently, experimental evidence was obtained showing that, above the Curie point, long-lived antiferromagnetic clusters coexist with ferromagnetic critical fluctuations in ferromagnetic $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ [8]. This situation resembles re-entrant phase separation, the notion of which is formulated in the present paper.

2. A model of the phase-separated state

In this section an investigation of the phase separation in a degenerate antiferromagnetic semiconductor first undertaken in [1, 2] will be continued. The s–d model will be used again. The treatment carried out here is based on the standard s–d model with the Hamiltonian

$$H = \sum E_k a_{k,\sigma}^* a_{k,\sigma} - \frac{A}{N} \sum (\mathbf{s} \cdot \mathbf{S}_g)_{\sigma,\sigma'} \exp\{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{g}\} a_{k,\sigma}^* a_{k',\sigma'} - \frac{I}{2} \sum \mathbf{S}_g \mathbf{S}_{g+\Delta} \quad (1)$$

where $a_{k,\sigma}^*$, $a_{k,\sigma}$ are the s-electron operators corresponding to the conduction electrons or holes with the quasimomentum \mathbf{k} and spin projection σ , \mathbf{s} represents the spin operator and \mathbf{S}_g that of the d spin at the site \mathbf{g} , Δ is the vector connecting the first-nearest neighbours, and N is the number of atoms in the crystal region considered. The first term in equation (1) is the s-electron kinetic energy, the second is the s–d exchange energy, and the third is the exchange interaction between d spins which in what follows will be called the direct exchange. For the sake of definiteness, the s–d exchange integral A is assumed to be positive.

First, like in [1–5], it will be assumed that the s-electron bandwidth W greatly exceeds the energy AS of the s–d exchange, where S is the d-spin magnitude. Then the treatment will be generalized to include the opposite limiting case $W \ll AS$ ('the double exchange'), which, as is usually believed, is more appropriate for the colossal-magnetoresistance materials. The phase separation was not considered in this case yet.

Only the case of relatively large s-electron densities will be considered, when the entire

crystal or its greater part is ferromagnetic. Like in [1–5], a variational procedure will be used to obtain the free energy F . To reduce the Coulomb energy, the two phases should be intermixed. We will use results already established in [1, 2]: to ensure the minimal energy, the geometry of the phase-separated state should correspond to small antiferromagnetic insulating droplets of spherical shape forming a superlattice inside the ferromagnetic highly conductive host. The variational parameters are the ratio x of the volumes of the antiferromagnetic and ferromagnetic phases and the radius R of the antiferromagnetic droplet.

In the wide-band case, $AS \ll W$, only temperatures at which the conduction electrons are completely spin polarized are considered for the sake of simplicity. This means that the inequality $AM > \mu$ holds, where μ is the Fermi energy, and M the average magnetization per atom. Then, with account taken of the strong degeneracy of the electron gas, the trial free energy is given by the expression

$$F = E_B + E_S + E_C + F_M \quad (2)$$

where E_B is the bulk s-electron kinetic energy:

$$E_B = \frac{3}{5} \mu(n) n (1+x)^{2/3} \quad (3)$$

where

$$\mu(n) = \frac{(6\pi^2 n)^{2/3}}{2m} \quad (\hbar = 1).$$

Here n is the average electron density, and m is the s-electron effective mass; the volume of the system is set equal to 1.

The notation E_S is used for the electron surface energy, i.e. for the correction to the electron kinetic energy arising due to the fact that the electron motion is restricted by the ferromagnetic portion of the crystal (in fact, this energy takes into account the electron level spatial quantization in a bounded region in the Born–Oppenheimer approximation):

$$E_S = \frac{15}{16} \left(\frac{\pi}{6} \right)^{1/3} \frac{x E_B}{n^{1/3} (1+x)^{1/3} R}. \quad (4)$$

The Coulomb energy E_C is calculated using the jellium model for the ionized donors. The crystal is separated into the Wigner cells, i.e. into spheres enveloping the antiferromagnetic inclusions drawn so as to make the total charge inside the sphere vanish:

$$E_C = \frac{2\pi}{5\epsilon} (neR)^2 x [3x + 2 - 3x^{1/3} (1+x)^{2/3}]. \quad (5)$$

Finally, the term F_M denotes the free energy related to the s–d and d–d exchange interactions. In the first approximation in AS/W , it may be represented in the form

$$F_M(T) = -\frac{AS}{2} n + \frac{JS}{v(1+x)} + \frac{xG_A(T)}{1+x} + \frac{G_F(T)}{1+x} \quad J = -ISz \quad (6)$$

where $v = a^3$ is the unit-cell volume, and z is the coordination number (it should be recalled that, according to the condition for the initial antiferromagnetic ordering, the d–d exchange integral for the first-nearest neighbours, I , is negative). The first term in (6) is the difference in the s–d exchange energy between the ferromagnetic and antiferromagnetic states, and the second term represents the energy of the d–d exchange required for conversion of the antiferromagnetic ordering into ferromagnetic ordering. The functions $G_A(T)$ and $G_F(T)$, vanishing at $T = 0$, in the spin-wave region are the magnon free energies in the

antiferromagnetic and ferromagnetic phases, respectively. Explicit expressions for these functions will be given later.

Now a generalization to the case with double exchange $W \ll AS$ will be given. For $A > 0$, equations (2)–(5) remain intact. In the first-nearest-neighbour approximation the electron effective mass in the ferromagnetic state is related to the hopping integral t by the standard expression $1/2ma^2 = t$. But the expression for F_M changes drastically.

In analysing its structure, one should keep in mind that in the zeroth approximation in W/AS each s electron is fixed at a certain site. Due to the s – d exchange interaction, the spins of the s electron and the atom at which it is located combine to form a united spin of magnitude $S + 1/2$. The corresponding gain in the energy is equal to $AS/2$, independently of the configuration of the set of d spins. In particular, the gain is the same for both ferromagnetic and antiferromagnetic orderings. For this reason, the s – d exchange integral cannot enter the quantity F_M .

This quantity is nonzero only in the first order in W/AS , where $W = 2zt$ (z is the coordination number). For the ferromagnetic ordering, the s -electron motion does not differ from the free-electron motion. Hence, the s -electron band bottom should be located at $(-AS/2, -W/2)$. As for the antiferromagnetic ordering, it hinders the s -electron motion, and s -electron band narrowing occurs. According to [4], the bandwidth with the antiferromagnetic ordering is $(2S + 1)^{1/2}$ times less than that with the ferromagnetic ordering. For $(2S)^{1/2} \rightarrow \infty$, it vanishes, and this result agrees with that obtained in [9] for classical spins. As a result, the quantity F_M can be represented by

$$F_M^{\text{DE}}(T) = -\frac{Wn}{2} \left(1 - \frac{1}{\sqrt{2S+1}} \right) + \frac{JS}{v(1+x)} + \frac{xG_A^{\text{DE}}(T)}{1+x} + \frac{G_F^{\text{DE}}(T)}{1+x} \quad (6a)$$

where, similarly to the functions G in (6), the functions G^{DE} vanish at $T = 0$ (the superscript DE denotes double exchange).

The total free energy F should be minimized with respect to R and x . The former procedure can be carried out explicitly, taking into account the fact that only E_S and E_C are R -dependent. After this partial minimization, the free energy becomes a function of the only remaining parameter x :

$$F(x) = E_B + F_M + 1.2 \gamma n x [3x + 2 - 3x^{1/3}(1+x)^{2/3}]^{1/3} (1+x)^{2/9} \quad (7)$$

where

$$\gamma = \left[\frac{\mu^2(n) e^2 n^{1/3}}{\epsilon} \right]^{1/3}$$

where ϵ is the dielectric constant of the crystal.

Strictly speaking, further investigation is possible only by numerical methods. Nevertheless, some important results can be found analytically.

3. Characteristics of the non-RKKY exchange in ferromagnetic semiconductors

In order to find the temperature dependence of the free energy, one should construct a theory of the indirect exchange in magnetic semiconductors. The standard RKKY theory is not appropriate, as the condition for its validity, $\mu \gg AS$, is not met. This is especially so in the case of the double exchange. But even in the wide-band case, the inequality $AS > \mu$, opposite to the RKKY validity condition, is typical of magnetic semiconductors due to the relatively small charge-carrier density. So far, only the magnon spectrum for the ferromagnetic ordering has been found for the magnetic semiconductors with wide and

narrow bands [4]. In what follows, an expression for the free energy in the spin-wave region will be deduced for both wide- and narrow-band cases. In addition, the magnon spectrum will be found for $S \gg 1$ independently of the ratio AS/W . In both limiting cases, $AS \ll W$ and $AS \gg W$, the results obtained below reproduce results from [4].

The Holstein–Primakoff transformation for the d-spin operators

$$S_g^+ = \sqrt{2S}b_g \quad S_g^- = \sqrt{2S}b_g^* \quad S_g^z = S - b_g^*b_g \quad (8)$$

is applied to the Hamiltonian (1) with b_g^*, b_g being the d-magnon operators. Then the Hamiltonian takes the form

$$H = H_0 + H_1 + H_2 \quad (9)$$

where

$$\begin{aligned} H_0 &= \sum E_{k,\sigma} a_{k,\sigma}^* a_{k,\sigma} + \sum \omega_q^0 b_q^* b_q \\ H_1 &= A \sqrt{\frac{S}{2N}} \sum (a_{k,u}^* a_{k+p,d} b_p^* + a_{k,d}^* a_{k-p,u} b_p) \\ H_2 &= \frac{A}{N} \sum' \sigma a_{k,\sigma}^* a_{k',\sigma} b_q^* b_{q'} \\ E_{k,\sigma} &= E_k - AS\sigma \quad \omega_q^0 = -J(1 - \gamma_q) \quad \gamma_q = \frac{1}{z} \sum \exp(iq \cdot \Delta). \end{aligned}$$

Here the subscripts u, d correspond to $\sigma = +1/2$ and $\sigma = -1/2$, respectively; the prime on the summation sign in the expression for H_2 indicates conservation of the quasimomentum.

One should stress that the d magnons introduced by (8) are not true magnons which represent the oscillations of the total moment of the system consisting not only of the localized d spins but also of spins of the delocalized s electrons. The number of true magnons should be conserved, whereas the number of d magnons is not a conserved quantity. To go over from the d magnons to the true ones, one should carry out a canonical transformation which eliminates the terms linear in the magnon operators from the Hamiltonian (9):

$$H'' = \exp(U)H \exp(-U). \quad (10)$$

Discarding small terms of the order J/A , one obtains for the operator U

$$U = A \sqrt{\frac{S}{2N}} \sum \left(\frac{a_{k,u}^* a_{k+q,d} b_q^*}{E_{k,u} - E_{k+q,d}} + \frac{a_{k,d}^* a_{k-q,u} b_q}{E_{k,d} - E_{k-q,u}} \right). \quad (11)$$

When $A > 0$, due to the condition $AS > \mu$ one can retain in the transformed Hamiltonian just the terms which do not contain the operators $a_{k,d}$. Then, to first order in $1/S$, one has

$$H'' = H_0 + \sum C_{kq} a_{k,u}^* a_{q,u} b_q^* b_q \quad (12)$$

where

$$C_{kq} = \frac{A}{2N} \frac{E_{k+q} - E_k}{AS + E_{k+q} - E_k}.$$

One finds the magnon spectrum to the same order in $1/S$ by averaging over the electron states:

$$\omega_q^F = \omega_q^0 + \sum C_{kq} f_k \quad (13)$$

where f_k is the s-electron distribution function.

As follows from (13) and (12), for any AS/W and n , the magnon frequency vanishes at $q \rightarrow 0$ as it should. Moreover, the energy spectrum for long-wavelength magnons does not depend on the ratio AS/W . The condition for this is the inequality

$$AS \gg |E_k - E_{k+q}| \quad \text{for all } k < k_F$$

where k_F is the Fermi momentum. This inequality is met for the entire Brillouin zone in the case of double exchange. If one takes the electron energy in the first-nearest-neighbour approximation, $E_k = -zt\gamma_k$, one obtains the following expression for the magnon frequencies, assuming that $W \ll AS$:

$$\omega_q^F = (-J + J^{\text{DE}})(1 - \gamma_q) \quad (14)$$

where

$$J^{\text{DE}} = \frac{zt}{2SN} \sum \gamma_k f_k.$$

One sees from (14) that the length of the indirect exchange for the double-exchange case is only one lattice constant, which manifests very distinctly the non-RKKY nature of the indirect exchange. This result agrees with results of neutronographic studies of a presumably double-exchange material, $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_4$ [10].

In the opposite limiting case of wide bands, the magnon frequency is approximated by the expression

$$\omega_q = -J(1 - \gamma_q) + \frac{Avq^2}{q_0^2 + q^2} \quad (15)$$

where $v = nv$ and $q_0^2 = 2mAS$.

In the case considered ($I < 0$), the quantity J is positive. Hence, as follows from (14) and (15), the ferromagnetic ordering in doped antiferromagnetic semiconductors becomes relatively stable only after the electron density reaches a critical value:

$$v_F = \frac{4J}{A} \quad \text{if } W \gg AS \quad (16)$$

$$v_F = \frac{2JS}{zt} \quad \text{if } W \ll AS. \quad (17)$$

But this does not mean that the ferromagnetic ordering is absolutely stable at $n > n_F$. It will be shown below that within a density range $n_F < n < n_u$ the phase-separated state is more energetically favourable than the ferromagnetic state.

One can hope that equations (14) and (15) are reasonable not only for large spins but also for spins of the order of 1. First, they meet the requirement for the q -dependence of the frequencies of the long-wavelength ferromagnetic magnons independently of the spin magnitude. Second, equation (14) displays an expected dependence on W : the magnon frequencies in the double-exchange limit are of the first order in W/AS . The accuracy of equation (14) can be estimated by comparing equation (17) with a similar expression obtained in [4] by a variational procedure valid for any spin magnitudes: the latter differs from equation (17) by the replacement of S by $S + 1$. This justifies the assumption that the relative correction to J^{DE} is close to $1/S$.

The fact that in the wide-band case equation (15) gives a reasonable estimate for the magnon frequencies for $S \sim 1$ may be confirmed by the following considerations based on the presence of an additional small parameter AS/W .

If one starts from an entirely ferromagnetic state and seeks for a change in the energy due to a reduction of the spin projection of one of the atoms by 1, then at $I = 0$ one finds it to

be equal to $Av/2$ independently of S . But this is just the frequency of the short-wavelength magnons, $q > q_0$, given by equation (15) at $I = 0$. Hence, in the short-wavelength limit equation (15) is valid for all S .

The situation with the long-wavelength magnons ($q < q_0$) is much more complicated: their frequencies are nonanalytical in AS/W , and it is precisely this nonanalyticity that ensures the vanishing of the magnon frequency for $q \rightarrow 0$. Due to the nonanalyticity, the rise in the magnon frequencies with q^2 should be very steep: the long-wavelength frequencies are proportional not to A but to a much larger quantity W . Obviously, as the nonanalyticity is a consequence of the symmetry of the system, it should remain also for smaller spins.

An additional confirmation of the applicability of (15) for small S can be obtained by comparison of the temperature dependence of the s-electron spectrum found from (12) by averaging over magnons at $S \gg 1$ and that obtained in reference [11]. In the latter case, applying a variational procedure to Hamiltonian (1), a result was obtained at $AS/W \ll 1$ valid for all of the spin magnitudes. In the leading approximation in AS/W , these two results coincide.

For these reasons, at least when calculating such integral quantities as the free energy, equation (15) can be considered a reasonable estimate for all spin magnitudes.

4. Thermally induced phase separation

In this section we will try to elucidate in what manner the concentration or conventional temperature phase transitions take place from the phase-separated state to the uniform state. In [1–5] an opinion was expressed, and confirmed by numerical calculations, that the concentration phase transition should be of second order. A more accurate investigation carried out below shows that, in reality, it should be of first order but very close to a second-order phase transition. The fact that the transition must be abrupt is seen from the following considerations. If one assumes the opposite, i.e. that $x = 0$ at the transition point, then one finds from equation (7) that $d^2F(x)/dx^2$ is negative, diverging as $x^{-2/3}$.

Hence, the condition that $dF/dx = 0$ at $x \rightarrow 0$ corresponds not to a minimum but to a maximum of the free energy. In other words, the volume of the antiferromagnetic phase in the phase-separated state cannot be arbitrarily small. Correspondingly, at a certain density $v_u = n_u v$, a transition from the phase-separated state to the uniform state takes place, on increase in density. To ensure the stability of the ferromagnetic state, the density v_u should exceed v_F (given by equations (16) and (17)).

As the volume of the antiferromagnetic phase cannot be arbitrarily small, the concentration and temperature phase transitions from the ferromagnetic to the phase-separated state should be first order. With allowance for (7), the condition is as follows:

$$F(x, T) \equiv F(x, 0) + \frac{xG_A}{1+x} + \frac{G_F[n(1+x)]}{1+x} = F(0, 0) + G_F(n). \quad (18)$$

The s–d exchange energy ($-ASn/2$) is the same for both of these states and for this reason does not enter equation (18). In (18), account is taken of the fact that in the phase-separated state the electron density in the ferromagnetic phase is not n but $n(1+x)$.

The considerations presented above are confirmed by numerical calculations for the case where $W \gg AS$ based on equation (18) at $T = 0$. The following values of the parameters were chosen: $a = v^{1/3} = 3 \times 10^{-8}$ cm, $m = 10^{-27}$ g, $\epsilon = 10$, $AS = 1$ eV (this corresponds to $q_0 a = 1.7$). Then, if one takes $JS = 0.0005$ eV, one finds from the condition for the minimum energy (7) at $T = 0$ that the energy E_{ps} of the phase-separated state reaches

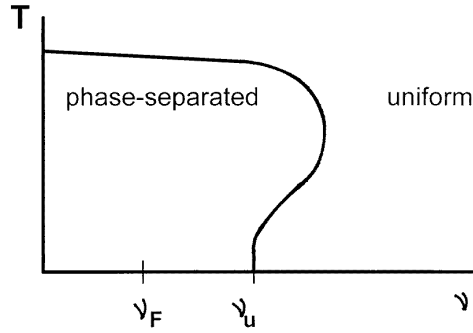


Figure 1. A qualitative diagram of the system: T against ν .

the energy E_u of the uniform state at $\nu_u = 0.003565$; that is, with allowance for (16), $\nu_u/\nu_F = 1.78$ (figure 1).

The E versus x curve attains two minima, at $x_1 = 0$ and $x_3 = 0.08$, separated by a maximum at $x_2 = 0.01$ (as the x_1 -point lies at the boundary of the x -interval, the equality $dE/dx = 0$ is not met there). If one takes $J = 0.001$ eV, then the $E(x)$ curve at $\nu_u = 0.00543$ displays a similar behaviour, with the maximum at $x_2 = 0.01$ and with the minimal values at $x_1 = 0$ and $x_3 = 0.06$ ($\nu_u/\nu_F = 1.37$). These numerical results confirm the above-mentioned conclusion: on increase in the electron density, the volume of the antiferromagnetic phase disappears abruptly at ν_u .

Our main aim is to prove the possibility of thermally induced re-entrant phase transitions from the uniform ferromagnetic state to the two-phase state at ν slightly exceeding ν_u . To do this, it is sufficient to restrict consideration to the spin-wave region. Obviously, a necessary condition for this transition is $G_F > G_A$.

In order to calculate the free energy of the system, one should take into account the fact that the electron gas remains strongly degenerate at all actual temperatures. For this reason, one can replace the operators $a_{k,u}^* a_{k,u}$ in the Hamiltonian (12) by the electron distribution function at $T = 0$. This means that the functions $G_F(T)$ and $G_A(T)$ in (6), (6a) are nothing but the free energies of magnons with the frequency spectrum (13)–(15) in the ferromagnetic state and with the spectrum

$$\omega_q^A = \sqrt{1 - \gamma_q^2} \quad (19)$$

in the antiferromagnetic state.

In both cases the free energy is given by the expression [12]

$$G = T \sum \ln \left[1 - \exp\left(-\frac{\omega_q}{T}\right) \right]. \quad (20)$$

First, the case of $T \ll T_C/S$ realized for small spins over the entire spin-wave region or for large spins at very low temperatures will be investigated. In the case of wide bands considered here, it will be assumed that only the magnon wave vectors with q less than q_0 are essential. Then, in the first-neighbour approximation, one can write, instead of equation (15),

$$\omega_q^F = \frac{J_{ef} q^2 a^2}{2} \quad (21)$$

where

$$J_{ef} = \frac{z t \nu}{2S} - J.$$

As seen from equation (21), due to the nonanalyticity of the spectrum in AS/W , the indirect exchange strength (the first term in equation (21)) at small q is proportional not to AS but to a much larger quantity W . This reduces the ferromagnetic magnon number and enhances the free energy as compared with the RKKY theory predictions. In other words, this should facilitate the phase separation. Substituting (21) into (20) and representing the logarithmic function by an exponential series, one obtains the following expression for the ferromagnetic magnon free energy:

$$G_F = -\frac{2^{3/2}\zeta(5/2)NT^{5/2}}{8\pi^{3/2}J_{ef}^{3/2}} \quad (T \ll J_{ef}q_0^2a^2) \quad (22)$$

where $\zeta(n)$ is the Riemann zeta function. Using (19), in the same long-wavelength approximation one obtains for the antiferromagnetic magnon free energy

$$G_A = \frac{2\zeta(4)NT^4}{\pi^2J^3} \quad (T \ll J). \quad (23)$$

Hence, under the condition that $W \gg AS$,

$$G_A/G_F \approx 5\left(\frac{T}{J}\right)^{3/2}\left(\frac{J_{ef}}{J}\right)^{3/2} = 5\left(\frac{T}{J}\right)^{3/2}\left[(W/AS)\left(\frac{v}{v_F}\right) - 1\right]^{3/2}. \quad (24)$$

This means that for $T \rightarrow 0$ the transition from the uniform state to the nonuniform state is impossible even if $v \rightarrow v_u$. But it becomes possible at higher temperatures. For $T > (J/3)(AS/W)(v_F/v)$ one may neglect G_F as compared with G_A , and the transition from the ferromagnetic state to the phase-separated state takes place at

$$T_u = \left\{ \frac{\pi^2(1+x)[F(x,0) - F(0,0)]J^3}{2\zeta(4)x} \right\}^{1/4}. \quad (25)$$

Obviously, on further increase in temperature, the phase-separated state should melt.

Now the case of $T_C/S \ll T \ll T_C$ for large spins will be investigated, where T_C is the Curie point. It corresponds to the spin-wave region due to the condition $S \gg 1$. As the frequencies of the antiferromagnetic magnons should also be below T , from equations (19) and (20) one easily obtains the following estimate for the antiferromagnetic magnon free energy:

$$G_A = TN\left(\ln\frac{J}{T} - \frac{1}{12}\right). \quad (26)$$

As to the free energy of the ferromagnetic magnons, for the case of the double exchange (14) it differs from (20) by the replacement of the antiferromagnetic exchange integral J by $J^{DE} - J$. In the wide-band case, to make the integration over q in equations (20) and (15) consistent, an isotropic interpolation for the direct-exchange contribution ω_q^0 , equation (9), is used. It matches the corresponding isotropic approximation for the indirect-exchange contribution (15) and goes over to an exact expression for ω_q^0 at the minimum and at the maximum of the magnon band:

$$\omega_q^0 \approx \frac{-J(aq)^2}{2[1 + 0.1841(qa)^2]}. \quad (27)$$

In this temperature range one may put $G = Tg$ where the function g is temperature independent. Then, using equation (18), one finds the following expression for the temperature of the transition from the uniform to the phase-separated state:

$$T_u = \frac{(1+x)[F(x,0) - F(0,0)]}{xZ} \quad (28)$$

where

$$Z = g_F(\nu) - g_A - \nu dg_F/d\nu. \quad (29)$$

Using the same value of $q_0a = 1.7$ as at the beginning of this section, one finds by a numerical integration of equation (20) over a sphere with a radius of $(6\pi^2)^{1/3}a$, with allowance for (15) and (29), that the quantity Z becomes positive for ν/ν_F exceeding 1.75. This means that the phase transition from the uniform state to the phase-separated state should take place at such large values of ν . According to the numerical value for ν_u presented at the beginning of the section, such values are quite realistic. Hence, the transition from the ferromagnetic state to the phase-separated state induced by increasing temperature is possible at more elevated temperatures, too.

If ν is below ν_u , and the quantity Z is negative, then this is evidence that a first-order phase transition from the phase-separated state to the uniform ferromagnetic state should take place with increasing temperature. A qualitative phase diagram of the system is presented in figure 1.

5. Conclusions

Phase separation into a highly conductive ferromagnetic phase and an insulating antiferromagnetic phase in degenerate antiferromagnetic semiconductors is investigated. The density of the charge carriers is assumed to be so high that at $T = 0$ the volume of the antiferromagnetic phase is very small or zero. On increase in the electron density, an abrupt concentration phase transition takes place from the phase-separated state to the uniform state. If the density exceeds its critical value at which the concentration phase transition takes place, then the ground state of the system is uniform. On increase in temperature, the state at first remains uniform, but at higher temperatures the phase separation can take place. At still higher temperatures the thermally induced phase-separated state melts, and the reverse transition to the uniform state takes place.

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