PHYSICS OF THE SOLID STATE VOLUME 41, NUMBER 1 JANUARY 1999

MAGNETISM AND FERROELECTRICITY

Characteristic features of the extrinsic electric resistance in ferromagnets with low carrier density

V. A. Gavrichkov*) and S. G. Ovchinnikov

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

(Submitted April 10, 1998)
Fiz. Tverd. Tela (St. Petersburg) **41**, 68–76 (January 1999)

Switching from simple semiconductors to more complicated chemical compositions, we encounter mainly nonstoichiometric or undoped compounds. Combined with other characteristic features of *d(f)* compounds, this can lead, together with the ordinary scattering by spin disorder in magnetic semiconductors, to an unusual impurity contribution to the total scattering of carriers even in intrinsic semiconductors. A unique scheme for calculating the energy structure of the conduction-band bottom of a ferromagnetic semiconductor and the temperature and field dependences of the impurity contribution to the resistivity is proposed on the basis of a model Hamiltonian. The computed magnetoresistance ratio is negative and has a maximum near T_c. A qualitative comparison is made between the results and the experimental temperature dependences of the Hall mobility and magnetoresistance ratio in the ternary semiconductor *n*-$HgCr_2Se_4$, which is nonstoichiometric with respect to the chalcogen. To identify previously unobserved temperature oscillations of the resistance, a careful analysis is made of the low-temperature part of the resistance using the relations obtained. [S1063-7834(99)01701-3]

1. Many compounds, which according to bond type are intermediate ion-covalent compounds, form extended concentration regions with their own components, often of the berthollide type.[1] This is facilitated by the characteristic features of the electronic shell structure of transition, rare-earth, and actinide elements. Interestingly, in these cases the effects due to nonstoichiometry and strong Coulomb correlations are present at the same time. In turn, in such compounds stoichiometry is only a special case or it is unattainable, if the ordinate of the compound corresponding to the highest degree of ordering of the ions falls outside the range of existence of these phases. Nonstoichiometry in semiconductor compounds is of special interest. In such compounds the main cation is a *d* element, since transition-element compounds form the largest group of semiconductors.[2,3]

We are interested in compounds of $d(f)$ elements, at whose Fermi level there is a contribution not only from diffuse *sp* states, which form wide bands, but also from more localized *d(f)* states, which form narrow bands. Ordinarily, in a two-band model it is not difficult to calculate the transport relaxation time, using Fermi's golden rule to calculate the probabilities of quantum transitions. But for substances with quite strong localization of the *d(f)* electrons the electronic correlations make it impossible to use a simple two-band model, since the correlations renormalize not only the parameters of the carrier dispersion law in a narrow band (the bandwidth and the effective mass) but also the hybridization parameters of the states of the wide and narrow bands. Such materials include compounds with variable valence, heavy fermions, and magnetic semiconductors. The discovery of giant magnetoresistance in the perovskites $La_{1-x}(Ca,Sr,Pb,Ba)_xMnO_y$[4] drew additional attention to this problem, since the microscopic mechanism of giant magnetoresistance is still not clear.

The carrier dispersion laws in magnetically ordered substances depend on both temperature and magnetic field on account of the exchange interaction. This makes an additional contribution to the temperature and field dependences of the electric resistance. Many physical properties of conducting magnets can be described in the narrow-band *s–d(f)* model,[2,3] where the carrier is a spin polaron — a quasiparticle, whose motion is similar to that of an ''irregular spin $S \pm 1/2$ on the background formed by a lattice of regular spins S.'' This model is applicable when the *d(f)* electrons are well localized and their contribution to the density of states at the Fermi level is zero. This naive picture is unsuitable in the case of partial delocalization of *d(f)* electrons, where narrow *d* bands must be taken into account together with strong electronic correlations and hybridization with the more diffuse *sp* states. A synthesis of the *s–d(f)* model and Anderson's periodic model makes it possible to do this, and we shall use it below to calculate the temperature and field dependences of the resistance. The computational results will be compared with the experimental data for the magnetic semiconductor *n*-$HgCr_2Se_4$.

The paper is organized as follows. In Sec. 2 the electronic structure of a degenerate semiconductor is described in the periodic Anderson model taking into account *s–d* exchange and scattering by impurities and intrinsic defects. In Sec. 3 the electrical conductivity is calculated. In Sec. 4 the experimental results pertaining to the present calculation are briefly listed and compared with the relations obtained.

2. Let us consider a multielectron model of a magnetic semiconductor taking into account the real multielectronic orbital structure of the $3d$ states.[5] Following this model, the Hamiltonian can be written as a superposition of the periodic Anderson model and the sd exchange model

$$H=H_0+H_1+H_2+H_3;$$

$$H_0=\sum_{\mathbf{k}\sigma}\xi_{\mathbf{k}}c^{+}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}+\sum_{\mathbf{f}}\Bigg[(E_n-n\mu)\sum_{\gamma}X_{\mathbf{f}}^{\gamma\gamma}$$

$$+(E_{n+1}-(n+1)\mu)\sum_{\Gamma}X_{\mathbf{f}}^{\Gamma\Gamma}\Bigg];$$

$$H_1=\sum_{\mathbf{f}}\left\{-J\sigma_{\mathbf{f}}S_{\mathbf{f}}+V\sum_{\sigma}(c^{+}_{\mathbf{f}\sigma}d_{\mathbf{f}\sigma}+\text{h.c.})\right\}. \qquad (1)$$

Here $c_{\mathbf{k}\sigma}$ is the operator annihilating a c electron with momentum $\mathbf{k}$, spin σ, and energy $\xi_{\mathbf{k}}=\varepsilon_{\mathbf{k}}-\mu$, measured from the chemical potential μ. It is assumed that the c band is formed mainly by the $4s$ states of the magnetic ion. $X_{\mathbf{f}}^{pq}=|\mathbf{f}p\rangle\langle\mathbf{f}q|$ are Hubbard operators, describing the transition of a magnetic ion at a lattice site $\mathbf{f}$ from a localized state $|q\rangle$ into a state $|p\rangle$; E_n and E_{n+1} are the energies of the ground state configurations d^n and d^{n+1} of the magnetic ion; the indices γ and Γ refer to the orbital degeneracy of these terms; $S_{\mathbf{f}}$ and $\sigma_{\mathbf{f}}$ are the spin operators of the d ion and c conduction electrons; V and J are hybridization and exchange interaction parameters of the c and d electrons. The signal-electron operators $d_{\mathbf{f}\sigma}$ can be expressed in terms of the Hubbard operators in the standard manner as $d_{\mathbf{f}\sigma}=\Sigma_{pq}\langle p|d_{\mathbf{f}\sigma}|q\rangle X_{\mathbf{f}}^{pq}$. For specific calculations we shall consider only the d^3 and d^4 configurations. This makes it possible to compare the results with experimental data on the semiconductor $HgCr_2Se_4$, where the $^4A_2$ ground state of the Cr^{3+} ion is orbitally nondegenerate and corresponds to spin $S=3/2$. When the "extra" electron (current carrier) is transported along the multielectronic $^4A_2$ states, $Cr^{2+}(d^4)$ ions are formed. For chromium, the energies of the terms $^3T_1(d^4)$ and $^5E(d^4)$ can compete with one another, attesting to the possible presence of two types of donor single-particle excitations of different symmetry with energies $E(^3T_1)-E(^3A_2)$ and $E(^5E)-E(^3A_2)$ in this compound. Here we shall confine ourselves to the latter case, although the method described below for calculating the linear response makes it possible, where it is important to do so, to take into account the excited states of Cr^{2+} and Cr^{4+} (for the valence band), as done in Ref. 5 in a calculation of absorption coefficients. If ^5E is the ground state of the Cr^{2+} ion,

$$d_{\mathbf{f}\uparrow}=X_{\mathbf{f}}^{1.5}+\frac{\sqrt{3}}{2}X_{\mathbf{f}}^{2.6}+\frac{1}{\sqrt{2}}X_{\mathbf{f}}^{3.7}+\frac{1}{2}X_{\mathbf{f}}^{4.8};$$

$$d_{\mathbf{f}\downarrow}=X_{\mathbf{f}}^{4.9}+\frac{\sqrt{3}}{2}X_{\mathbf{f}}^{3.8}+\frac{1}{\sqrt{2}}X_{\mathbf{f}}^{2.7}+\frac{1}{2}X_{\mathbf{f}}^{1.6},$$

where the superscripts enumerate states of the Cr^{3+} and Cr^{2+} ions:

$$Cr^{3+}:|1\rangle=\left|S=\frac{3}{2};S_z=\frac{3}{2}\right\rangle;\quad |2\rangle=\left|\frac{3}{2};\frac{1}{2}\right\rangle;$$

$$|3\rangle=\left|\frac{3}{2};-\frac{1}{2}\right\rangle;\quad |4\rangle=\left|\frac{3}{2};-\frac{3}{2}\right\rangle;$$

$$Cr^{2+}:|5\rangle=|2,2\rangle;\quad |6\rangle=|2;1\rangle;$$

$$|7\rangle=|2;0\rangle;\quad |8\rangle=|2;-1\rangle;\quad |9\rangle=|2;-2\rangle.$$

The operators $d_{\mathbf{f}\sigma}$ in this representation are quasi-Fermi operators. This is because the highest excited states of chromium are neglected, and it corresponds to the single-electron transition $^2A_2\leftrightarrow{}^5E$. We also call attention to the existence of similar concepts in the theory of defects in semiconductors, referring to "local population levels."[6] The presence of a hybridization term in the Hamiltonian is due to the possible entanglement of the c and d states by the distant coordination spheres (trigonal corrections to the crystal field in the case of $HgCr_2Se_4$). Of the different processes responsible for electron scattering by impurities, we take into account in out calculation the standard potential scattering of carriers in c states and fluctuations of the energies of the d level

$$H_2=\sum_{\mathbf{kpfq}}p_{l\mathbf{f}}\Delta_1(\mathbf{k}-\mathbf{q})e^{-i\mathbf{f}\cdot(\mathbf{k}-\mathbf{q})}c^{+}_{\mathbf{k}\sigma}c_{\mathbf{q}\sigma}$$

$$+\sum_{\mathbf{f}\sigma}p_{2\mathbf{f}}\Delta_2(\mathbf{f})d^{+}_{\mathbf{f}\sigma}d_{\mathbf{f}\sigma}. \qquad (2)$$

Here $p_{1\mathbf{f}}$ and $p_{2\mathbf{f}}$ are projection operators, equal to 0 in the absence of impurities and 1 in the nearest-neighbor environment of an impurity atom or defect. The second term in H_2 presumes random fluctuations of the crystal field without a change in symmetry of the field. We chose the form of the Hamiltonian H_2 describing the interaction with impurities so as to illustrate the characteristic features of potential scattering and multicomponent semiconductors.

Depending on the specific physical situation the following are possible: independent fluctuations of the impurity parameters $p_{1\mathbf{f}}\cdot p_{2\mathbf{f}}=0$ or correlated fluctuations $p_{1\mathbf{f}}\cdot p_{2\mathbf{f}}=p_{\mathbf{f}}$. We turn to the first case, which we shall identify below with the presence of intrinsic defects in the sublattices of both the A cations and the B anions. For the system of equations for the two-time Green's functions not averaged over the impurities

$$G_{11}=\langle\langle c_{\mathbf{k}\sigma}|c^{+}_{\mathbf{k}\sigma}\rangle\rangle,\quad G_{22}=\langle\langle d_{\mathbf{k}\sigma}|d^{+}_{\mathbf{k}\sigma}\rangle\rangle,$$

$$G_{12}=\langle\langle c_{\mathbf{k}\sigma}|d^{+}_{\mathbf{k}\sigma}\rangle\rangle$$

is obtained in the standard manner[7]

$$G_{11}(\mathbf{k},\mathbf{k}')=G_{11}^{(0)}\delta_{\mathbf{kk}'}+G_{11}^{(0)}\sum_{\mathbf{fq}}p_{1\mathbf{f}}\Delta_1(\mathbf{k}-\mathbf{q})e^{i\mathbf{f}\cdot(\mathbf{q}-\mathbf{k})}$$

$$\times G_{11}(\mathbf{q},\mathbf{k}')$$

$$+G_{12}^{(0)}\sum_{\mathbf{fq}}p_{2\mathbf{f}}\Delta_{2\mathbf{f}}e^{i\mathbf{f}\cdot(\mathbf{q}-\mathbf{k})}G_{21}(\mathbf{q},\mathbf{k}'),$$

$$G_{21}(\mathbf{k},\mathbf{k}')=G_{21}^{(0)}\delta_{\mathbf{kk}'}+G_{21}^{(0)}\times\sum_{\mathbf{fq}}p_{\mathbf{f}1}e^{i\mathbf{f}\cdot(\mathbf{q}-\mathbf{k})}\Delta_1(\mathbf{k}-\mathbf{q})G_{11}(\mathbf{q},\mathbf{k}')+G_{22}^{(0)}\sum_{\mathbf{fq}}p_{2\mathbf{f}}\Delta_{2\mathbf{f}}e^{i\mathbf{f}\cdot(\mathbf{q}-\mathbf{k})}G_{21}(\mathbf{q},\mathbf{k}'). \qquad (3)$$

The second pair of equations is obtained by interchanging the indices $1\leftrightarrow 2$. Here the initial Green's functions describe the c and d states in the generalized Hartree–Fock approximation:

$$G_{11}^{(0)}=\frac{E-\Omega}{(E-\tilde{\xi}_{\mathbf{k}})(E-\Omega)-K_\sigma V^2},$$

$$G_{12}^{(0)}=\frac{\sqrt{K_\sigma}V}{(E-\tilde{\xi}_{\mathbf{k}})(E-\Omega)-K_\sigma V^2},$$

$$G_{22}^{(0)}=\frac{K_\sigma(E-\tilde{\xi}_{\mathbf{k}})}{(E-\tilde{\xi}_{\mathbf{k}})(E-\Omega)-K_\sigma V^2}, \qquad (4)$$

and $\Omega=E_4-E_3-\mu$ is the transition energy between the terms of the d^4 and d^3 configurations, $\tilde{\xi}_{\mathbf{k}}=\xi_{\mathbf{k}}-\sigma J\langle S_z\rangle$, $K_\sigma=\langle d^+_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma}+d_{\mathbf{k}\sigma}d^+_{\mathbf{k}\sigma}\rangle=1/4(5/2+2\sigma\langle S_z\rangle)$,[5] $\sigma=\pm 1/2$, and $\langle S_z\rangle$ is the average spin of the Cr^{3+} ion. The spectrum of the bands $E^{+}_{\mathbf{k}\sigma}$ can be represented by the expression

$$E^{+}_{\mathbf{k}\sigma}=\frac{1}{2}(\tilde{\xi}_{\mathbf{k}}+\Omega\pm\sqrt{(\tilde{\xi}_{\mathbf{k}}-\Omega)^2+4K_\sigma V^2}).$$

We call attention to the fact that strong correlations not only determine the energy of a localized d level Ω but they also renormalize the hybridization. In the case of no correlations $K_\sigma=1$ and hybridization is determined by the parameter V. On account of the restrictions imposed on the Hilbert space by strong correlations, $K_\sigma=1$ and the effective hybridization $VK_\sigma^{1/2}$ depends on both T and H as a result of $\langle S_z\rangle$, and it is different for the spin subbands.

The functions (4) make it possible to construct a plot of the density of states at the conduction-band bottom of the semiconductor. Figure 1 shows a plot of the density of states obtained under the assumption of a semielliptic density of states for the initial c band:

$$g_0(\varepsilon)=\frac{2}{\pi W}\left[1-\left(\frac{\varepsilon}{W}\right)^2\right]^{1/2},$$

where W is the width of the initial c band.

As is well known, in the band theory the influence of magnetic order reduces to splitting of the spin subbands. In our approach the amplitude Ω of the d peak, corresponding to the one-electron transition ${}^2A_2\leftrightarrow{}^5E$, changes without a change in energy of the d states. Since in a semiconductor with a completely filled valence band and empty conduction band, the band contribution to the magnetization is $\langle\sigma_i\rangle=0$. Shifts of the peak Ω are possible only as a result of Heisenberg exchange, but they are of the order of $T_c\approx 0.01$ eV and much less than the sd exchange interaction, which is responsible for the spin splitting of the c band. The difference in the temperature behavior of the density of c and d states is the key for further understanding, and for this reason we shall explain in greater detail the physical reasons for this and our approach to the compound $\mathrm{HgCr_2Se_4}$. In the paraphase, as one can easily understand, all states $|i\rangle(i=1-4)$ of the Cr^{3+} ion which differ by the spin projection are equally likely. However, as temperature decreases, in the ferrophase the state $|1\rangle$ with maximum spin projection $S_z=3/2$ is predominantly populated, and the single-particle density of d states loses symmetry to spin flip, since $d^+_{\mathbf{f}\uparrow}$ and $d^+_{\mathbf{f}\downarrow}$ acting on the same initial state $|1\rangle$ place carriers in completely different four-particle (d^4) states $|5\rangle$ and $|6\rangle$, respectively. The differences between the multielectron states can lead to a zero density of states in the limit $T\to 0$ K for a carrier with one of the spin projections, as happens, for example, in the case of ${}^3T_1$ symmetry of the ground state for Cr^{2+} (Fig. 1). We note that in our approach it is not necessary to introduce a giant spin splitting of the d bands, which still cannot describe the presence of a large spin on the Cr^{3+} ion in the paraphase (the Curie–Weiss law). Similar features of the density of states are also observed in other magnetic semiconductors — both ferromagnetic and antiferromagnetic.[8]

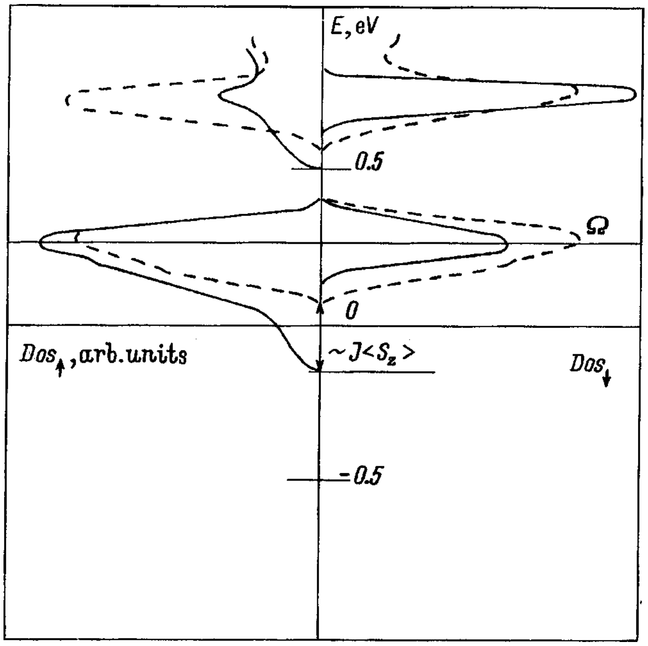

FIG. 1. Density of states near the conduction-band bottom of the compound $\mathrm{HgCr_2Se_4}$[5] for $T=4.2$ (solid line) and 300 K (dashed line). The symbol Ω denotes the initial d level: $E({}^5E)-E({}^3A_2)\mu$.

To perform the configurational averaging, we shall employ an impurity diagram technique.[7] We shall average each term in the series of the system (3) using the rules

$$\left\langle\sum_{\mathbf{f}}Z_{\mathbf{f}}p_{i\mathbf{f}}e^{i\mathbf{f}\cdot(\mathbf{k}'-\mathbf{k})}\right\rangle=c_iZ\delta_{\mathbf{kk}'};\quad i=1,2,$$

where c_1 and c_2 are the concentrations of defects of the first and second kinds. Intersecting plots were dropped when writing the corresponding equations. This is valid only for a degenerate semiconductor $\langle\mu\rangle\hbar/\tau$, where the Fermi level lies in the conduction band and the substitution KT $\Leftrightarrow\mu$

makes sense. As a result, the solution of these equations for the average Green's functions G_{11} and G_{12} has the form

$$G_{11}^{\sigma}(\mathbf{k},E)=\left\{E-\tilde{\xi}_{\mathbf{k}}+\frac{i}{2\tau_1^{\sigma}}\,\mathrm{sign}(\tilde{E})-\frac{K_{\sigma}V^2}{E-\Omega+\dfrac{i}{2\tau_2^{\sigma}}\dfrac{(K_{\sigma}V)^2}{(E-\Omega)^2}\,\mathrm{sign}(\tilde{E})}\right\}^{-1},$$

$$G_{22}^{\sigma}(\mathbf{k},E)=K_{\sigma}\left\{E-\Omega+\frac{i}{2\tau_2^{\sigma}}\frac{(K_{\sigma}V)^2}{(E-\Omega)^2}\,\mathrm{sign}(\tilde{E})-\frac{K_{\sigma}V^2}{E-\tilde{\xi}_{\mathbf{k}}+\dfrac{i}{2\tau_1^{\sigma}}\,\mathrm{sign}(\tilde{E})}\right\}^{-1}. \quad (5)$$

Here $(\tau_i^{\sigma})^{-1}=c_i g_0^{\sigma}\int d\omega|\Delta_i(\theta)^2|/4\pi$; $\tilde{E}=E-K_{\sigma}V^2/(E-\Omega)$, g_0^{σ} is the density of states in the initial c band at the Fermi level. The Green's functions (5) have a two-band structure. For a degenerate semiconductor, the contribution of the top band $E_{\mathbf{k}\sigma}^{+}$ can be neglected and a single-pole expression can be used:

$$G_{11}^{\sigma}(\mathbf{k},E)=\frac{u_{\mathbf{k}\sigma}^2}{D_{\mathbf{k}\sigma}};\quad G_{22}^{\sigma}(\mathbf{k},E)=\frac{K_{\sigma}v_{\mathbf{k}\sigma}^2}{D_{\mathbf{k}\sigma}};$$

$$G_{12}^{\sigma}(\mathbf{k},E)=\frac{u_{\mathbf{k}\sigma}^2 v_{\mathbf{k}\sigma}\sqrt{K_{\sigma}}}{D_{\mathbf{k}\sigma}};$$

$$D_{\mathbf{k}\sigma}=E-E_{\mathbf{k}\sigma}^{-}+i\left(\frac{u_{\mathbf{k}\sigma}^2}{2\tau_1^{\sigma}}+\frac{K_{\sigma}v_{\mathbf{k}\sigma}^2}{2\tau_d^{\sigma}}\right)\mathrm{sign}(E). \quad (6)$$

$u_{\mathbf{k}\sigma}^{+}$ and $v_{\mathbf{k}\sigma}^2$ determine the probability of finding a carrier quasiparticle in the lowest conduction band $E_{\mathbf{k}\sigma}$ in the c and d relaxation channels

$$u_{\mathbf{k}\sigma}^2=\frac{\partial E_{\mathbf{k}\sigma}^{-}}{\partial\tilde{\xi}_{\mathbf{k}}}=\frac{(\Omega-E_{\mathbf{k}\sigma})}{(E_{\mathbf{k}\sigma}^{+}-E_{\mathbf{k}\sigma}^{-})};\quad v_{\mathbf{k}\sigma}^2=1-u_{\mathbf{k}\sigma}^2;$$

$$(u_{\mathbf{k}\sigma}v_{\mathbf{k}\sigma})^2=\frac{K_{\sigma}V^2}{(E_{\mathbf{k}\sigma}^{+}-E_{\mathbf{k}\sigma}^{-})^2},$$

$\dfrac{1}{\tau_d^{\sigma}}=\dfrac{K_{\sigma}v_{\mathbf{k}\sigma}^2}{u_{\mathbf{k}\sigma}^2}\dfrac{1}{\tau_2^{\sigma}}$ is the effective relaxation rate of a carrier in a d channel. Specifically, when the Ω level lies far below the c band of the diffuse states $u_{\sigma}^2|_{\mathbf{k}=\mathbf{k}_{\mathbf{F}}}\to 0$ and in accordance with the high density of states at Ω level, the effective relaxation rate $\dfrac{1}{\tau_d^{\sigma}}\to\infty$.

In the limit $\Omega\to\infty$, where an unoccupied d level lies high above the Fermi energy, for $E_{\mathbf{k}\sigma}\to\tilde{\xi}_{\mathbf{k}}$, $v_{\mathbf{k}\sigma}^2\to 0$ and the Green's function G_{11} assumes the standard form for the single-band model

$$G_{11}^{\sigma}(\mathbf{k},E)=\left(E-\tilde{\xi}_{\sigma}+\frac{i}{2\tau_{\sigma}}\mathrm{sign}(E)\right)^{-1}. \quad (7)$$

We do not discuss here the specific form of the dispersion relation $\xi_{\mathbf{k}}$, since the further calculations concerning the conductivity will make it possible to leave it in the general form. In what follows, we shall consider the particular case of a quadratic dispersion law near the bottom of the initial c band, and we shall present the conductivity formula corresponding to this case.

3. The dispersion laws of the hybridized $E_{\mathbf{k}\sigma}^{+}$ bands can give the impression that the problem of calculating the electrical conductivity reduces to the standard problem for a simple two-band model. Then it would be possible to use Fermi's golden rule to calculate the probabilities of quantum transitions and to write down easily the transport relaxation time. In the present problem, there is one circumstance that makes it necessary to use a more complicated computational method in terms of the Green's function, specifically, the localization of d electrons on account of the strong electronic correlations. Strong correlation effects result in a renormalization of the hybridization parameter $V^2\to K_{\sigma}V^2$, where K_{σ} is determined by the magnetization and depends on both temperature and the applied magnetic field. The renormalized hybridization parameter appears in the effective relaxation time. In all other respects, the picture is indeed similar to the model of two bands for quasiparticles with band structure, depending on the carrier density, temperature, and magnetic field.

On account of the initial atomic description of the $3d$ states appearing in the lower conduction band $E_{\mathbf{k}\sigma}$, the width of the initial d band is 0, and conduction in this band occurs by charge transfer along c states. The expression for the current density can be written in the form[7]

$$j_{\alpha}(\mathbf{q},\nu)=-\frac{e^2}{2c}\sum_{\mathbf{k}\sigma}\int\frac{dE}{2\pi}\rho_{\alpha}^{\sigma}(\mathbf{k},\mathbf{k}+\mathbf{q})\times\prod_{\beta}^{\alpha}(\mathbf{k}+\mathbf{q},\mathbf{k},E+\nu,E)A^{\beta}(\mathbf{q},\nu), \quad (8)$$

$$\prod_{\beta}^{\sigma}(\mathbf{k}+\mathbf{q},\mathbf{k},E+\nu,E)=\sum_{p}\langle G_{11}^{\sigma}(\mathbf{k},\mathbf{p},E)\rho_{\beta}^{\sigma}(\mathbf{p},\mathbf{p}+\mathbf{q})\times G_{11}^{\sigma}(\mathbf{k}+\mathbf{q},\mathbf{p}+\mathbf{q},E+\nu)\rangle, \quad (9)$$

where $A^{\beta}(\mathbf{q},\nu)=i\nu E^{\beta}(\mathbf{q},\nu)/c$, $\rho_{\alpha}^{\sigma}(\mathbf{k},\mathbf{k}+\mathbf{q})=\dfrac{\partial\tilde{\xi}_{\mathbf{k}}}{\partial\mathbf{k}_{\alpha}}+\dfrac{\partial\tilde{\xi}_{\mathbf{k}+\mathbf{q}}}{\partial(\mathbf{k}+\mathbf{q})_{\alpha}}$, and $E(\mathbf{q},\nu)$ is the intensity of the external electromagnetic field. The vertex part (9) can be found in a ladder approximation from the system of equations

$$\prod_{11}^{\sigma}(\mathbf{k},E+\nu,E)=\frac{\partial\tilde{\xi}_{\mathbf{k}}}{\partial\mathbf{k}}\{G_{11}^{\sigma}(\mathbf{k},E)G_{11}^{\sigma}(\mathbf{k},E+\nu)\times(1+\Lambda_{11}^{\sigma}(E,\nu))+G_{12}^{\sigma}(\mathbf{k},E)\times G_{21}^{\sigma}(\mathbf{k},E+\nu)\Lambda_{22}^{\sigma}(E,\nu)\},$$

$$\prod_{22}^{\sigma}(\mathbf{k},E+\nu,E)=\frac{\partial\tilde{\xi}_{\mathbf{k}}}{\partial\mathbf{k}}\{G^{\sigma}_{21}(\mathbf{k},E)G^{\sigma}_{12}(\mathbf{k},E+\nu)\times(1+\Lambda^{\sigma}_{11}(E,\nu))+G^{\sigma}_{22}(\mathbf{k},E)\times G^{\sigma}_{22}(\mathbf{k},E+\nu)\Lambda^{\sigma}_{22}(E,\nu)\}, \qquad (10)$$

where, confining our attention to the normal skin effect $\nu(q)\ll 1/\tau$, we have introduced the notation

$$\mathbf{k}\Lambda^{\sigma}_{ii}(E,\nu)=\frac{c_i}{2\pi}\int|\Delta_i(\mathbf{k}-\mathbf{k}')|^2\Pi^2_{ii}(\mathbf{k}',E+\nu,E)d\mathbf{k}'. \qquad (11)$$

Since in our model the impurity potential Δ_2 does not depend on the momentum, the integration over angles leads to $\Delta_{22}=0$, so that a transport relaxation time does not arise for d states. For c electrons the transport relaxation time is

$$\tau_{tr}^{-1}=c_1 g_0^{\sigma}\int d\Omega|\Delta_1(\theta)|^2(1-\cos(\theta))/4\pi.$$

As a result, we have for the statistical conductivity

$$\sigma=e^2\sum_{\sigma}g_0^{\sigma}\int\frac{d\Omega}{4\pi}\left(\frac{\partial\tilde{\xi}_{\mathbf{k}}}{\partial\mathbf{k}}\right)^2 u^2_{\mathbf{k}\sigma}\tau^{\sigma}_{\mathrm{eff}}|_{\mathbf{k}=\mathbf{k}_F}, \qquad (12)$$

where the effective relaxation rate (all labels referring to the momenta on the Fermi surface are dropped in what follows)

$$(\tau^{\sigma}_{\mathrm{eff}})^{-1}=\frac{u^2_{\sigma}}{\tau_{tr}}+\frac{K_{\sigma}v^2_{\sigma}}{\tau_d}. \qquad (13)$$

In the particular case of a quadratic dispersion law for the c band

$$\sigma=\frac{e^2}{m}\sum_{\sigma}n_{\sigma}u^2_{\sigma}\tau^{\sigma}_{\mathrm{eff}}, \qquad (14)$$

where $n^{\sigma}_{\mathrm{eff}}=n_{\sigma}u^2_{\sigma}$ is the effective density of carriers with spin σ, which occupy c states with the effective mass m and rate $\partial\xi_{\mathbf{k}}/\partial\mathbf{k}$ characteristic of the latter. The effective relaxation rate (13), in agreement with Mathiessen's rule, is additive in the relaxation rates τ_{tr}^{-1} and $(\tau^{\sigma}_d)^{-1}$ with weights u^2_{σ} and $K_{\sigma}v^2_{\sigma}$. They are simply the probability with which the carrier participates in scattering by the corresponding potential for the c and d states. The main individual features of the material, such as the chemical composition, symmetry, and lattice constant, strongly influence the conductivity in this relation through the position of the d level relative to the conduction-band bottom and the effective hybridization parameter, and therefore via the u^2_{σ} and v^2_{σ} coefficients. Moreover, since the u^2_{σ} and v^2_{σ} coefficients depend on temperature, the conductivity also turns out to be temperature-dependent.

To study the case of completely correlated impurities $p_{f1}\times p_{f2}=p_f$, we added diagrams where the dashed line connects different impurity vertices.

As a result, solving the system in the standard manner, we obtain for the conductivity the expression (14) but with a renormalized relaxation time

$$(\tau^{\sigma}_{\mathrm{eff}})^{-1}_{tr}=\frac{cg_0^{\sigma}}{u^2_{\sigma}}\int\frac{d\Omega}{4\pi}|u^2_{\sigma}\Delta_1(\theta)+K_{\sigma}v^2_{\sigma}\Delta_2|^2\times(1-\cos(\theta)),$$
$$c=c_1=c_2. \qquad (15)$$

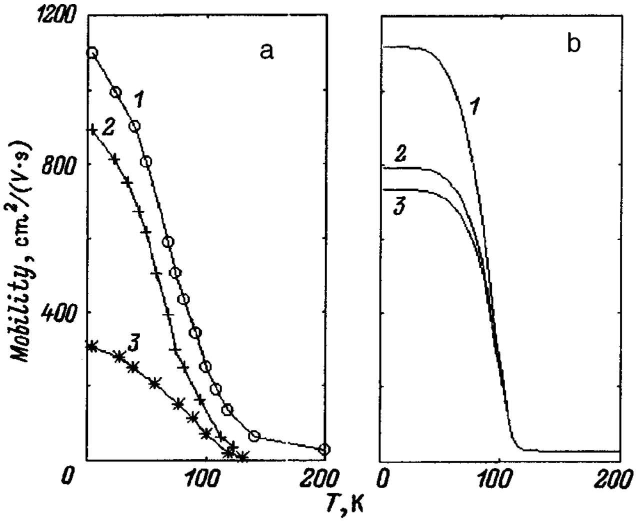

FIG. 2. Temperature dependence of the mobility for $\mathrm{HgCr_2Se_4}$ with different carrier density. a — Experiment,[17] b — theory. $n=5\times10^{18}$ cm^{-3} (*1*), 1.23×10^{18} (*2*), and 1.4×10^{17} cm^{-3} (*3*).

The latter relation attests to the fact that the arrangement of the impurities strongly influences the relaxation rate. If Eq. (13) describes scattering of carriers under the condition that the impurities or defects are distributed randomly, then for a correlated arrangement of impurities or defects the interference of electronic waves, scattered by different impurity atoms (defects), becomes important.

4. The conductivity of the semiconductor n-$\mathrm{HgCr_2Se_4}$ has been investigated in detail in a series of works.[9–12] In what follows, we shall briefly sketch the experimental situation, and we shall discuss its possible interpretation. Figure 2a shows the typical temperature dependences of teh Hall mobility for different $\mathrm{HgCr_2Se_4}$ samples. The mobility in the paraphase is 10–30 cm^2/V·s. As temperature decreases, the mobility increases strongly (approximately from $T_c\sim110$ K), reaching values of the order of 1200 cm^2/V·s at $T=4.2$ K for $n\sim5\times10^{18}$ cm^{-3}.[9] Starting approximately at 2×10^{18} cm^{-3}, the carrier density at low temperatures and up to 200 K remains virtually constant, in agreement with our initial assumption that the object of our calculation is a degenerate semiconductor.

In this way, the mobility increases by two orders of magnitude in the temperature interval ~100 K. A magnetic field shifts the mobility versus temperature curve as a whole in the direction of higher temperatures. As a consequence, a large negative magnetoresistance ratio, displayed in Fig. 3a, with a peak near T_c is observed.

Such dependences in magnetically ordered substances ordinarily are attributed to scattering of carriers by spin disorder.[10,11] As correctly noted in Ref. 9, the absence of a minimum in the mobility versus temperature curve at the

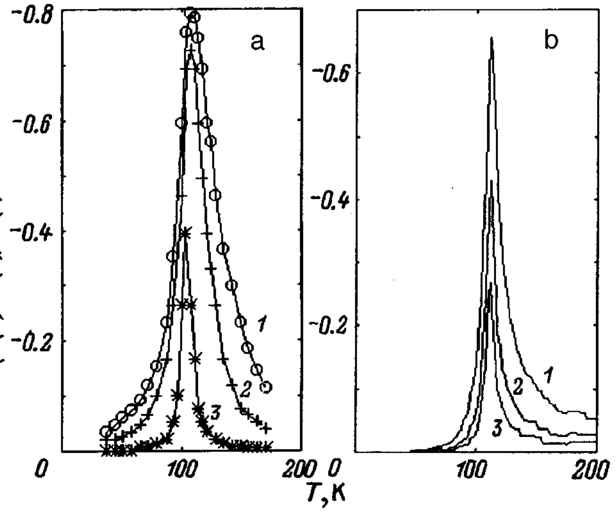

FIG. 3. Temperature dependence of the magnetoresistance ratio for $HgCr_2Se_4$. a — Experiment,[17] b — theory. $H = 10.2$ (*1*), 5.6 (*2*), and 1 kOe (*3*).

point T_c, associated with increasing diffusion through spin disorder with increasing temperature, casts doubt on the existence of the standard mechanism of scattering of carriers by spin disorder in this compound. We also mention that the increase in the mobility by two orders of magnitude up to values characteristic for widegap semiconductors attests to serious temperature changes in the semiconductor band structure itself. As an acceptable mechanism, the authors of Ref. 9 proposed a mechanism of carrier scattering by spin disorder in a narrow band of *d* states, the nature of the band, just as in our case, being associated with the states of Cr^{2+}. However, the 1/*T* relation presented for the mobility in Ref. 9, with no features at T_c, appears to be incorrect for this scattering mechanism. Moreover, it has long been known for transition-metal alloys (the Mott model[13]) that the residual impurity scattering may be temperature-dependent,[14] so that it cannot be neglected when identifying the real scattering mechanism according to the temperature dependence. This is also supported by the unusual, for semiconductors, dependence of the mobility on the defect density. The highest mobility occurs in the sample obtained at the highest excess mercury vapor pressure, and hence with the highest content of uncompensated Se vacancies. Since the high-temperature part of the mobility is essentially independent of the defect density, the presence of defects increases the temperature-dependent part of the mobility.

An alternative to the generally accepted explanation could be the presence of a record-high ''red'' shift of the optical absorption edge in $HgCr_2Se_4$.[15] For a semiconductor gap $E_g(300\ \mathrm{K}) \approx 0.8$ eV, the shift reaches 0.5 eV and $E_g(4.2\ \mathrm{K}) \approx 0.3$ eV, which attests to a large rearrangement of the lower conduction band (Fig. 1). Together with the restructuring of the spectrum and the density of states, the carrier scattering mechanisms change: impurity and phonon.[14] Just as in the case of transition-metal alloys, we can encounter a situation where the spin disorder scattering mechanism will compete with the impurity scattering mechanism among the *d* states, which exhibits an analogous temperature dependence. Even though they are different in nature, these mechanisms nonetheless have different concentration dependences, which ultimately makes it possible to identify the predominant presence of one of them in the experimental material.

For a specially undoped *n*-$HgCr_2Se_4$ sample, the carrier scattering is due to vacancies among the anions and the *A* cations. The Se vacancies lead to both the standard potential scattering and scattering by fluctuations of the crystal field as a result of energy shifts of the *d* level. The Hg-cation vacancies apparently influence the *d* levels very little, since they are located in the second coordination sphere. At the same time they act as scattering centers for carriers undergoing the standard potential scattering. For Se vacancies the second term in Eq. (2) is most important because of the strong localization of the *d* states, and all other defects give rise mainly to carrier scattering in the channel for ordinary potential scattering by the potential Δ_1. Defects in the Se and Hg sublattice can be distributed differently. We shall assume that these defects are distributed independently, and we shall employ the results of a calculation with uncorrelated impurities (13) and (14). These relations contain, together with the parameters $V = 0.15$ eV, $J = 0.8$ eV, and $\Omega = -0.25$ eV (Ω is measured from the bottom of the initial *c* band in the paraphase)[5] two unknown parameters μ_S and μ_d:

$$\sigma = e \sum_{\sigma} n_\sigma u_\sigma^2 \mu_{\mathrm{eff}},$$

$$\mu_{\mathrm{eff}} = \frac{e}{m}\left(\frac{u_\sigma^2}{\tau_{tr}} + \frac{K_\sigma v_\sigma^2}{\tau_d} \right)^{-1} = \left(\frac{u_\sigma^2}{\mu_s} + \frac{K_\sigma v_\sigma^2}{\mu_d} \right)^{-1}. \qquad (16)$$

At low temperatures ($T \to 0$) the *c* band of the diffuse states drops below the Ω level as a result of the *sd* exchange interaction (Fig. 1), and for this reason the fraction of carriers in the *c* states is high: $u_\sigma^2 \to 1$ and $\mu_{\mathrm{eff}} \to \mu_s \sim 1/c_1$. As temperature increases, the action of the *sd* exchange interaction on the *c* band becomes weaker ($\langle S_z \rangle \to 0$), causing the band to rise above the Ω level. In the process, the carriers pass into current-free *d* states, and their fraction in the *c* states $u_\sigma^2 \to 0$. Therefore, in the paraphase for $T \gg T_c \mu_{\mathrm{eff}} \to \mu_d / K_\sigma \sim 1/c_2$. Hence $\dfrac{\mu_s}{\mu_d} \approx \dfrac{\mu_{\mathrm{eff}}(T \to 0)}{K_\sigma \mu_{\mathrm{eff}}(T \gg T_c)}$. According to the experimental data, this ratio is approximately 100. The quantity μ_s was determined from the absolute value of $\mu_{\mathrm{eff}}(4.2\ \mathrm{K})$ for $n \sim 5 \times 10^{18}\ \mathrm{cm}^{-3}$ and was found to be $\sim 2000\ \mathrm{cm}^2/\mathrm{V \cdot s}$. Next, the temperature dependence $\mu_{\mathrm{eff}}(T)$ shown in Fig. 2b (solid line) was calculated. We shall assume that the role of the excess mercury vapor reduces to simply decreasing the number of Hg vacancies, the number Se vacancies remaining constant and equal to $10^{19}\ \mathrm{cm}^{-3}$. Then the temperature dependences for samples with a different carrier density can be easily calculated (Fig. 2b).

Characteristically, μ_{eff} is always less than the parameter μ_s. Thus, it follows from Eq. (16) that as $u_\sigma^2 \to 0$ (the *d* level drops much below the bottom of the *c* band) $\mu_{\mathrm{eff}} \to 0$. This signifies that all carriers are in the *d* scattering channel, and in accordance with the high density of *d* states their contribution to the mobility is minimal. In the intermediate case $u_\sigma^2 \sim v_\sigma^2$ the effective mobility $\mu_{\mathrm{eff}} \sim \mu_d$ and scattering by fluctuations of the d levels makes the main contribution to the carrier scattering. Finally, only in the limit $v_\sigma^2 \rightarrow 0$, when the d level $\Omega \rightarrow \infty$, we have $\mu_{\mathrm{eff}} \sim \mu_s$, i.e. the parameter μ_s is the maximum possible mobility that can occur if the d level were located infinitely high above the bottom of the c band. Then the carriers undergo mainly the standard potential scattering. We note also that for u_σ^2, $v_\sigma^2 \neq 0$, in the limit $\mu_s \rightarrow \infty$, we obtain from Eq. (16)

$$\sigma=\sum_\sigma e n_\sigma u_\sigma^2 \mu_\sigma^*, \quad \mu_\sigma^*=\frac{\mu_d}{K_\sigma v_\sigma^2}, \tag{17}$$

i.e. the conductivity is finite even with an infinitely long free path of carriers in c states. This effect is due for carrier scattering by the fluctuation potential Δ_2 of the crystal field.

The computed value of the magnetoresistance ratio $(R(H)-R(0))/R(0)$ as a function of temperature is shown in Fig, 3b (solid line). One can see that, just as in the case of scattering by critical fluctuations of the magnetization, a large negative magnetoresistance with a maximum at $T \sim T_c$ occurs near the Curie temperature. However, these features of the magnetoresistance are due to potential scattering by impurities or defects, as well as by the magnetic field induced redistribution of carriers over different scattering channels. A direct consequence of these results is that the simple estimate of the form $\rho=\rho(H=0)-\rho(H\rightarrow\infty)$ is incorrect for determining the contribution of only the scattering of current carriers by spin disorder to the resistance of the semiconductor. The computed mechanism of magnetoresistance is observed, in complete agreement with experiment, in the form of a uniform shift (without a large change in shape) of the conductivity versus temperature curve in the direction in higher temperatures in a magnetic field.

The concentration dependence of the mobility is of special interest. As the density of defects among the nonmagnetic cations increases, the effective mobility μ_{eff} of the current carriers increases from 300 $\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ at $n \sim 1.4\times10^{17}$ cm^{-3} up to 1850 $\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ at $n \sim 10^{19}$ cm^{-3}.[9] It can be inferred that this is due to processes, continuing at this defect density, that lead to the formation of an impurity conduction band and therefore to drawbacks in the simplified treatment of a degenerate semiconductor as a metal with KT simply replaced by μ. It is also possible that as the mercury vapor pressure increases, the defect concentration c_1 in the Hg cation sublattice decreases, and $\mu_{\mathrm{eff}}(\sim 1/c_1)$ at low temperatures, where scattering of carriers occurs mainly in the standard potential scattering channel, intensifies. In turn, the Se vacancy concentration c_2 remains constant, but only at high temperatures $(T \gg T_c)$ $\mu_{\mathrm{eff}} \sim 1/c_2$.

In strong magnetic fields, where Landau quantization occurs for itinerant electrons, unusual quantum oscillations of the magnetization and resistance are observed in n-$\mathrm{HgCr_2Se_4}$.[16] A theoretical description of the magnetization was given in Ref. 17 on the basis of the same model as the one in the present paper. As one can see from Eq. (4), the conduction-band bottom shifts in proportion to $\langle S_z\rangle$, while the chemical potential is pinned near the d level Ω. For this reason, the effective chemical potential, measured from the band bottom and determining the phase of the oscillating part of the thermodynamic potential, the magnetization, and the resistance, acquires strong field and temperature dependences, in contrast to the weak T^2/ε_F corrections in the Fermi-liquid theory. As a result, the quantum oscillations of the magnetization and resistance which are observed in an external magnetic field are no longer periodic as functions of the reciprocal of the field.[16] Similarly, as the temperature varies, crossings of the chemical potential with the Landau levels can occur. Such crossing can lead to temperature quantum oscillations, observed thus far only for the magnetization.[18]

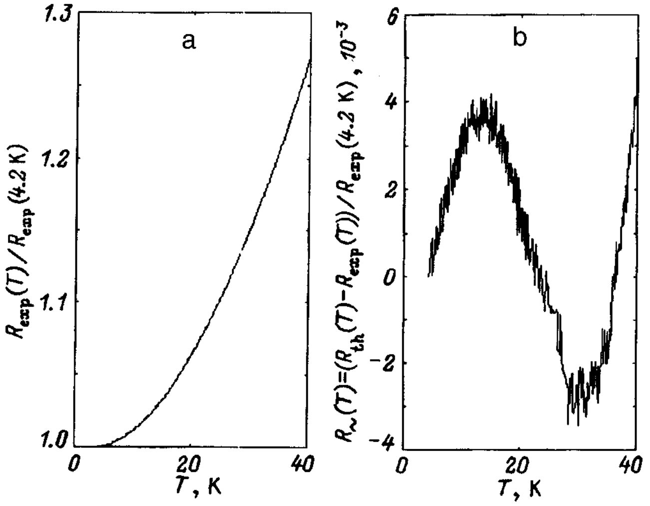

FIG. 4. Experimental temperature dependence of the electrical resistance for n-$\mathrm{HgCr_2Se_4}$ in a 60 kOe field (a) and oscillating part of the resistance $R_{\sim}(T)$ (b).

To single out the oscillating part in the temperature dependence of the resistance, it is necessary to subtract the monotonic dependence, not associated with Landau quantization, specifically, the resistance $R_{th}(T)$ determined by Eq. (15), from the experimental curve $R_{\mathrm{exp}}(T)$ (Fig. 4a[16]). The temperature dependence appearing in Eq. (14) was found on the basis of the spin-wave theory

$$\langle S_{\acute{E}}\rangle=3/2-at^{3/2}Z_{3/2}(x)-bt^{5/2}Z_{5/2}(x)-ct^{7/2}Z_{7/2}(x), \tag{18}$$

$t=T/4\pi IS$, $x=2\mu_B H/T$. The parameters in the expansion (18) a, b, and c were determined by fitting the experimental data on the temperature dependence of the magnetization using a simplex method. The results are $a=0.8499$, $b=-0.5545$, and $c=0.1294$. The theoretical temperature dependence $R_{th}(T)$ obtained in this manner describes the temperature dependence of the resistance neglecting Landau quantization. The oscillating part of the resistance $R_{\sim}(T)=R_{\mathrm{exp}}(T)-R_{th}(T)$ is shown in Fig. 4b, where indeed a single period of the oscillations is observed, just as for the magnetization.[18] The relative amplitude of the oscillations of the electrical resistance is small because of the smallness of the carrier density itself, but, as it turned out, it is approximately five times greater than the magnitude of the magnetization oscillations.

In conclusion, we note that the potential impurity scattering mechanism acquires such unusual, for the practice of multicomponent compounds, temperature and field dependences because of a characteristic combination of several factors, the initial ones being the breakdown of the stoichiometric laws and the presence of transition elements in the chemical composition of the semiconductor. Such a combination could be the first indication of a substantial impurity contribution to the resistance in a semiconductor with temperature and field dependences that are similar to those calculated here.

We thank A. D. Balaev for providing the low-temperature dependence of the resistivity of n-$HgCr_2Se_4$ in a 60 kOe field.

This work was supported by the Russian Fund for Fundamental Research (Grant No. 96-02-16075) and the Krasnoyarsk Krai Science Foundation (Grant No. 7F0175).

*⁾E-Mail: gav@iph.krasnoyarsk.su

---

[1] N. N. Sirota, *Physicochemical Nature of Phases with Variable Composition*, Nauka i Tekhnika, Minsk (1970), 231 pp.

[2] S. Metfessel and D. C. Mattis, *Magnetic Semiconductors, Handbuch der Physic*, Springer-Verlag, N. Y. (1968), 562 pp.

[3] É. L. Nagaev, *Physics of Magnetic Semiconductors*, Nauka, Moscow (1979), p. 127.

[4] R. von Helmholt, J. Wecker, B. Holzapfel, L. Shultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. Mc. Cormack, R. A. Fasthnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).

[5] V. A. Gavrichkov, S. G. Ovchinnikov, M. Sh. Erukhimov, I. S. Édel'man, and M. Sh. Erukhimov, Zh. Éksp. Teor. Fiz. **90**, 1275 (1986) [Sov. Phys. JETP **63**, 744 (1986)]; V. A. Gavrichkov, S. G. Ovchinnikov, and M. Sh. Erukhimov, Fiz. Tverd. Tela (Leningrad) **29**, 527 (1987) [Sov. Phys. Solid State **29**, 298 (1987)].

[6] M. Lanoo and J. Bourgoin, *Point Defects in Semiconductors I, Theoretical Aspects*, Springer Series in Solid-States Science 22. Springer-Verlag, N. Y. (1981), 264 pp.

[7] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Methods of Quantum Field Theory in Statistical Physics* [Prentice-Hall, Englewood Cliffs, N. J., 1963; Gostekhizdat, Moscow, 1962].

[8] S. G. Ovchinnikov, Phase Transit. **36**, 15 (1991).

[9] A. Selmi, *Galvanomagnetic Properties of the Semiconductor* $HgCr_2Se_4$, Diplome de Doctoeur (in French), University of P.-M. Curie, 1979, pp. 61–71; A. Selmi *et al.*, J. Appl. Phys. **57**, 3216 (1985); A. Selmi *et al.*, J. Magn. Magn. Mater. **66**, 295 (1987).

[10] N. Koguchi, K. Masumoto, and J. Phys. Chem. Solids **41**, 1279 (1980).

[11] B. A. Gizhevskiĭ, A. A. Samokhvalov *et al.*, Fiz. Tverd. Tela (Leningrad) **26**, 2647 (1984) [Sov. Phys. Solid State **26**, 1604 (1984)].

[12] V. K. Chernov, V. A. Gavrichkov, N. B. Ivanova, G. S. Veĭst, and Yu. V. Boyarshinov, Fiz. Tverd. Tela (Leningrad) **28**, 289 (1986) [Sov. Phys. Solid State **28**, 159 (1986)].

[13] N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935); Proc. Roy. Soc. A **153**, 368 (1936); N. F. Mott, K. W. H. Stevens Philos. Mag. **2**, 1364 (1957); B. R. Coles Adv. Phys. **7**, 40 (1958).

[14] J. Frank and F. Blatt, *Physics of Electronic Conduction in Solids*, Mc Graw–Hill Book Co., N. Y. (1968), 470 pp.

[15] T. Arai and M. Wakaki *et al.*, J. Phys. Soc. Jpn. **34**, 68 (1973).

[16] A. D. Balaev, V. V. Val'kov, V. A. Gavrichkov, N. B. Ivanova, S. G. Ovchinnikov, and V. K. Chernov, Usp. Fiz. Nauk **167**, 1016 (1997); A. D. Balaev, V. A. Gavrichkov, S. G. Ovchinnikov, V. K. Chernov, T. G. Aminov, and G. G. Shabunina, Zh. Éksp. Teor. Fiz. **113**, 5 (1998), at press [J. Exp. Theor. Phys. **86**, 1026 (1998)].

[17] V. V. Val'kov and D. Dzebisashvili, Zh. Éksp. Teor. Fiz. **111**, 654 (1997) [J. Exp. Theor. Phys. **84**, 360 (1997)].

[18] S. G. Ovchinnikov, V. K. Chernov, A. D. Balaev, N. B. Ivanova, V. A. Levshin, and B. P. Khrustalev, JETP Lett. **62**, 642 (1995).

Translated by M. E. Alferieff