Resistivity extrema in double exchange ferromagnetic nondegenerate semiconductors

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A version of the magnetoimpurity theory of the colossal magnetoresistance materials suitable for the double exchange ferromagnetic nondegenerate semiconductors is presented. It provides an explanation of the nonmonotonic temperature dependence for the charge carrier density in them when it displays first a maximum and then a minimum, on increase in temperature. Respectively, the resistivity displays first a minimum and then a maximum. The theory is based on the relation between the charge carrier activation energy and the change in the magnon free energy caused by the ionization of an impurity. This is tantamount to the relation between the charge carrier density and the so called giant red shift of the optical absorption edge.

I. INTRODUCTION

The colossal magnetoresistance (CMR) arises in ferromagnetic materials as a result of the suppression of the resistivity peak by the magnetic field in the vicinity of the Curie point \( T_C \). Usually this phenomenon is related to the manganites, though not only they but also all conventional degenerate ferromagnetic semiconductors display a similar resistivity peak and CMR (see [1]). Still more unusual is the behavior of the nondegenerate ferromagnetic semiconductors, in which a resistivity minimum precedes the resistivity peak in the vicinity of \( T_C \) (Fig. 1). It is natural to assume that the origin of this peak is similar for all ferromagnetic semiconductors and manganites. One believes that the manganites are the double exchange systems, i.e., the exchange energy between the localized spins and charge carriers far exceeds the bandwidth in them. Hence the physical nature of the nonmonotonic temperature dependence of the conductivity in doped manganites should be especially close to that in the double exchange ferromagnetic semiconductors.

The resistivity peak in degenerate ferromagnetic semiconductors can be explained within the framework of the magnetoimpurity theory [1–5]. It is based on the fact that, due to the screening, the charge carrier density in the vicinity of the ionized donors (acceptors) is higher than far from them. The charge carriers give rise to the indirect exchange, which tends to support the ferromagnetic ordering. For this reason, at finite temperatures the local magnetization in the vicinity of impurities is higher than far from them. But the charge carrier energy is the lower the higher is the magnetization. For this reason, in addition to the Coulomb force, at \( T \neq 0 \) a “magnetic” force appears, which attracts the electron to the donor. If the Coulomb force alone is insufficient for the electron localization, the total Coulomb + “magnetic” force can cause the temperature-induced electron localization of electrons, i.e., the transition of the crystal from the highly-conductive state to the insulating one.

FIG. 1. Resistivity \( \rho (\Omega \text{ cm}) \), constant of normal Hall effect \( R_0 = 1/nee \text{ (cm}^2/\text{A s)} \), where \( n \) is the electron density, and the thermoelectric power \( \alpha \text{ (mV/deg)} \) of \( \text{CdCr}_2\text{Se}_4 \) doped by In (a donor impurity). Data on \( \text{Cd}_{0.99}\text{In}_{0.01}\text{Cr}_2\text{Se}_4 \) from [4] are presented.

On further increase in temperature, the excess local magnetization around the donors decreases. Depending on the impurity density, two scenarios are possible.

(1) The crystal becomes again highly-conductive. This
manifests itself as a high resistivity peak in the vicinity of $T_C$. (2) The crystal remains insulating up to the highest temperatures.

The magnetoimpurity theory is valid for all doped ferromagnetic semiconductors, independent of their being or not being double exchange and of the existence or nonexistence of the Jahn-Teller effect in them. It predicts the colossal magnetoresistance in the cases when the impurity density is sufficiently close to that, at which the Mott transition takes place. 

Some sort of the magnetoimpurity theory should also be valid for the nondegenerate ferromagnetic semiconductors but certainly its specific manifestation in the nondegenerate semiconductors should be different from that in the degenerate ones. Here the magnetoimpurity theory will be formulated for the double exchange semiconductors.

In addition to the fact that this theory makes it possible to explain the properties of some specific ferromagnetic semiconductors, it allows one to understand more deeply the processes in such double exchange systems as manganites. (Let us remind that many of them behave as the degenerate semiconductors below $T_C$ and as the nondegenerate ones above $T_C$).

The main results of the present paper can be explained qualitatively as follows. The drastic difference in the temperature dependence of the resistivity for the ferromagnetic and nonmagnetic semiconductors is attributed to the giant red shift of the optical absorption edge specific for the ferromagnetic semiconductors. It implies the decrease of the optical gap width with decreasing temperature. To explain this phenomenon, it is sufficient to note that the electron energy is the lower the higher is the magnetization $H$. At very low temperatures, the nondegenerate ferromagnetic semiconductor behaves like the nonmagnetic one: the charge carrier density increases exponentially with temperature. But the activation energy also increases with temperature (Fig. 2). The reason for it is the fact that the local magnetization in the vicinity of an unionized donor is higher than that averaged over the crystal. This is related to the indirect ferromagnetic exchange, which is realized by the donor electron. It increases the local magnetization close to the donor impurity as compared with its mean value over the crystal. Hence the rate of the temperature-induced rise of the donor level is considerably less than that of the conduction band bottom. This means that the donor level depth first increases with temperature, and this process is determined by the band bottom shift toward higher energies.

As the position of the band bottom determines the optical gap, one can say that the temperature-induced increase in the donor level depth is equal to the temperature increase of the optical gap. One calls this shift of the optical gap in the ferromagnetic semiconductors "the giant red shift of the optical absorption edge". The term "red" is a consequence of the fact that, experimentally, this optical shift was observed on decrease in temperature. The term "giant" follows from the fact that total optical shift amounts to several tens eV, which is by many orders of magnitude larger than in nonmagnetic semiconductors.

The temperature-induced increase in the activation energy first slows down the rate of the temperature-induced increase in the charge carrier density. On further increase in temperature, a temperature-induced rise in the charge carrier density gives place to by a decrease in it. This means that the density passes a maximum and then decreases (Fig. 1). But, on further increase in temperature, the long-range ferromagnetic ordering becomes destroyed, and destruction of the local ordering in the vicinity of the donors begins. Then the position of the band bottom becomes virtually temperature independent, and the donor level depth decreases with increasing temperature. Respectively, after passing a minimum, the charge carrier density increases again.

In reality, this simple physical explanation is valid only qualitatively since the density is expressed not in terms of the electron energy averaged over the magnetic state of the crystal but in terms of the change in the free energy of the magnetic subsystem caused by the impurity ionization. This is the basis for calculations carried out below.

One can point out CdCr$_2$Se$_4$ as an example of the standard ferromagnetic semiconductors with the double exchange. This material can be transferred in the degenerate state only by a very heavy doping. This implies a large electron effective mass in CdCr$_2$Se$_4$, which is a necessary condition for the double exchange. The double exchange scenario for it corresponds to the appearance of the Cr$^{2+}$ ions instead of the regular Cr$^{3+}$. The former play the role of the conduction electrons. CdCr$_2$Se$_4$ displays a giant red optical shift of about 0.15 eV and a nonmonotonic temperature dependence of the resistivity of the type described above, i.e., with a minimum and a maximum. Figure 1 in the present paper is taken from [1].

II. QUANTUM DOUBLE-EXCHANGE HAMILTONIAN IN THE SPIN-WAVE REGION

Usually in magnetic semiconductors only one type of the charge carriers is sensitive to the magnetic ordering (only the charge carriers of one sign move over the magnetic cations. The charge carriers of the opposite sign move over the nonmagnetic ions). For example, in CdCr$_2$Se$_4$ the electrons interact strongly and the holes very weakly with the magnetic subsystem. For this reason, it is sufficient to take only the former into account.
The problem of the energy spectrum in the double exchange systems is treated as a single-electron problem. The treatment is based on the $s-d$ model with the $s$-electrons modeling the conduction electrons or holes moving over the crystal and exhibiting a strong exchange interaction with the localized $d$-spins. With accounting for the donor (acceptor) impurities the total Hamiltonian of the system is written in the form

$$H = H_{sd} + H_I. \quad (1)$$

The quantum $s-d$ exchange Hamiltonian $H_{sd}$ for double-exchange case was deduced by the present author as early as in 1969 (See Refs. 11, 13, 14). Unlike corresponding Hamiltonians deduced by other authors, this Hamiltonian for the antiferromagnetic $s-d$ exchange is exact to the first order in $AS/W$, and no additional approximations (the mean field etc.) were used. To construct it, an effective spin $S_g$ of the magnitude $S$ is ascribed to each magnetic atom $g$, independently of its being free or occupied by a $s$-electron (in the former case it is the true spin). In the last case, it formally increases the number of spin degrees of freedom by 1 as compared with its actual number. However, the structure of the effective Hamiltonian is such that the contribution from the extra degree of freedom vanishes. As for the charge carriers, they are treated as spinless fermions with the operators $c^+_g$, $c_g$. This effective Hamiltonian is:

$$H_{sd}^{ef} = \frac{A(S+1)}{2} \sum c^+_g c_g - t_0 \sum F(S_g, S_g+\Delta)c^+_g c_g - I \sum S_g S_g + \Delta, \quad (2S+1)F(S_g, S_g+\Delta) = \sqrt{(S+S_g^2)(S+S_g^2+\Delta)}$$

$$+ \frac{1}{\sqrt{S+S_g^2}} S_g^2 S_g^2 + \Delta \frac{1}{\sqrt{S+S_g^2+\Delta}}$$

where $\Delta$ is the vector connecting the nearest neighbors in a simple cubic lattice of the magnetic atoms, $A$ is the $s-d$ exchange integral assumed to be negative here (see below), $I$ is the $d-d$ exchange integral which is assumed to be positive, $t_0$ is the hopping integral, which would have been realized if the crystal would have been nonmagnetic. The corresponding band width $W$ is equal to $12t_0$. In Eq.(2), small terms of the order of $IS^2/t$, which describe a change in the $d-d$ exchange of the atom bearing the charge carrier, are disregarded (they are presented in the original papers). The first term in Eq.(2) is an additive constant and for this reason can be omitted.

As usually, the inequality $t_0 \gg IS^2$ must be met as the hopping integral $t_0$ is of the first order of magnitude, and the $d-d$ exchange integral $I$ of the second order in the small $d$-orbital overlapping. In what follows, the condition of the double exchange $W \ll |A|S$ will be also assumed to be met, with the $s-d$ exchange integral $A$ being negative. Under these conditions, to a zero approximation in $W/AS$, the charge carrier is fixed at one of the magnetic atoms, their total spin being $S - 1/2$. This just corresponds to the situation in the manganites, where appearance of a hole at a regular ion Mn$^{3+}$ reduces its spin by 1/2.

It should be pointed out that the case $A < 0$ can be also applied to the conduction electrons if the occupancy of the $d$-shell exceeds 5/2. Then, due to the Pauli’s exclusion principle, the spin of the atom bearing a conduction electron should be equal to $S - 1/2$. In this case, the quantity $A$ looses the meaning of the Hund’s exchange integral and expresses only the Pauli’s principle. But, as the quantity $A$ enters Eq.(2) only through an additive constant in the electron energy, this fact is nonessential.

In the case of smaller $d$-shell occupancies, the quantity $A$ for the conduction electron is directly related to the Hund’s integral and hence is positive. One can construct a similar effective Hamiltonian also for $A > 0$ by introducing an effective spin $S$ for each atom. But in this case one of the states of an atom with the total spin $S + 1/2$ remains unaccounted for, and this restricts the applicability of this effective Hamiltonian. Nevertheless, it can be used, for example, for $2S \gg 1$ or for any spin magnitude in the spin-wave region. Then the quantity $F(S_g, S_g+\Delta)$ in Eq.(2) should be replaced by its conjugate $F(S_g, S_g-\Delta)$. As the spin-wave region will be considered below, both Hamiltonians for $A > 0$ and $A < 0$ lead to the same results.

In the classical limit $S \to \infty$, introducing the polar angles $\theta_g, \phi_g$ and carrying out a canonical transformation of the spinless operators shifting their phases one arrives to the classical Hamiltonian “with the Berry phases” deduced for the first time in Refs. 14, 11, 13.

The term $H_I$ in Eq.(1) describes the interaction between the $s$-electrons and impurities,

$$H_I = \sum_j V(g - R_j) c^+_g c_g, \quad (3)$$

where $R_j$ are the coordinates of impurity $j$.

Now the quantum double exchange Hamiltonian (2) will be specified for the spin-wave region. Introducing the magnon operators $b^+_g, b_g$ and performing the Holstein–Primakoff transformation in the Hamiltonian (2)

$$S^+_g = S - b^+_g b_g, \quad S^-_g = (2S)^{1/2} b_g, \quad S^0_g = (2S)^{1/2} b^+_g$$

one obtains the $s-d$ Hamiltonian in the spin-wave region:

$$H_{sd}^{SW} = -t \sum a^+_g a_g + \frac{t}{2S} \sum \left[ \frac{1}{2} (m_g + m_g + \Delta) - b^+_g b_g \right] a^+_g a_g + \Delta$$

$$+ IS \sum \left[ \frac{1}{2} (m_g + m_g + \Delta) - b^+_g b_g \right] \quad (4)$$
or in the quasimomentum representation

\[ H_{sd}^{\text{eff}} = -zt \sum \gamma_k c_k^\dagger c_k + \frac{zt}{4SN} \sum' (\gamma_k + \gamma_{q-k} - 2\gamma_{q-k'})c_k^\dagger c_{k'} b_q^\dagger b_{q'} + \sum \Omega_q b_q^\dagger b_q \]  

(4a)

\[ t = \frac{2St_0}{2S + 1}, \Omega_q = zJS(1 - \gamma_q), \]  

(5)

\[ \gamma_k = \frac{1}{z} \sum_{\Delta} \exp(i\Delta k) \quad (z = 6) \]

where z is the coordination number, the primed sum denotes conservation of the total quasimomentum. As is seen from Eq. (5), for \( A < 0 \) even with the complete ferromagnetic ordering, the \( s-d \) interaction reduces the effective hopping integral by a factor of \( 1 + 1/2S \). For \( A > 0 \) this reduction is absent, and \( t = t_0 \).

### III. TEMPERATURE DEPENDENCE OF THE CONDUCTION BAND BOTTOM

In order to calculate the charge carrier density, first the temperature dependence of the conduction band bottom in the spin-wave region will be investigated. The further consideration will be carried out under assumption that \( 1/2S \ll 1 \). One should keep in mind that in the theory of the magnetism the formal expansion in \( 1/2S \) powers usually gives reasonable results even for small spins. Then the total Hamiltonian of a perfect crystal can be represented in the form

\[ H_{sd}^{\text{eff}} = \sum E_k n_k + \sum B_{k,k+q} n_k m_q + \sum \Omega_q m_q \]  

(6)

\[ n_k = c_k^\dagger c_k, m_q = b_q^\dagger b_q, \]

\[ E_k = -zt\gamma_k, B_{k,k+q} = \frac{zt}{2SN}(\gamma_k - \gamma_{k+q}) \]  

(7)

Introducing the chemical potential \( \mu \), one can write for the average number of the \( s \) electrons with the quasimomentum \( k \):

\[ < n_k > = \frac{\partial F}{\partial E_k}, F = -T \ln Z_{de} \]  

(8)

\[ Z_{de} = \prod_{k,q} \sum_{\{n,m\}} \exp\{-\beta[(E_k - \mu)n_k + \Omega_q m_q + B_{k,k+q} n_k m_q]\} \]

\[ = \prod_{k,q} \left\{ \frac{1}{1 - \exp(-\beta\Omega_q)} \right\} \frac{\exp[\beta(\mu - E_k)]}{1 - \exp[-\beta(\Omega_q + B_{k,k+q})]}, \beta = \frac{1}{T}. \]  

(9)

One obtains from Eqs. (8) and (9):

\[ \begin{array}{c}
\{ 1 + \exp[\beta(E_k - \mu)] \Pi_q \{ 1 - \exp(-\beta(\Omega_q + B_{k,k+q})) \} \}^{-1} < n_k > = \\
\{ 1 + \exp[\beta(E_k - \mu)] \Pi_q [1 - \exp(-\beta\Omega_q)] \}^{-1} \\
\end{array} \]  

(10)

It should be noted that

\[ \prod_q [1 - \exp(-\beta\Omega_q)] = \exp(\beta F^0_m), \]

where

\[ F^0_m = T \sum_q \ln[1 - \exp(-\beta\Omega_q)] = Nf(J,T) \]  

(11)

is the magnon free energy in the absence of the conduction electrons.

Similarly, introducing the magnon free energy \( F^0_m \) in the presence of the \( s \)-electron with the quasimomentum \( k \),

\[ F^r_m = T \sum_q \ln\{ 1 - \exp[-\beta(\Omega_q + B_{k,k+q})] \} \]  

(12)

one can rewrite Eq. (10):

\[ < n_k > = \{ 1 + \exp[\beta(E_k - \mu)] \}^{-1}, \]

(13)

\[ E_k^r = E_k + F^r_m - F^0_m, \]  

(14)

or, using Eq. (11) and keeping in mind the fact that \( B \sim 1/N \):

\[ E_k^r = E_k + \frac{zt}{2SN} \sum_q \gamma_k (1 - \gamma_q) < m_q >, \]

\[ < m_q > = \frac{1}{\exp(\beta\Omega_q) - 1}. \]  

(15)

This corresponds to the temperature renormalization of the hopping integral:

\[ t_{ef}(T) = t \left[ 1 - \frac{1}{2SN} \sum_q (1 - \gamma_q) < m_q > \right]. \]  

(16)

Obviously, the quantity \( E_k^r \) represents the \( s \)-electron energy renormalized due to the electron-magnon interaction. As is seen from Eq. (15), the electron energy increases with temperature. As the energy of the holes is assumed to be temperature independent, this means that gap \( G(T) \) becomes wider. On the contrary, the temperature decrease causes its narrowing. Using the standard terminology, the temperature shift of the conduction band bottom represents the red shift of the optical absorption edge \( \delta G(T) \). This shift is proportional to \( T^{5/2} \) for \( T < J = ISz \) and to \( T \) for \( T > J \) (for the applicability of the spin-wave approximation in the latter
case, spins should be large, $2S \gg 1$). With $z = 6$, we have

$$\delta G(T) = G(T) - G(0) = F_k^m - F_0^m$$

$$= \frac{t_\zeta(3/2)}{16\pi^{3/2}} \left( \frac{6T}{J} \right)^{5/2}, \quad \text{for } T < J,$$

$$\delta G(T) = \frac{ztT}{2S\gamma} \quad \text{for } T > J.$$  (17)

where $\zeta(x)$ is the Riemann zeta-function.

As is seen from Eqs.(17), (18), the giant magnitude of the shift is a consequence of the fact that it is proportional to the $s$-electron bandwidth.

Comparison Eqs.(17) and (15), one sees that two different interpretations of the temperature dependence of the optical absorption edge are possible. The first of them is traditional and corresponds to the temperature dependence of the electron energy, which is obtained from Eq.(6) by averaging it over the magnons. Thereby an intuitive approach adopted in [1] is confirmed for the band electrons here. But the red shift can also be attributed to the change in the magnon free energy due to the electron excitation. In considering the impurity conductivity, one will see that only the latter approach is correct as it makes it possible to describe the temperature dependence of the electron discrete level correctly (see the paragraph after Eq.(27)).

IV. CHARGE CARRIER DENSITY IN AN IMPURITY SEMICONDUCTOR

Now our task is to calculate the charge carrier density in an impurity semiconductor. The calculation begins with the magnon energy spectrum in the presence of an unionized donors. The main feature of the impurity samples is the fact that the electron of a unionized donor realizes an indirect exchange between $d$-spins. As the electron density diminishes exponentially with increasing distance from the impurity, the intensity of the indirect exchange diminishes in a similar manner.

For $T = 0$ the electronic wave function can be found exactly in the effective mass approximation when the impurity has is the Coulomb potential. At higher temperatures the increased exchange will increase the magnetization in the vicinity of the impurity. The electron energy is the lower the higher the local magnetization. Hence an additional force appears which attracts the electron to the donor. Respectively, the effective Bohr radius should decrease, on increase in temperature. The problem can be solved by using a variational procedure for the free energy under condition that the donor electron be in the ground state with the hydrogen-like wave function

$$\psi(r) = \left( \frac{x^3}{\pi a_B^5} \right)^{1/2} \exp \left( -\frac{xt}{a_B} \right), \quad a_B = \frac{2a_t^2 \epsilon}{\epsilon^2},$$  (19)

where $x$ is the variational parameter and $\epsilon$ is the dielectric constant. The effective Bohr radius $a_B/x$ is assumed to be large comparing with the lattice constant $a$.

As is seen from the structure of the electron-magnon Hamiltonian (4) and from the form of the wave function (19), an exact treatment of the problem is impossible in this case. To obtain semiquantitative results, it is convenient to replace the nonuniform electron density distribution (19) by an uniform that with an average density $3/4\pi \rho^3$ inside of the sphere of the radius $\rho$:

$$\rho = \sum g\psi^2(g) = \frac{3a_B}{2\epsilon}.$$  (20)

Let us separate such a region from the totality of the magnetic atoms, and choose $V = \text{const}$ in the Hamiltonian $H_I$ (3) in such a way as to ensure the minimal $s$-electron energy $E_I$ to be equal to that value, which is obtained from the Hamiltonian $H_I$ with $V(g) = -e^2/\epsilon g$ with the use of the trial wave function (19). At $T \to 0$, when $x = 1$,

$$E_I \equiv -E_B = -e^2/2\epsilon a_B.$$  (21)

The relative number of the donors $\nu$ is assumed to be small. We can divide all regular magnetic atoms into those which enter spheres of radius $\rho$ surrounding donors and those which are outside these spheres (the number of the latter greatly exceeds the total number of the former).

Now the canonical transformation of the electron operators corresponding to sites inside the impurity region will be carried out:

$$a_g = \frac{1}{\sqrt{N_I}} \sum \exp(ipg)a_p,$$

$$b_g = \frac{1}{\sqrt{N_I}} \sum \exp(iqg)b_q,$$  (22)

$$N_I = \frac{4\pi \rho^3}{3a^3} = \frac{9\pi}{2} \left( \frac{a_B}{x a} \right)^3.$$  (23)

We will use the expression for the conduction-electron-magnon Hamiltonian (6) and retain only terms corresponding to the lowest discrete levels in the Hamiltonian $H_{sd} + H_I$ (1), (3) with the donor potential $V = \text{const}$. Then we arrive to the following Hamiltonian:

$$\begin{align*}
H &= (E_I - \mu) \sum n_{li} + \sum (E_k - \mu)n_k + \\
&\quad + \sum B_{ip} n_{li}^m + \sum B_{k,k+q} n_k m_q + \\
&\quad + \sum \Omega q m_q + \sum \Omega p m_p,
\end{align*}$$

$$B_{ip} = \frac{zt}{2S N_I} (1 - \gamma_p),$$  (24)

where $m_q$ and $m_q$ are the magnon operators for the $i$-th sphere and outside the spheres, which surround donors,
respectively. Since the magnon number operators for different donor regions and outside them are constructed of magnon operators $b^*_g$ and $b_g$ with different $g$, all the operators $m_{q,i}$ and $m_q$ are independent.

Further, $n_{I,i}$ and $n_k$ are the operators for an electron in the localized state at the donor $i$ and for the delocalized electrons outside the spheres with the quasimomentum $k$, respectively.

It should be noted that Eq. (23) is also valid for degenerate semiconductors and leads to the well-known equation for the magnon frequencies in them

$$\omega_q = \Omega_q + \frac{zT}{2SN} \sum_k \gamma_k (1 - \eta_q).$$

One ascribes usually this equation to Furukawa [13], though in reality it was first obtained by the present author [14].

The mean number of electrons at a donor is calculated in the same manner as in Eqs. (8) to (14). It is given by the expression (the index of the donor is omitted):

$$<n_I> = \frac{1}{1 + \exp[(E_I + \delta F_{mi}(T) - \mu)/T]}^{-1}, \quad (25)$$

$$\delta F_{mi}(T) = F_{mi} - F_{mi}^0 = N_I [f(J_I, T) - f(J, T)] \quad (26)$$

where $F_{mi}$ and $F_{mi}^0$ are the magnon free energies for a region of radius $\rho$ containing an unionized and ionized donor, respectively. The magnon free energy $f(J, T)$ is given by Eq. (11) and the quantity $f(J_I, T)$ differs from it by the replacement of the $d - d$ superexchange integral $J$ by the total impurity exchange integral $J_I$. The latter includes the contribution from both $d - d$ superexchange and indirect exchange via the $s$-electron (24):

$$J_I = J + \frac{zta^3x^3}{9\pi 5a_B^3}. \quad (27)$$

Obviously, the quantity $\delta F_{mi}$ describes the temperature shift of the donor level. This shift differs strongly from that obtained from a Hamiltonian of the electron-magnon interaction similar to Eq. (6) by its averaging over the magnons. Really, as the quantity $B_{1p}$ (24) is not asymptotically small, one cannot restrict oneself to a linear approximation in it. Hence, a generally correct interpretation of the temperature shift of the donor level is as follows: it is the difference between the magnon free energies resulting from the donor ionization. This resolves the dilemma formulated in the end of Section 3.

Equating the number of ionized donors determined from Eq. (25) to the total number of the conduction electrons (13), we find an expression for the charge carrier density $n_{cc}$ for the quadratic dispersion relation $E_k = tk^2a^2 = k^2/2m$:

$$n_{cc} = (n_{eff})^{1/2} \exp [E_A(T)/2T], \quad n_{eff} = \frac{(mT)^{3/2}}{2\sqrt{2\pi}} \quad (28)$$

$E_A(T) = E_I + \delta(T), \quad \delta(T) = \delta F_{mi}(T) - \delta G(T)$,

where $n_{eff}$ is the effective density of states in the conduction band, and $n = \nu/a^2$ is the donor density. It should be recalled that $E_I(0) = -E_B$ is negative.

It can be ascertained that the activation energy for the charge carrier density $[-E_A(T)/2]$ in Eq. (28) increases with temperature in the spin-wave region (Fig. 2). First, it should be noted that for very large $a_B$ the temperature dependence of $E_A$ disappears since the expansion of $f(J_I, T)$ in the powers of $1/a_B^3$ gives an expression for $\delta F_{mi}$, which coincides with $\delta G(T)$. For smaller $a_B$, if the second term in Eq. (26) dominates, then one can neglect $F_{mi}$ in Eq. (26), i.e. $\delta(T) = -N f(J) - \delta G(T)$.

![Fig. 2. Qualitative temperature dependences of the conduction band bottom $\delta G$ (it corresponds to the giant red shift of the optical absorption edge); of donor level $D = E_I + \delta F_{mi}$; of the doubled activation energy for the charge carrier density and conductivity $|E_A|$.](image)

According to Eq. (11), the first term, which describes the temperature shift of the donor level, is positive and has a value of order $N_J (T/J)^\nu$. The quantity $y(T)$ decreases from $5/2$ to $1$ with increasing temperature. According to Eqs. (17), (18), the second term, which de-
scribes the optical gap shift, is negative and of the order of \((W/S)(T/J)^\gamma\). As \(W \gg JS\), the quantity \(\delta(T)\) should be negative with its absolute value increasing with temperature. This means that the activation energy in Eq.(28) increases with temperature. In this case, its temperature dependence is almost completely determined by the shift of the optical absorption gap \(\delta G(T)\).

Physically, this effect can be explained as follows. The donor electron realizes the ferromagnetic indirect exchange in the vicinity of the impurity. For this reason the ferromagnetic coupling there is stronger than on the average over the crystal. Hence, with increasing temperature, the local ferromagnetic ordering degree in the donor vicinity decreases more slowly than on the average over the crystal. But the electron energy is the lower the higher is the degree of the ferromagnetic ordering. As a result, the donor level depth decreases with the temperature in the spin-wave region. This fact can cause appearance of a maximum in the charge carrier density at a certain temperature \(T_m\). According to Eq.(28), its condition is

\[
E_I + \delta(T_m) = T_m \frac{d\delta(T_m)}{dT}.
\]

(29)

It should be noted that some experimentalists [16,17] pointed out that the activation energy in the ferromagnetic semiconductors must be temperature-dependent, and a condition of the type of Eq.(29) was proposed for the density maximum. But no expression for the quantity \(\delta\) was obtained by them.

Below the explicit formula for this quantity will be used. If, in accordance with Eqs.(17), (18), in the low temperature range one puts \(\delta \sim WT^\gamma/SJ^\gamma\) with \(y = 5/2\), then

\[
T_m \sim J \left[ \frac{E_BS}{W} \right]^{2/5},
\]

(30)

where \(E_B\) is given by Eq.(21). As \(W \gg E_B\), this means that the maximum charge carrier density is reached still in the spin-wave region below \(T = J\) in accordance with the choice of \(n\) made above. It manifests itself as a resistivity minimum.

This maximum assumes existence the subsequent charge carrier density minimum, as at elevated temperatures the ferromagnetic ordering is destroyed, and \(<n_{cc}(T)>\) should increase with temperature exponentially (Fig. 1). This is nothing else as a qualitative proof of the existence of the resistivity peak at temperatures higher than the resistivity minimum. Physically, such a nonmonotonic behavior of \(<n_{cc}(T)>\) can be explained by the fact that, on increase in temperature, after destruction of the ferromagnetic ordering far from impurities, its destruction close to the impurities begins. Hence the donor level rises. As the conduction band bottom band remains fixed at such temperatures, the donor level depth decreases, and the rate of the temperature growth for the \(<n_{cc}(T)>\) increases (Fig. 2). But, as these processes take place at temperatures of order of the Curie point, their analytical treatment is hardly possible at present.

In particular, at temperatures comparable with the Curie point, one should take the ferron effect into account: the electron is dragged in by the region of the enhanced magnetization and simultaneously supports it, realizing the ferromagnetic indirect exchange inside it. This process decreases the donor free energy and hence the charge carrier density. In the paramagnetic region, such a state of a donor was investigated in [18,1] for non-double exchange systems. For the double exchange systems it is not investigated yet. But in the spin-wave region one can take the ferron effect into account if one considers temperatures sufficiently low, when the term \(\delta F_{m1}\) in the total free energy can be considered as a perturbation. As follows from Eqs.(3), (19), (26), the free energy of a system containing a donor has the form

\[
F_I(x) = E_B(x^2 - 2x) + \delta F_{m1}.
\]

(31)

Then the optimum value of \(x\) is

\[
x = 1 - \frac{1}{2} \frac{d\delta F_{m1}(1)}{dx}.
\]

(32)

The free energy coincides with the quantity \(F_I(1)\) virtually used above up to the second order in \((x - 1)\). The parameter \(x\) increases with temperature, and the electron orbital radius \(a_B/x\) decreases as should be the case.

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