Indirect exchange in ferromagnets with low carrier densities

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A theory of indirect exchange is developed for ferromagnetic heavily doped semiconductors and semimetals, and also for impurity-free semiconductors in which light excites nonequilibrium carriers. The Ruderman-Kittel-Kasuya-Yosida (RKKY) theory is inapplicable to these materials because the Fermi energy of electrons is low compared with the *s-f* energy AS. The proposed theory is based on the alignment of the spins of the conduction electrons with fluctuations of the magnetization which vary slowly in space. The non-Heisenberg nature of the indirect exchange is manifested by a nonanalytic dependence of T_C on AS. In the case of semimetals the dependence of the carrier density on the magnetization may result in an abrupt phase transition. In the case of semiconductors in which the indirect exchange is due to photoelectrons, a thermodynamically nonequilibrium phase transition is characterized by discontinuities of the derivatives of the rates of generation of entropy with respect to temperature, frequency, and intensity of light.

INTRODUCTION

It is known that the properties of magnetic metals with localized moments and simple Fermi surfaces are described quite satisfactorily by a theory of the indirect exchange developed by Ruderman, Kittel, Kasuya, and Yosida (RKKY). The condition of its validity is the inequality $\mu \gg AS$, where μ is the Fermi energy of the carriers, A is the integral of their exchange with localized magnetic moments, and S is the magnitude of such a moment. This inequality makes it possible to derive, in the second order of perturbation theory with respect to AS/μ, an effective Hamiltonian of the indirect exchange between localized moments and this Hamiltonian has the Heisenberg structure.

However, there is a wide class of conducting materials with conduction-electron densities much lower than in metals. Therefore, the conditions of validity of the RKKY theory are not satisfied by these materials. They include in particular heavily doped semiconductors which satisfy the inequality $\mu < AS$ at densities up to $\approx 10^{21}$ cm^{-3}. This inequality should also be satisfied by semimetals. Such magnetic materials include also impurity-free semiconductors in which carriers appear under the action of strong illumination. The importance of the indirect exchange in such materials can be judged by the fact that doping of ferromagnetic semiconductors EuO and EuS with electrically active impurities doubles their Curie temperature T_C (see Ref. 1 for experimental data). Moreover, the hypothesis of a photoinduced indirect exchange is also in agreement with the increase in T_C observed for pure EuS on illumination.[2]

Since perturbation theory utilizing the ratio AS/μ is inapplicable to these magnetic materials, the indirect exchange is *a priori* known to be of the non-Heisenberg nature. This itself makes the study of their magnetic properties an interesting task. However, the same metals and photoconductors have an additional specific property that the carrier density depends on the magnetization. Finally, it is in principle important that a magnetic phase transition in photoconductors occurs under thermodynamically nonequilibrium conditions and, consequently, cannot be described in terms of the characteristic features of the derivative of the thermodynamic potential. Studies of such phase transitions have barely begun.

We shall report a study of the influence of the indirect exchange on order-disorder phase transitions in the low-carrier-densities ferromagnets mentioned above. In contrast to the RKKY theory, we shall be unable to derive an effective magnetic Hamiltonian valid at all temperatures. However, near T_C we shall find the contribution of the indirect exchange to the total thermodynamic potential of a magnetic material (or to its nonequilibrium analog in the case of photoconductors) and use it to determine the naturer and temperature of the phase transition. We shall show that there are situations (for example, in the case of metals) in which the conduction electrons convert a continuous phase transition into an abrupt one. In those cases when the transition is continuous, the shift of the Curie point T_C caused by the conduction electrons may be several orders of magnitude different from the RKKY result. In the case of photoconductors we shall obtain expressions for the discontinuities of the derivatives of the rate of generation of entropy with respect to temperature, and with respect to the intensity and frequency of light needed[3] for a photoinduced phase transition.

The non-Heisenberg nature of the indirect exchange in degenerate magnetic semiconductors has already been pointed out.[1] However, only the magnon spectrum is investigated in Ref. 1. This spectrum differs greatly from that obtained using the RKKY theory. For example, the frequency shift of long-wavelength magnons because of the indirect exchange is proportional not to A^2S^2/μ, but to the width W of the conduction band. If the inequality $W \gg AS$ is obeyed, which is true of EuO and EuS, the dependence of the frequency on the *s-f* exchange integral A is manifested only by short-wavelength magnons and this dependence is linear in A, and not quadratic.

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These results already manifest the specific nature of the interaction of long-wavelength charge carriers with fluctuations of the magnetization in ferromagnets, which is retained also near T_C: the electron spins become aligned parallel to the direction of the local moment and follow the changes of this moment in space. If such changes are slow, the spin alignment is complete and an electron experiences the maximum possible "gain" in respect of the *s-f* exchange energy amounting to $AS/2$, as in the case of ideal ferromagnetic ordering. Consequently, the change in the electron energy due to the appearance of a long-wavelength magnon (and it is this change that determines the contribution of the indirect exchange to the magnon frequency) should be independent of A.

We can show that the spin of long-wavelength electrons is indeed aligned parallel to the direction of the local moment simply by analyzing the familiar formula[4] for the electron energy in the case of helicoidal ordering of the spins of the magnetic atoms. Using the effective electron mass m^*, we can write down the formula as follows ($\mathbf{Q}$ is the vector of the helicoid, a is the lattice constant, and $\hbar = 1$):

$$\mathscr{E}_\mathbf{k} = \frac{1}{4m^*}\{\mathbf{k}^2+(\mathbf{k}+Q)^2 \pm ([\mathbf{k}^2-(\mathbf{k}-\mathbf{Q})^2]^2+q_0^4)^{1/2}\}, \quad (1)$$

where

$$q_0^2 = 2m^*AS \sim AS/Wa^2.$$

It is clear from Eq. (1) that the energy shift of electrons with $k \ll q_0$ caused by the *s-f* exchange amounts to $\pm AS/2$ if $Q \ll q_0$, exactly as in the case of ideal ferromagnetic ordering. Since the total moment of helicoidally ordered crystal vanishes, it is clear that the *s-f* shift is determined not by the long-range but by the local magnetic order. The quantity q_0^{-1} can be regarded as the radius of a locally ordered region and the conduction-electron spin becomes aligned with the moment of this region. It follows from the condition $Q \ll q_0$ that all the spins in this region are parallel to one another, i.e., the local order is ideally ferromagnetic.

Ferromagnets at temperatures close to T_C naturally do not contain regions with ideal ferromagnetic order, but they do have regions with unsaturated ferromagnetic order and the direction of the local magnetic moment varies slowly in space. It is precisely the interaction with the magnetization fluctuations varying slowly in space which makes the dependence of the electron energy on the *s-f* exchange integral nonanalytic. However, such nonanalyticity means that the indirect exchange is of the non-Heisenberg type.

We can allow for the nonanalyticity of the electron energy in A by using a variational method based on the physical idea of the alignment of the electron spin with a slowly varying direction of the local moment. It represents a generalization of a method developed earlier[1] for the determination of the position of the bottom of the conduction band at $T = T_C$. Such generalization consists in an allowance for the finite magnetization and for the many-electron nature of the problem. A special analysis in Ref. 1 shows that the method used there gives a correct representation of the dependence of the electron energy on the parameters of the problem. In the case of the generalized method used below, the following circumstance support the conclusion that its use is reasonable: 1) in the spin-wave region it gives the same results as the spin-wave theory, not only in the principal order in respect of $1/S$, but also in the next order; 2) if $\mu \gg AS$, this method duplicates the results of the RKKY theory.

ENERGY SPECTRUM OF CARRIERS

We shall consider a semiconductor with a wide conduction band $W \gg AS$. In analyzing the electron spectrum of such a semiconductor near T_C, we must bear in mind that there are not only delocalized carrier states, but also those which are localized near fluctuations of the magnetization which have a very large radius and a moment close to that of a saturated ferromagnet. However, there are only few such giant fluctuations. In any case, the number of trapped (localized) electrons in degenerate semiconductors is known to be negligible compared with the number of free carriers. This is supported also by the experimental observation that an increase in the degree of doping suppresses the resistance peak which appears near T_C and is due to partial localization of carriers.[1]

Close to T_C the properties of free electrons are governed by the existence of local moments of considerable magnitude and due to strong correlations between the spins. For example, in a simple cubic lattice with an exchange between the nearest neighbors the function describing the correlation between these neighbors is $S^2/3$ in the classical limit. This value is even higher if antiferromagnetic exchange between the second-nearest neighbors is important.[1)] In view of the large radius of correlations near T_C the direction of the local moment varies slowly in space. It follows from this discussion that the conduction-electron spins tend to become aligned with the direction of the local moment.

Our calculations will be based on a Hamiltonian of the *s-f* model written down in the approximation of the nearest neighbors for electrons:

$$\begin{gathered} H = -\frac{W}{12}\sum a_{\mathbf{g}\sigma}^* a_{\mathbf{g}+\Delta\sigma} - A\sum \mathbf{S}_\mathbf{g}\mathbf{s}_{\sigma\sigma'} a_{\mathbf{g}\sigma}^* a_{\mathbf{g}\sigma'} + H_M, \\ H_M = -\frac{1}{2}\sum I(\mathbf{g}-\mathbf{f})\,\mathbf{S}_\mathbf{g}\mathbf{S}_\mathbf{f}, \end{gathered} \quad (2)$$

where $a_{\mathbf{g}\sigma}^*$ and $a_{\mathbf{g}\sigma}$ are the operators of an *s*th conduction electron with a spin projection σ of an atom $\mathbf{g}$; $\boldsymbol{\Delta}$ is the vector joining the nearest neighbors; $\mathbf{S}_\mathbf{g}$ is the spin of an atom $\mathbf{g}$; I is the integral of the direct exchange between the *f* spins, the lattice of which is assumed to be simple cubic; $\mathbf{s}_{\sigma\sigma'}$, are the Pauli matrices.

In the variational method used below the physical concept of the alignment of the conduction electron spins along the direction of the local moment is formulated as a requirement that the spin of an electron located at an atom $\mathbf{g}$ is oriented along the total moment $\mathbf{M}_\mathbf{g}$ of a region of radius $R \gg a$ with its center at the atom $\mathbf{g}$. This radius is regarded as a variational parameter of the problem which has to be determined from a condition for a minimum of the free energy of the system. However, since the electron gas is degenerate, the value of R is determined in reality from the condition for a minimum of the electron energy for a given value of the magnetization of a crystal.

It is convenient to rewrite the Hamiltonian (2) introducing for each atom g its own coordinate system in which the z_g axis coincides with the direction of the local moment $\mathbf{M}_g$. With this in mind we shall transform the electron operators by a procedure analogous to the transformation of spinors described in Ref. 6, except that instead of the Euler angles we shall use the angular coordinates in a spherical coordinate system. The explicit form of the coefficients of a unitary transformation from a general to a local coordinate system can be found from the following conditions: 1) invariance of the scalar product of the vector $\mathbf{M}_g$ and of the spin of an electron at an atom g relative to the coordinate system; 2) rotation by 2π about the z_g axis reverses the sign of the operators $a^*_{g\lambda}$, by analogy with the wave functions, since these functions can be represented in a local coordinate system in the form $a^*_{g\lambda}\ |0\rangle$, where $|0\rangle$ is the electron vacuum function. The transformation from a general to a local coordinate system is then described by the relationship

$$a_{g\lambda}{}^* = \exp(i\varphi_g\lambda) \sum_{(\pm)} \cos\left(\frac{\theta_g}{2} + \frac{\pi}{4} \mp \frac{\lambda\pi}{2}\right) a^{\bullet}_{g,\pm 1/2}. \tag{3}$$

The transformation (3) converts the Hamiltonian (2) to

$$H = \sum_{\lambda} H_\lambda + H_M + H_{\lambda,-\lambda},$$

$$H_\lambda = -A \sum \lambda S_g^{z_g} a^*_{g\lambda} a_{g\lambda} - \frac{W}{12} \sum \cos(\theta_{gg+\Delta}/2)$$
$$\times \exp(i2\lambda\gamma_{gg+\Delta})\, a^*_{g\lambda} a_{g+\Delta\lambda}, \tag{4}$$

$$\gamma_{gf} = \operatorname{arctg}\{\cos\eta_{gf}\,\operatorname{tg}\zeta_{gf}/\cos\xi_{gf}\},$$

$$\zeta_{gf} = \frac{\varphi_g - \varphi_f}{2}, \qquad \eta_{gf} = \frac{\theta_g + \theta_f}{2}, \qquad \xi_{gf} = \frac{\theta_g - -\theta_f}{2},$$

where θ_g and φ_g are the angles which define the direction of the vector $\mathbf{M}_g$ in the general coordinate system; θ_{gf} is the angle between $\mathbf{M}_g$ and $\mathbf{M}_f$; λ is the projection of the conduction electron spin in the local coordinate system. The Hamiltonian $H_{\lambda,-\lambda}$, which is not spelled out in detail, describes electron transitions caused by a change in λ.

The condition $R \gg a$ (this is confirmed by the results obtained below) ensures that the directions of the moments $\mathbf{M}_g$ and $\mathbf{M}_{g+\Delta}$ are close to one another. Expanding the quantity γ_{gf} in Eq. (4) in terms of the small differences $\varphi_g - \varphi_f$ and $\theta_g - \theta_f$, and applying a canonical transformation to the electron operators

$$a_{g\lambda}{}^* \exp\{i\lambda\varphi_g \cos\theta_g\} \to a_{g\lambda}{}^*,$$

we obtain an expression for the electron energy with a fixed value of λ and this expression is identical with H_λ of Eq. (4) if we assume that $\gamma_{gg+\Delta} = 0$. This result is valid up to and including the squares of the small differences between the angles.

A test wave function of a delocalized electron will be selected in the form of a plane wave with a fluctuating spin direction:

$$\psi_{k\lambda} = \frac{1}{N^{1/2}} \sum_{g} \exp(i\mathbf{k}\mathbf{g})\, a_{g\lambda}{}^* |0\rangle. \tag{5}$$

It is asymptotically orthogonal to the states localized within giant fluctuations of the magnetization. The form of Eq. (5) suggests the existence of two Zeeman subbands with opposite orientations of the electron spin relative to the local moment. In zeroth order with respect to AS/W Eq. (1) includes also the exact result and this should ensure a sufficient accuracy at low values of AS/W.

Using Eqs. (4) and (5), we obtain the following expression for the electron energy:

$$\mathscr{E}_{k\lambda} = -{}^1\!/_2 W (1 - {}^1\!/_4 \bar{P}_{gg+\Delta}) \gamma_k - A\lambda \overline{\mathbf{S}_g \mathbf{M}_g / |\mathbf{M}_g|}, \tag{6}$$

where

$$P_{gf} = 1 - \mathbf{M}_g \mathbf{M}_f / |\mathbf{M}_g||\mathbf{M}_f|, \qquad \gamma_k = {}^1\!/_6 \sum_{\Delta} \exp i\mathbf{k}\mathbf{\Delta}.$$

The bar in Eq. (6) denotes averaging over all the atoms and this is obviously equivalent to thermodynamic averaging denoted below by angle brackets. The structure of the first term in Eq. (6) is determined by the fact that if $\theta_{gf} \ll 1$, then

$$\cos\theta_{gf}/2 = (1 - P_{gf}/2)^{1/2} \approx 1 - P_{gf}/4.$$

The structure of the second term follows from the fact that the projection of the spin of an atom g along the spin direction of an electron s parallel to $\mathbf{M}_g$ is $\mathbf{S}_g \mathbf{M}_g |\mathbf{M}_g|$. Equation (6) gives in particular the energy of an electron in the helicoid of Eq. (1) if $k, Q \ll q_0$.

We can estimate approximately the complicated correlation functions in Eq. (6) by noting first that the local moments $\mathbf{M}_g$ of different regions have different magnitudes and directions. However, the fluctuations of $|\mathbf{M}_g|$ are not important, because disappearance of ferromagnetic ordering near T_C is due to disordering of the directions of the local moments. Therefore, we can modify Eq. (6)—with an accuracy up to terms of higher order in a/R-by replacing $|\mathbf{M}_g|$ with its average value $\langle|\mathbf{M}_g|\rangle$. Next, the smallness of fluctuations of $|\mathbf{M}_g|$ at high values of R makes it possible to replace quite accurately $\langle|\mathbf{M}_g|\rangle$ with $\langle M_g^2\rangle^{1/2}$, since for $x = M_g^2/\langle M_g^2\rangle$ we can write down

$$\langle x^{1/2}\rangle = \langle\exp({}^1\!/_2 \ln x)\rangle \approx 1 + {}^1\!/_2\langle\ln x\rangle \approx \langle\exp\ln x\rangle^{1/2} = \langle x\rangle^{1/2}.$$

Consequently, the complicated correlation functions in Eq. (6) can be expressed in terms of binary functions. If the correlation length is large compared with R, then in the case of binary correlation functions we can use expressions in which a small critical exponent η is assumed to vanish:

$$K_\parallel(\mathbf{f}) = \langle S_0^z S_f^z\rangle = \mathscr{M}^2 + S(S+1) r/f,$$
$$K_\perp(\mathbf{f}) = \langle S_0^x S_f^x\rangle + \langle S_0^y S_f^y\rangle = 2S(S+1) r/f, \tag{7}$$

where r is a characteristic constant with the dimensions of length, like the three-dimensional number of an atom f; $\mathscr{M}$ is the average magnetization of a crystal per atom. Calculations carried out using Eq. (7) give (when summation over g is replaced with integration)

$$\begin{gathered}\langle \mathbf{S}_0\mathbf{M}_0\rangle=\frac{3}{2}\frac{lN_R}{R}+N_R\mathscr{M}^2,\\ \langle \mathbf{M}_0^2\rangle=\frac{6}{5}\frac{lN_R^2}{R}+N_R^2\mathscr{M}^2,\\ \langle \mathbf{M}_0\mathbf{M}_\Delta\rangle=\langle \mathbf{M}_0^2\rangle-\frac{la^2}{2R^3}N_R^2,\\ l=3rS(S+1),\quad N_R=\frac{4\pi}{3}\left(\frac{R}{a}\right)^3.\end{gathered}\tag{8}$$

It follows from Eqs. (6) and (8) that, including terms up to $\mathscr{M}^4$, the electron energy can be represented in the form

$$\begin{gathered}\mathscr{E}_{\mathbf{k}\lambda}=-A\lambda X-\frac{W}{2}\gamma_{\mathbf{k}}Y,\\ X=\left(\frac{5R}{6l}\right)^{1/2}\left\{\frac{3}{2}\frac{l}{R}+\frac{3}{8}\mathscr{M}^2-\frac{5}{192}\frac{R}{l}\mathscr{M}^4\right\},\\ Y=1-\frac{5}{48}\frac{a^2}{R^2}+\frac{25}{288}\frac{a^2\mathscr{M}^2}{Rl}-\frac{125a^2\mathscr{M}^4}{1728l^2}.\end{gathered}\tag{9}$$

When the total energy of electrons is minimized with respect to R, we shall consider electron densities which are so low that electrons are only in the lower Zeeman subband ($\lambda = 1/2$). It is then sufficient to minimize the position of the bottom of this subband and the system (9) yields

$$\begin{gathered}R=R_0\left\{1-\frac{R_0\mathscr{M}^2}{9l}-\frac{23R_0^2\mathscr{M}^4}{432l^2}\right\},\\ R_0=\left(\frac{Wa^2}{3A}\right)^{2/3}\left(\frac{5}{6l}\right)^{1/3}\gg a.\end{gathered}\tag{10}$$

After substitution of Eq. (10) into Eq. (9), the spectrum of the conduction electrons dependent on the magnetization is given by the expression ($\lambda=\frac{1}{2}$)

$$\begin{gathered}\mathscr{E}(\mathbf{k})=\mathscr{E}_0(\mathbf{k})+\mathscr{E}_2(\mathbf{k})\mathscr{M}^2+\mathscr{E}_4(\mathbf{k})\mathscr{M}^4,\\ \mathscr{E}_0(\mathbf{k})=-\frac{3}{4}A\left(\frac{5l}{6R_0}\right)^{1/2}\left(1+\frac{\gamma_{\mathbf{k}}}{4}\right)-\frac{W}{2}\gamma_{\mathbf{k}},\\ \mathscr{E}_2(\mathbf{k})=-\frac{11A}{48}\left(\frac{5R_0}{6l}\right)^{1/2}\left(1+\frac{\gamma_{\mathbf{k}}}{4}\right),\\ \mathscr{E}_4(\mathbf{k})=\frac{11\sqrt{30}}{768}A\left(\frac{R_0}{l}\right)^{3/2}.\end{gathered}\tag{11}$$

We can see from the systems (10) and (11) that the s-f exchange at $T=T_C$ lowers the electron energy by $E_c \sim AS(AS/W)^{1/3}$, i.e., the reduction in the energy is greater than that obtained in the second order of perturbation theory with respect to AS/W. This result was obtained earlier in Ref. 1 by a variational method and also using a graphical technique. It was shown there that a perturbation introduced by the term $H_{\lambda,-\lambda}$ in Eq. (4) is slight, so that the concept of the Zeeman subbands retains its meaning also at T_C.

A completely new (compared with Ref. 1) feature is the result that the electron energy is a quadratic function of the magnetization near T_C. Until now, it has been usual to assume that the bottom of the conduction band shifts linearly downward on increase in the magnetization. The cause for the quadratic dependence of the energy on the magnetization can be understood qualitatively if we consider it as an analog of an external field which perturbs the state of an electron (5) with the zeroth projection of the spin along this field.

It is interesting to note that the variational method used here is valid in the spin-wave range of temperatures $T_C/S<T\ll T_V$ of a magnetic material with $S\gg 1$ and it gives the same results as those obtained in Ref. 1 if magnon operators and perturbation theory in terms of $1/S$ are used. In this case we can assume that $K_\parallel=\mathscr{M}^2$ and $K_\perp\sim rT/T_Cf$. The optimal radius R is proportional to q_0^{-1}, as in Eq. (1), and the s-f shift is $A\mathscr{M}/2$ in the principal order, whereas the correction to this shift is of the order of $(TAS/T_C)(AS/W)^{1/2}$. Therefore, generalization of the method of Ref. 1 makes it fairly universal.

MAGNETIC PROPERTIES OF DEGENERATE SEMICONDUCTORS

Investigations of phase transitions in degenerate magnetic semiconductors are made using an incomplete thermodynamic potential of the system which is not minimized in respect of the magnetization. Equation (11) can be used to find the total energy of degenerate electrons as a function of the magnetization. The average energy of localized spins is obtained from the Hamiltonian H_M of Eq. (2) and the energy corresponding to a given value of the magnetization is described by the usual combinatorial methods (in this case the short-range order is ignored). The result is an expression for the thermodynamic potential Φ which in the absence of the conduction electrons reduces to the potential Φ_0 of a Heisenberg magnetic material considered in the self-consistent field approximation[2)]:

$$\Phi=\Phi_0+\int_0^{\mathscr{M}} n\frac{d}{d\mathscr{M}}\mathscr{E}(0)\,d\mathscr{M}+O(n^{5/3}),\tag{12}$$

where

$$\begin{gathered}\Phi_0=-NT\ln(2S+1)+\frac{3N}{2}(T-\tilde{T}_C^0)\tilde{\mathscr{M}}^2\\ +\frac{9N}{20}T\left[1+\frac{1}{2S(S+1)}\right]\tilde{\mathscr{M}}^4,\\ \tilde{T}_C^0=\tilde{I}_0S(S+1)/3,\quad \tilde{I}_0=I_0+\frac{dI_0}{da}\Delta a,\\ I_0=\sum I(\mathbf{f}),\quad \tilde{\mathscr{M}}=\mathscr{M}/[S(S+1)]^{1/2}.\end{gathered}$$

If $S\neq\frac{1}{2}$, then it is technically more convenient to obtain an expression Φ_0 directly from the self-consistent field equations without explicit use of the combinatorial methods.

The contribution of the conduction electrons to Φ is described by the second term on the right-hand side of Eq. (12). Its structure is clear from the fact that the quantity $d\mathscr{E}(0)/d\mathscr{M}$ represents the force exerted by a conduction electron on the magnetic subsystem and, consequently, $(d\mathscr{E}(0)/d\mathscr{M})d\mathscr{M}$ is the work carried out by this force.

Equation (12) is written down allowing for the fact that introduction of an impurity into a crystal not only provides the conduction electrons but also creates a homogeneous deformation of a crystal by impurity ions.[7] The resultant change in the lattice constant by Δa alters the direct exchange integral I_0.

It follows from Eqs. (11) and (12) that, in spite of the non-Heisenberg nature of the indirect exchange, it cannot result in an abrupt phase transition because the coefficient in front of $\mathscr{M}^4$ in Φ is positive even when the indirect exchange is allowed for. The increase in the Curie temperature because of the indirect exchange is given by the expression

$$\delta T_c=\frac{110}{594}\left(\frac{5}{2}\right)^{1/3}A[S(S+1)]^{1/3}\left(\frac{R_0}{r}\right)^{1/3}\nu\sim\frac{A^2S^2\nu}{E_c},$$

$$\nu=n/N. \tag{13}$$

Therefore, δT_C is a quantity of the order of $(AS)^{2/3}W^{1/3}\nu$. The result (13) differs from the RKKY result by the nature of the dependence on the electron density: δT_C is proportional to n and not to $n^{1/3}$. If $\mu \ll E_C$, the quantity δT_C of Eq. (13) is considerably less than found from the RKKY theory.

The non-Heisenberg nature of the indirect exchange is manifested in this case by a nonanalytic dependence of δT_C on the s-f exchange integral and spin. Moreover, the contribution of the indirect exchange to the coefficient in front of $\mathscr{M}^4$ in Φ is in this approximation independent of AS and proportional to W. As pointed out in the Introduction, a similar disappearance of the dependence on W occurs also in the case of frequencies of long-wavelength magnons. Therefore, the effect is fairly common in the case of the indirect exchange.

However, the paramagnetic Curie temperature is still described by the RKKY theory result $\delta\theta \sim A^2S^2\nu/\mu$ (Ref. 1). This is due to the fact that this temperature θ is defined in the range $T \gg T_C$, when the correlation radius is small and there is no alignment of the electron spin to the local moment. The spin retains its spatial direction and this makes it possible to expand the electron energy in terms of $A\mathscr{M}/\mu$, where $\mathscr{M}$ is the magnetization induced by a vanishingly weak external field. In other words, if $\mu < E_c$, the value of θ should be considered greater than T_C, even if these quantities are equal in the original impurity-free semiconductor.

It should be noted that at high electron densities when the inequality $W \sim \mu \gg AS$ is satisfied, the above method gives the same results as the RKKY theory. It is necesary then to minimize with respect to R the total energy of the electron gas allowing for the filling of both subbands of Eq. (9) with electrons. The radius R is then proportional to $(W/AS)^2a$ and that part of the electron energy which is proportional to $\mathscr{M}^2$ is—as expected—of the order of $A^2\nu/\mu$.

When the experimental results are compared with the above theory, we must allow for renormalization of the direct exchange because of a change in the volume of a crystal as a result of doping. Its role is particularly great in those cases when some impurity atoms form clusters, which is typical of many impurities in degenerate semiconductors. The electrons of those atoms which form clusters do not become delocalized and, therefore, they do not participate in the indirect exchange. Because of the presence of such clusters the number of impurity atoms deforming the lattice may be several orders of magnitude higher than the number of the conduction electrons. It is possible to separate the renormalization of the direct exchange if Δa and dT_C/da are measured additionally for a pure crystal. The second of these quantities is known for many materials, but unfortunately there have been no measurements of Δa in the case of doped crystals. However, the shift of T_C due to the lattice deformation is comparable with T_C for a pure crystal only if the values of $\Delta a/a$ are very large (of the order of 10%) when the experimental values are $d(\ln T)/d(\ln a) \sim 5$–6 for EuO and EuS (Ref. 8). Such values of $\Delta a/a$ are hardly realistic.

The fact that according to Ref. 9 the shift of T_C exhibited by Gd-doped EuO is proportional to the carrier density indicates its origin due to the indirect exchange. The use of the parameters $AS = 0.5$ eV and $W = 4$ eV found from independent experiments for EuO (Ref. 1) in calculations based on Eq. (13) and on the assumption that $r \sim a$ gives values of δT_C close to those found experimentally (12 K for $n = 1.6\times10^{20}\ \mathrm{cm}^{-3}$, etc.). The dominant role of the indirect exchange in the shift of T_C was supported also by a maximum through which the difference $\theta - T_C$ passes in the case of EuS (Ref. 8) and EuO (Ref. 10) on increase in the dopant concentration (at very high concentrations when the indirect exchange becomes of the RKKY type and the value of θ should be close to T_C, as in pure crystals).

PHASE TRANSITIONS IN FERROMAGNETIC SEMIMETALS

The main difference between a semimetal and a degenerate semiconductor is that in the former case the carrier density depends on the magnetization because a change in the magnetization alters the degree of overlap of the valence and conduction bands. We shall show below that the dependence of the carrier density on the magnetization may have a considerable influence on the nature of a magnetic phase transition. We shall assume that only the conduction electrons interact strongly with localized spins, whereas the interaction of holes in negligible (such a situation is typical of compounds of rare-earth elements in which holes move between nonmagnetic anions). For simplicity, we shall assume that the effective masses of electrons and holes are equal to one another and that the extrema of both bands are located at $k = 0$.

The most interesting situation arises when near T_C the valence band maximum $\mathscr{E}_{vt}$ lies above the minimum $\mathscr{E}_{cb}$ of the lower spin conduction subband, but above the minimum of the upper conduction subband. The dependence of $\mathscr{E}_{cb}$ on the magnetization is given by Eq. (11). The condition for the balance of the number of particles derived bearing in mind that the valence band is spin-degenerate yields the following expression describing the dependence of the number of the conduction electrons on the magnetization:

$$n=n_0\left(1-\frac{\mathscr{E}_2}{D}\mathscr{M}^2-\frac{\mathscr{E}_4}{D}\mathscr{M}^4\right)^{3/2}, \tag{14}$$

$$n_0=\frac{1}{3\pi^2}\left(\frac{2m^*D}{1+\sqrt{2}}\right)^{3/2},\quad D=\mathscr{E}_{vt}-\mathscr{E}_{cb}, \tag{15}$$

where all the quantities $\mathscr{E}_n$ are taken at $k = 0$.

After substitution of Eq. (14) into Eq. (12), the thermodynamic potential of the system becomes

$$\Phi=\Phi_0+n_0\left\{\mathscr{E}_2\mathscr{M}^2+\left(\mathscr{E}_4-{}^3/_4\frac{\mathscr{E}_2^{\,2}}{D}\right)\mathscr{M}^4\right\}. \tag{16}$$

It is clear that if $D/\mathscr{E}_2\sim 1$, then the term $\mathscr{M}^4$ in Eq. (16) remains positive so that the phase transition is of the second order, exactly as for $D=0$. However, in the case of intermediate values of $D/\mathscr{E}_2$ we can have a situation when the negative nature of the electron contribution to the term $\mathscr{M}^4$ makes the whole of this term in Φ negative and then the phase transition is of the first order. For given parameters of the electron subsystem, this is favored by the smallness of the direct exchange between the f spins. If the phase transition is of the second order, the shift of T_C because of the indirect exchange is still given by Eq. (13), i.e., the dependence of the number of carriers on the magnetization does not affect the value of T_C.

PHOTOINDUCED PHASE TRANSITIONS

The dependence of the carrier density on the magnetization is significant also in the case of photoinduced phase transitions in impurity-free semiconductors. An analysis of this problem simplifies greatly if we bear in mind that the cooling time of photoelectrons is short compared with their recombination time. Therefore, we can assume that photoelectrons are concentrated mainly near the bottom of the lower conduction subband. The photomagnetic effect becomes significant only at very high photoelectron densities, of the order of 10^{18} cm^{-3} or more. At these densities the electron gas can be regarded as degenerate so that the quasi-Fermi level of photoelectrons lies within the conduction band. The conduction band tails corresponding to the capture of electrons by magnetic fluctuations are very weak for pure crystals.[1] Therefore, we can ignore the contribution of the trapped electrons to the total electron energy although the states in the tails are very important in multistage recombination of nonequilibrium carriers.

Obviously, in view of the nonequilibrium nature of the phase transition under discussion, we cannot describe this transition using a condition for a minimum of the thermodynamic potential. However, if the temperature of a sample is constant in time and varies weakly throughout a sample, the steady-state magnetization can be found from a minimum of the expression which differs from Eq. (12) only because the number of electrons n is not the thermodynamic equilibrium value. The term "synergetic potential" is suggested for this quantity in Ref. 3. If n is independent of $\mathscr{M}$, the conclusion that $\mathscr{M}$ can be found from a condition for a minimum of the synergetic potential is self-evident because then the quantity n behaves as a given external field with respect to the magnetic subsystem and Eq. (12) represents the thermodynamic potential of the magnetic subsystem in an external field. However, in the self-consistent field approximation this conclusion remains valid also when n depends on $\mathscr{M}$. This is shown in Ref. 3 for the specific case of an Ising model with a large-radius direct exchange, using directly the equations of motion for the electron and spin operators.

The principal difference between the synergetic and thermodynamic potentials is that the derivatives of the former with respect to temperature do not represent entropy and specific heat. Nevertheless, we shall show below that the second derivative of the synergetic potential with respect to temperature shows a discontinuity in the adopted approximation. In addition to singularities in respect of temperature, the synergetic potential exhibits similar singularities in respect of the parameters of the system, the energy of which is being dissipated, which are the intensity and frequency of light. These singularities are consequences of the corresponding singularities of the rate of generation of entropy.

Before considering calculations, we must point out that the simplest situation occurs when the inequality $\omega-\mathscr{E}_{cb}\gg\mathscr{E}_c$ is satisfied; here $\mathscr{E}_c$ is the Zeeman splitting and $\mathscr{E}_{cb}$ is the position of the bottom of the conduction band. In this case the density of electrons generated by unpolarized light depends weakly on the magnetization. The shift of T_C is still described by Eq. (13); the density of carriers in the case of equal effective masses of electrons and holes is given by an expression which follows from the condition of balance of the numbers of generated and recombining carriers:

$$\begin{gathered}n=\tau_r G_0(\omega),\quad G_0(\omega)=L(\omega-D_0)^{1/2},\\ L(\omega)=\frac{8\pi e^2\mathscr{I}(\omega)g^2}{3c\omega^2m_0^{\,2}}\frac{m^{*\,3/2}}{(2\pi)^2},\end{gathered} \tag{17}$$

where $G_0(\omega)$ is the number of carriers generated per unit time; τ_r is the recombination time of carriers which can be regarded as independent of $\mathscr{M}$; g is the interband matrix element of the momentum; D_0 is the width of the band gap at $T=0$; m_0 is the true mass of an electron; $\mathscr{I}(\omega)$ is the spectral density of the intensity of ligth. The validity of Eq. (17) is limited by the condition that the quasi-Fermi level of photoelectrons lies below the electron level at which optical transitions terminate: $\mu<\omega-D_0$.

However, if the frequency of light is sufficiently close to the absorption edge, we have to allow for the dependence of the carrier density on the magnetization. We shall assume that the frequency of the absorbed light corresponds to the lower spin subband but does not reach the upper subband. We can calculate the probability of band-band transitions using plane waves with a fixed direction of spin for the valence band and waves with a fluctuating spin (5) for the conduction band. The transformation to a general coordinate system is made using Eq. (3). The probability of a transition under the influence of illumination is proportional to

$$W_{kp}\sim\frac{1}{N^2}\sum_{\mathbf{fg}}\exp\{i(\mathbf{f}-\mathbf{g})(\mathbf{k}-\mathbf{p})\}\left\langle\cos\frac{\theta_{\mathbf{fg}}}{2}\exp(i\gamma_{\mathbf{fg}})\right\rangle, \tag{18}$$

where **k** and **p** are the quasimomenta in the valence and conduction bands, respectively, and the quantities $\theta_{\mathbf{fg}}$ and $\gamma_{\mathbf{fg}}$ are defined by Eq. (4).

In view of the difficulties encountered in the calculation of the correlation functions of Eq. (18), we shall consider only the case of magnetic materials with a strong easy-plane anisotropy (x-y model), when $\gamma_{\mathbf{gf}}=0$ in all cases. Using Eq.

(7), we obtain—allowing for the smearing of the state (5) between the states with a fixed quasimomentum and spin direction:

$$\langle\cos\theta_{gf}/2\rangle\approx(1/\sqrt{2})\{1+\langle \mathbf{S}_g\mathbf{S}_f\rangle/2S^2\},$$
$$n=\tau_r G(\omega),\ G(\omega)\approx G_c(\omega)[1+CR[m^*(\omega-D_c)]^{1/2}+\ldots],\quad(19)$$
$$G_c=L(\omega-D_c)^{1/2},$$

where $C\sim 1$; the band gap D_c near T_C depends on the magnetization in the same way as $\mathscr{E}(0)$ [see Eq. (11)]. In this case the nonequilibrium analog $\tilde{\Phi}$ of the thermodynamic potential Φ has the following structure:

$$\tilde{\Phi}=\Phi_0+n_0\{\mathscr{E}_2\mathscr{M}^2+(\mathscr{E}_4-\mathscr{E}_2^2/4\nu)\mathscr{M}^4\},$$
$$n_0=\min\left\{\tau_r L\nu^{1/2},\frac{1}{6\pi^2}(2m^*\nu)^{3/2}\right\},\qquad \nu=\omega-D_c|_{\mathscr{M}=0}.\quad(20)$$

It follows from Eq. (20) that, as in the case of semimetals, the phase transition can now be of the first order, although it is now much more difficult to satisfy the conditions for such a transition. It is nevertheless of interest that light can convert a continuous phase transition to an abrupt one. If the phase transition remains continuous even during illumination, then the shift of T_C due to photoelectrons is given by Eq. (13).

We shall now consider singularities of the derivatives of the rate of generation of entropy $\dot{S}=\delta Q/T$, where δQ is the power of the light flux absorbed and converted into heat per unit time. According to Eqs. (19) and (11), we have

$$\dot{S}(\mathscr{M})=G\omega/T=\dot{S}(0)[1-\mathscr{E}_2\mathscr{M}^2/2\nu].\quad(21)$$

Using Eqs. (20) and (13), we find that the magnetization regarded as a function of temperature is

$$\mathscr{M}^2=K(T_C{}^0+\delta T_C-T),\quad K=10S^2(S+1)^2/3T_C(2S^2+2S+1).\quad(22)$$

It is clear from Eqs. (21) and (22) that at the transition points the derivatives of $\dot{S}$ with respect to temperature, and with respect to the intensity and frequency of light all exhibit singularities:

$$\delta\frac{\partial\dot{S}}{\partial T}=\frac{\dot{S}(0)\mathscr{E}_2K}{2\nu},\quad \delta\frac{\partial\dot{S}}{\partial L}=\frac{\dot{S}(0)\mathscr{E}_2^2Kn_0}{2\nu L},$$
$$\delta\frac{\partial\dot{S}}{\partial\omega}=\frac{\dot{S}(0)\mathscr{E}_2^2Kn_0}{4\nu^2}.\quad(23)$$

Since according to Eqs. (19) and (21), the rate $\dot{S}$ is proportional to the photoelectron density, such discontinuities should be experienced also by the corresponding derivatives with respect to this density.

The nature of the singularities of this energetic potential at T_C is governed by the fact that in the adopted approximation Eqs. (20), (22), and (13) yield

$$\tilde{\Phi}\propto(T_C{}^0+\delta T_C-T)^2.\quad(24)$$

Hence it follows that the second derivatives of $\tilde{\Phi}$ with respect to T, ω, and L (including the mixed derivatives) also have discontinuities at T_C. According to Eqs. (21), (22), and (24), that part of the entropy generation rate which is responsible for its discontinuity in the derivative with respect to T_C is proportional to the derivatives of $\tilde{\Phi}$ with respect to T, ω, or L. This result generalizes the conclusion of Ref. 3 according to which a special part of the entropy generation rate is proportional to $\partial\tilde{\Phi}/\partial\omega$.

[1)] These results are obtained using, for example, a spherical model which reproduces highly accurately many properties of the Heisenberg model.[5]

[2)] The quantity Φ_0 in Eq. (12) can be regarded as an accurate expression of the Landau type for the thermodynamic potential of a Heisenberg magnetic material. The specific form of the unrenormalized T_C does not affect its shift because of the indirect exchange. The expression (12) is convenient because it makes it possible to estimate readily the shift of T_C due to the deformation of the lattice by the dopant.

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