Resonant scattering by mixed-valence impurities in zero-gap $Hg_{1-x}Fe_xSe$ semiconductors

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The nondegenerate Anderson model for mixed-valence impurities is used to derive an expression for the electrical conductivity which allows not only for radical changes in the energy spectrum and damping of the conduction electrons as a result of hybridization of the *s* and *d* electrons, but also for background scattering mechanisms. A theoretical analysis accounts for the "anomalous" change in the conduction electrons observed in Hg–Fe–Se semiconductors and dependent on the iron concentration. The anomalous change is explained without assuming the formation of a Wigner crystal from Fe^{3+} ions at low temperatures.

1. INTRODUCTION

The system of compounds $Hg_{1-x}Fe_xSe$ is attracting attention because of a number of interesting features exhibited by the dependences of the physical quantities on the concentration N_d of the iron impurity. Numerous experimental investigations[1-4] have demonstrated that the majority of the physical properties of Hg–Fe–Se semiconductors are governed by the position of the resonant level Fe^{2+} $(3d^6)$ relative to the bottom of the conduction band: for example, the density of free electrons is $n_e = N_d$ if $10^{18}\ \text{cm}^{-3} \leqslant N_d \leqslant N_d^*$ ($N_d^* = 5\times 10^{18}\ \text{cm}^{-3}$) and the Fermi energy ζ_F increases on increase in N_d reaching the resonant level $\Omega_0 = 220 \pm 10$ meV. A further increase in N_d has practically no effect on the Fermi energy or on the density of the band carriers $n_e \approx N_d^*$.

The low-temperature dependences of the mobility $\mu(N_d)$ and of the Dingle temperature $T_D(N_d)$ on the concentration N_d are unusual. An increase in the iron concentration in Hg–Fe–Se increases the mobility μ, which reaches its maximum at $N_d = N_{d(m)}$, and rises in the process by a factor of 4–5, but a further increase in N_d reduces the mobility μ. According to Refs. 1 and 2, the Dingle temperature decreases on increase in N_d and passes through a minimum at $N_d \sim N_{d(m)}$, decreasing in the course of this process by a factor $T_D(N_d^*)/T_D(N_{d(m)}) \approx 3-4$.

A theoretical explanation of the anomalous dependence of the mobility on the iron concentration has been provided in the literature on the basis of the following models.

1. In one model it is assumed that a localized Wigner crystal of charged Fe^{3+} ions forms in the range $N_d \gg N_d^*$ (Refs. 5 and 6).

2. In the other model it is assumed that the conduction electrons are scattered resonantly by the *d* impurities in the form of the Fe^{2+} ions, the Breit–Wigner formula is used, and it is assumed that the Coulomb gap in the impurity density of states is the mechanism that weakens the resonant scattering.[7,8] Clearly, in spite of the weakening of such scattering because of the formation of the Coulomb gap, it represents an additional scattering mechanism and, in accordance with the Matthiessen rule, can only reduce the band carrier mobility.

In spite of its attractiveness, the model of formation of a three-dimensional Wigner crystal from the Fe^{3+} ions is not free of shortcomings which force us to approach critically the suitability of this model in a quantitative interpretation of the experimental data.[6] First of all, the experimental values of the temperature at which the mobility anomalies disappear ($T \geqslant 100$ K) are far too high for the ordering temperature of the Fe^{3+} ions. Secondly, simple estimates show that the average distance between charged donors is comparable with the screening radius. Obviously, under these conditions the screening weakens the Coulomb interaction between the iron ions Fe^{3+}; obviously, one cannot expect formation of a completely regular lattice.[9] There are also experimental data which are not explained by the model postulating formation of a Wigner crystal. For example, an increase in the iron concentration from $N_d \sim 1\times 10^{18}\ \text{cm}^{-3}$ to N_d^* increases—according to Ref. 1—the mobility by a factor of 2–3, but in this range we have $N_{Fe^{3+}} \approx N_d$ and it is meaningless to talk of the formation of a Wigner crystal if an allowance is made for the random nature of the iron impurity distribution. It should be pointed out that at present there is no direct confirmation of the Wigner crystallization model.

A common shortcoming of the theoretical treatments given in Refs. 5–8 is the absence of calculations carried out starting from first principles: the influence of the *d* level on the energy spectrum of the conduction electrons is ignored; the contribution of the various mechanisms to the transport relaxation time $\tau(E)$ is allowed for on the basis of the Matthiessen rule ($\tau^{-1} = \Sigma_i \tau_i^{-1}$). We shall show that these approximations and the use of the Breit–Wigner formula for the contribution of the resonant scattering (used in Refs. 7, 8, and 10) fail to provide a satisfactory description of the transport properties of semiconductors containing mixed-valence impurities.

We shall consider the scattering of the conduction electrons on mixed-valence iron impurities on the basis of the Anderson model[11] and we shall allow for the background scattering mechanisms (such as the scattering by charged impurities or defects); we shall also analyze the energy spectrum and the damping of the branches of the conduction electron spectrum and calculate the density of states allowing for the hybridization of the *d* level with the conduction band states. We shall find the transport relaxation time of carriers for the scattering by mixed-valence impurities and we shall show that the Matthiessen rule is inapplicable when one of the scattering mechanisms is resonant. We shall adopt a model with a single fitting parameter, which is the *s–d* hybridization constant, and explain qualitatively the experimentally observed[1-4] dependences $n_e(N_d)$, $\zeta_F(N_d)$, $\mu(N_d)$, as well as the temperature dependence $\mu(T)$ for different iron concentrations in $Hg_{1-x}Fe_xSe$ compounds.

2. HAMILTONIAN AND ELECTRON GREEN FUNCTIONS

The Fe^{2+} and Fe^{3+} ions in Hg–Fe–Se have the $3d^6$ and $3d^5$ electrons in the d shell. Using the Anderson model,[11] we shall assume that the Fe^{2+} ion corresponds to the state with two d electrons (d^2) and the Fe^{3+} ion to the d^1 state; the state d^0 corresponding to the Fe^{4+} ion is much lower on the energy scale than the states of the Fe^{2+} and Fe^{3+} ions and we can ignore it.[1)] Therefore, the d states of the iron impurity can be occupied only by one or two electrons and the $d^1 \rightleftarrows d^2$ transitions govern the d-resonance energy[11]

$$\Omega_0=\varepsilon_{21}=\varepsilon_d+u.$$

The Anderson Hamiltonian[11] for a system of electrons interacting with randomly distributed iron d impurities and a random field of defects V_{ss}, expressed in terms of the Hubbard operators $X^{\alpha\beta}$ representing changes in the atomic configuration,[12] is

$$\begin{gathered}
H=H_{0s}+H_{0d}+V_{sd}+V_{ss}, \qquad H_{0s}=\sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} a_{\mathbf{k}\sigma}{}^{+} a_{\mathbf{k}\sigma}, \\
H_{0d}=\sum_{j}\left[\varepsilon_d(X_j{}^{++}+X_j{}^{--})+(2\varepsilon_d+u)X_j{}^{22}\right], \\
V_{sd}=\frac{V_0}{V^{1/2}}\sum_{\mathbf{k}j\sigma}\left[\exp(i\mathbf{k}\mathbf{R}_j)\,a_{k\sigma}{}^{+}\sigma X^{-\sigma 2}+\text{H.c.}\right], \\
V_{ss}=\sum_{\mathbf{k}\mathbf{k}'\sigma} V_{\mathbf{k}\mathbf{k}'} a_{\mathbf{k}\sigma}{}^{+} a_{\mathbf{k}'\sigma}, \\
X_j{}^{\alpha\beta}X_j{}^{\gamma\delta}=\delta_{\beta\gamma}X_j{}^{\alpha\delta}, \quad X^{++}+X^{--}+X^{22}=1.
\end{gathered} \tag{1}$$

The state d_j^0 and the transitions to this state are ignored. Here, $\varepsilon_{\mathbf{k}}$ is the dispersion law of the conduction electrons and is assumed, for the sake of simplicity, to be isotropic and quadratic; V_0 is the s–d hybridization constant; V is the volume of the system; the symbols (+ , −) correspond to the d-electron spins (↓, ↑); $V_{\mathbf{k}\mathbf{k}'}$ is the matrix element of the interaction of the conduction electrons with charged centers and neutral defects (the phonon scattering mechanisms are included in V_{ss}).

We shall calculate the electron spectrum and the electron damping by writing down the equations of motion for the electron commutator Green functions[13]

$$\begin{aligned}
G_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}(E\pm i\varepsilon)&=\langle\!\langle a_{\mathbf{k}\sigma}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle_{E^\pm} \\
&=-i\int_0^\infty \langle[a_{\mathbf{k}\sigma}(t),\overset{+}{a}_{\mathbf{k}'\sigma'}]_+\rangle\exp(t(iE-\varepsilon)/\hbar)
\end{aligned} \tag{2}$$

up to the third order in respect of the s–d hybridization constant V_0.

Decoupling of equations of the second order with respect to V_0 (Ref. 12) allows us to find the renormalized spectrum of charge-carrier quasiparticles and corresponds to the "mean-field" approximation. Decoupling of equations of the third order in V_0 makes it possible to find correctly the damping of the branches of the hybridized spectrum and, consequently, the influence of fluctuations of the population of quasilocal centers on the carrier mobility. For example, in the third order in V_0, we have

$$\begin{aligned}
&(E-\varepsilon_{\mathbf{k}})G_{\mathbf{k}\mathbf{k}'}^{\uparrow\sigma'}=\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}+\frac{V_0}{V^{1/2}}\sum_j\exp(i\mathbf{k}\mathbf{R}_j)\langle\!\langle X_j{}^{-2}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle \\
&\quad+\sum_{\mathbf{q}}V_{\mathbf{k}\mathbf{q}}G_{\mathbf{k}\mathbf{q}'}^{\uparrow\sigma'}(E);\ (E-\Omega_0)\langle\!\langle X_j{}^{-2}|a_{\mathbf{k}'\sigma'}\rangle\!\rangle \\
&\quad=\frac{V_0}{V^{1/2}}\sum_{\mathbf{q}}\{\exp(-i\mathbf{q}\mathbf{R}_j)[\langle X_j{}^{--} \\
&\qquad+X_j{}^{22}\rangle G_{\mathbf{q}\mathbf{k}'}^{\uparrow\sigma'}+\langle\!\langle\{(\tilde{X}_j{}^{--}+\tilde{X}_j{}^{22})a_{\mathbf{q}\uparrow}-X_j{}^{-+}a_{\mathbf{q}\downarrow}{}^{+}\}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle\}, \\
&\quad\tilde{A}=A-\langle A\rangle;
\end{aligned} \tag{3}$$

$$\begin{aligned}
&(\check{E}-\varepsilon_{\mathbf{q}})\langle\!\langle(\bar{\tilde{X}}_j{}^{--}+\bar{X}_j{}^{22})a_{\mathbf{q}\uparrow}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle\approx\frac{V_0}{V^{1/2}}\exp(i\mathbf{q}\mathbf{R}_j)\langle\!\langle X_j{}^{-2}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle \\
&\qquad+\sum_{\mathbf{q}'}V_{\mathbf{q}\mathbf{q}'}\langle\!\langle(\tilde{X}_j{}^{--}+\tilde{X}_j{}^{22})\overset{+}{a}_{\mathbf{q}'\uparrow}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle, \\
&(E-\varepsilon_{\mathbf{q}})\langle\!\langle X_j{}^{-+}a_{\mathbf{q}\downarrow}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle\approx\frac{V_0}{V^{1/2}}\exp(i\mathbf{q}\mathbf{R}_j)(2-f_{\mathbf{q}}{}^{\uparrow})\langle\!\langle X_j{}^{-2}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle \\
&\qquad+\sum_{\mathbf{q}'}V_{\mathbf{q}\mathbf{q}'}\langle\!\langle X_j{}^{-+}a_{\mathbf{q}'\downarrow}|\overset{\pm}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle, \\
&f_{\mathbf{q}}{}^{\downarrow}=\frac{1}{2\pi i}\int dE\,f(E)\,[G_{\mathbf{k}\mathbf{k}}{}^{\downarrow\downarrow}(E^-)-G_{\mathbf{k}\mathbf{k}}{}^{\downarrow\downarrow}(E^+)].
\end{aligned} \tag{4}$$

The following decoupling is carried out above:

$$\langle\!\langle a_{\mathbf{q}\downarrow}{}^{+}a_{\mathbf{q}'\downarrow}X_j{}^{-2}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle\approx\delta_{\mathbf{q}\mathbf{q}'}f_{\mathbf{q}}{}^{\uparrow}\langle\!\langle X_j{}^{-2}|\overset{+}{a}_{\mathbf{k}'\sigma'}\rangle\!\rangle.$$

The solution of the system of equations (3) is as follows:

$$\begin{aligned}
&G_{\mathbf{k}\mathbf{k}'}^{\uparrow\sigma'}(E^\pm)=\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma'\sigma}\{E^\pm-\varepsilon_{\mathbf{k}}-\Sigma_b^\pm(E)-\xi[\mathrm{E}-\Omega_0-\Sigma_d{}^\pm(E)]^{-1}\}^{-1}, \\
&\qquad\Sigma_b^\pm=\sum_{\mathbf{q}}\langle V_{\mathbf{k}\mathbf{q}}V_{\mathbf{q}\mathbf{k}}\rangle G_{\mathbf{k}\mathbf{k}}{}^{\uparrow\uparrow}(E^\pm)=\Delta_b(E)\mp\frac{i}{2}\gamma_b(E), \\
&\Sigma_d^{(0)\pm}(E)=\frac{V_0{}^2}{V}\sum_{\mathbf{k}}(2-f_{\mathbf{k}})[E-\varepsilon_{\mathbf{k}}-\Sigma_b^\pm(E)]^{-1} \\
&\qquad=\Delta_d^{(0)}(E)\mp\frac{i}{2}\gamma_d{}^{(0)}(E), \\
&\quad\xi=N_dV_0{}^2\langle X_j{}^{--}+X_j{}^{22}\rangle.
\end{aligned} \tag{5}$$

A different selection of the charge states made in the nondegenerate Anderson model, $Fe^{2+}\to d^1$, $Fe^{3+}\to d^0$, gives the same expressions for the Green function after the substitutions $\Omega_0\to\varepsilon_d$, and $\xi\to N_dV_0^2(\langle X_j^{00}\rangle+\langle X_j^{--}\rangle)$, whereas in the expressions for $\Sigma_d(E)$ we have to replace the factor $2-f_{\mathbf{k}}$ with $1+f_{\mathbf{k}}$.

We shall introduce the notation $G_{\mathbf{k}\mathbf{k}}^{\sigma\sigma}(E\pm i\varepsilon)\equiv G_{\mathbf{k}\mathbf{k}}^{\pm}(E)$. An analysis of equations obtained of the fourth order in V_0 (we shall not give them here because they are cumbersome) shows that the expressions for $\Sigma_d^\pm$ become

$$\Sigma_d{}^\pm(E)=\frac{V_0{}^2}{V}\sum_{\mathbf{k}}(2-f_{\mathbf{k}})G_{\mathbf{k}\mathbf{k}}{}^\pm(E)=\Delta_d(E)\mp\frac{i}{2}\gamma_d(E). \tag{6}$$

The expression (6) is essential for self-consistent calculation of the quantities Δ_d and γ_d if an allowance is made for the influence of the correlation effects on the electron spectrum and on the structure of a d resonance.

3. INFLUENCE OF A *d* RESONANCE ON THE SPECTRUM AND DAMPING OF THE CONDUCTION ELECTRONS

The spectrum and damping of the conduction electrons are found in the usual way from the condition $\{G^{\pm}_{\mathbf{kk}}(E)\}^{-1}=0$. Estimates obtained from the electron mobility in Hg–Se and Hg–Fe–Se showed that $\gamma_b \sim 0.4$–0.6 meV and $\gamma_d \sim 0.1$–0.2 meV (in any case, the inequality $\gamma_d < \gamma_b$ is obeyed because otherwise the electron mobility in Hg–Fe–Se could only decrease relative to the mobility in Hg–Se). In the range of electron energies $E \sim \Omega_0 \sim \zeta_F \sim 230$ meV of interest to us we have $\gamma_b(E)/E \sim 10^{-2}$–$10^{-3}$. Therefore, ignoring the energy dependences $\Sigma_b^{\pm}(E)$ and $\Sigma_d^{\pm}(E)$, we find that the renormalized spectrum $E_{1,2}$ and the damping $\Gamma_{1,2}$ are described by

$$E^{\pm}_{1,2}=E_{1,2}\mp\frac{i}{2}\Gamma_{1,2},\qquad E'_{1,2}={}^1/_2(\varepsilon_{\mathbf{k}}+\Omega\mp R_1),$$

$$\Gamma_{1,2}=\gamma^{+}\mp\frac{\varepsilon_{\mathbf{k}}-\Omega}{R_1}\gamma^{-},\qquad \gamma^{\pm}={}^1/_2(\gamma_b\pm\gamma_d),\quad \Omega=\Omega_0+\Delta_d,$$

$$R_1=\{{}^1/_2[r_1+(r_1^2+r_2^2)^{1/2}]\}^{1/2},\quad r_1=(\varepsilon_{\mathbf{k}}-\Omega)^2-(\gamma^{-})^2+4\xi,$$

$$r_2=2(\varepsilon_{\mathbf{k}}-\Omega)\gamma^{-}. \tag{7}$$

If $|\varepsilon_{\mathbf{k}}-\Omega|\gg\gamma^{+},\xi$, it follows from Eq. (7) that

$$E_1\approx\begin{cases}\varepsilon_{\mathbf{k}}-\dfrac{\xi}{2|\varepsilon_{\mathbf{k}}-\Omega|}, & \Gamma_1\sim\gamma_b,\\[2ex] \Omega-\dfrac{\xi}{2|\varepsilon_{\mathbf{k}}-\Omega|}, & \Gamma_1\sim\gamma_d;\end{cases}$$

$$E_2\approx\begin{cases}\Omega+\dfrac{\xi}{2|\varepsilon_{\mathbf{k}}-\Omega|}, & \Gamma_2\sim\gamma_d,\quad \varepsilon_{\mathbf{k}}<\Omega,\\[2ex] \varepsilon_{\mathbf{k}}+\dfrac{\xi}{2|\varepsilon_{\mathbf{k}}-\Omega|}, & \Gamma_2\sim\gamma_b,\quad \varepsilon_{\mathbf{k}}>\Omega,\end{cases} \tag{8}$$

whereas if $\varepsilon_{\mathbf{k}}=\Omega$ and $\xi>(\gamma^{-}/4)^2$, we find that

$$E_{1,2}=\Omega\mp[\xi-(\gamma^{-}/4)^2]^{1/2},\quad \Gamma_{1,2}=\gamma^{+}.$$

Consequently, as a result of the *s–d* hybridization the energy spectrum of the band carriers splits into two branches (Fig. 1). This form of the spectrum is typical of the *s–d* systems.[12] It is clear from Fig. 1 that the damping of the renormalized branches of the spectrum does not exhibit a resonant peak in the vicinity of the *d* level (in contrast to the calculations based on perturbation theory of the spectrum and on the Breit–Wigner formula for the scattering[10]). Far from a resonance, if $|E-\Omega|\gg\xi^{1/2}$, the electron states, for each of the branches of the spectrum are *s*-like and their damping is governed by the background scattering mechanisms: $\Gamma_{1,2}(\varepsilon_{\mathbf{k}})\propto\gamma_b$. In the vicinity of a resonance the electron states are *d*-like and the values of $\Gamma_{1,2}(\varepsilon_{\mathbf{k}})$ are governed by the width of the *d* level.

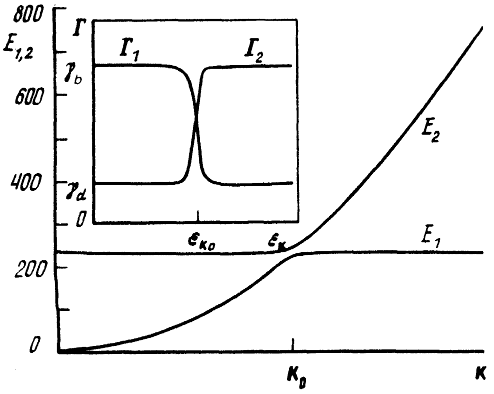

FIG. 1. Energy spectrum and collisional broadening of electron states ($\gamma_b = 0.56$ meV, $\gamma_d = 0.14$ meV, $N_d = 10^{19}$ cm^{-3}).

4. TRANSPORT RELAXATION TIME AND THE DENSITY OF THE CONDUCTION ELECTRON STATES IN Hg-Fe-Se

It is known that when the conduction electrons are scattered by impurities with a short-range potential, the differential scattering cross section is equal to the total cross section and the transport relaxation time $\tau(E)$ can be expressed in terms of the lifetime or in terms of the collisional width of one-particle states[10,14] $\Gamma(E)=\hbar/\tau(E)$, which is defined using the imaginary part of the mass operator $\Sigma^{\pm}(E)$:

$$\Sigma^{\pm}(E)=\Sigma_b^{\pm}(E)+\xi[E-\Omega_0-\Sigma_d^{\pm}(E)]^{-1}=\Delta(E)\mp\frac{i}{2}\Gamma(E). \tag{9}$$

Usually the transport relaxation time of the conduction electrons is calculated as follows:[15] the scattering amplitude is calculated for a conduction electron interacting with one impurity and then, assuming that all the *d* impurities make the same contribution, the result is multiplied by N_d and this gives $\tau^{-1}(E)$. It is assumed that introduction of *d* impurities into a crystal does not alter its electron spectrum. This approach is justified in the case of metals (noble metals with *d*-element impurities), because the *d* level in a metal is located far from the Fermi level; moreover, the *d*-level width γ_d is large and it is considerably greater than the collisional broadening of the conduction electrons due to the other scattering mechanims. If this approach is used to find the poles of the Green functions $G_{\mathbf{kk}}(E+i\varepsilon)$ in the limit $\varepsilon\to 0$, the result for $\Gamma_c(E)$ is

$$\Gamma_c(E)=\gamma_b+\xi\gamma_d[(E-\Omega)^2+(\gamma_d/2)^2]^{-1}. \tag{10}$$

The expression (10) corresponds to the Matthiessen rule for the total relaxation time of two scattering mechanisms and application of the Breit–Wigner formula for the resonant scattering by a *d* level. The function $\Gamma_c(E)$ has a sharp peak at $E=\Omega$; when the parameters have the values $N_d\sim 10^{19}$ cm^{-3} and $\gamma_d\sim 0.1$ meV, we obtain the ratio $\Gamma_c(E)/\Omega\sim 1$. Obviously, in this case we do not need a self-consistent allowance for the damping in the vicinity of a resonance and the approach is unsuitable for dealing with transport phenomena in Hg–Fe–Se.

An analysis of the energy spectrum of the conduction electrons shows that for all the values of $\varepsilon_{\mathbf{k}}$ the damping of the branches of the spectrum $\Gamma_{1,2}(\varepsilon_{\mathbf{k}})<\gamma_b$ (when $\gamma_b>\gamma_d$) varies monotonically and falls to γ_d in the vicinity of a resonance.

Since the poles of the Green function $G_{\mathbf{kk}}-(E)$ have a finite imaginary part, it follows that in order to find $\Gamma(E)$ in accordance with Eq. (13), we have to assume

$$E=E'\mp iE''=E'+\frac{i}{2}\Gamma(E').$$

Then, by equating to zero the real and imaginary parts of $\{G_{\mathbf{kk}}-(E)\}^{-1}$, we obtain the following equations

$$E'-\varepsilon_{\mathbf{k}}-\Delta_b(E')-\frac{\xi(E'-\Omega)}{(E'-\Omega)^2+{}^1/_4[\Gamma(E')-\gamma_d(E')]^2}=0, \tag{11}$$

$$\Gamma(E')-\gamma_b(E')+\frac{\xi[\Gamma(E')-\gamma_d(E')]}{(E'-\Omega)^2+{}^1/_4[\Gamma(E')-\gamma_d(E')]^2}=0, \quad (12)$$

where the quantities $\gamma_b(E')$, $\Delta_b(E')$, $\gamma_d(E')$, and $\Delta_d(E')$ occurring in Eq. (12) are themselves functions of $\Gamma(E)$, for example,

$$\Delta_b(E')=\mathrm{Re}\,\Sigma_b\left(E'+\frac{i}{2}\Gamma(E')\right), \qquad (13)$$
$$\gamma_b(E')={}^1/_2\,\mathrm{Im}\Sigma_b\left(E'+\frac{i}{2}\Gamma(E')\right).$$

However, in view of the smallness of the values of γ_d and γ_b compared with the energy of an electron being scattered, we shall ignore this dependence. Consequently, Eq. (12) transforms into a cubic equation for $\Gamma(E)$, which has a unique solution given by the expression

$$\Gamma(E')=(-q/2+Q^{1/2})^{1/3}-(q/2+Q^{1/2})^{1/3}+{}^1/_3(\gamma_b+2\gamma_d), \quad (14)$$

where

$$Q=(p/3)^3+(q/2)^2, \quad p=(\gamma^-)^2/3+4[\xi+(E'-\Omega)^2],$$
$$q={}^4/_3\gamma^-[\xi-2(E'-\Omega)^2-(\gamma^-)^2/18].$$

It follows from Eq. (14) that far from a resonance, where $(E'-\Omega)^2\gg\xi$, we have $\Gamma(E')\propto\gamma_b(E')$, whereas in the limit $|E-\Omega|\to 0$, we have $\Gamma(E')\to\gamma_d$. An approximate expression for $\Gamma(E')$, which gives correctly these asymptotes and reproduces to within ~0.1% the solution (14) in the intermediate range can be represented in the following form, which is valid in a wide range of the parameters γ_b, γ_d, and ξ:

$$\Gamma(E')\approx\gamma_b(E')\frac{(E'-\Omega)^2+\xi\gamma_d(E')/\gamma}{(E'-\Omega)^2+\xi}. \quad (15)$$

The quantity $\Gamma(E)$ has a minimum when $\gamma_d(E')<\gamma_b$, whereas $\tau(E')$ has a maximum at $E'=\Omega$ (curve 1 in Fig. 2). Such variation of $\Gamma(E')$ accounts for the dependence of the mobility $\mu(N_d)$ and of the Dingle temperature on the concentration of iron in Hg–Fe–Se by assuming that the Fermi level crosses the d level when the iron concentration is increased. It should be noted that neglect of the background scattering in the ground state and its inclusion in accordance with the Matthiessen rule gives a result which is qualitatively incorrect: in fact, if we assume that $\gamma_b=0$ in Eq. (12) and find its solution $\Gamma_r(E')$, and then deduce $\Gamma_M(E')=\Gamma_r(E')+\gamma_b(E')$ in accordance with the Matthiessen rule, we find that

$$\Gamma_M(E')\approx\gamma_b\frac{(E'-\Omega)^2+\xi(1+\gamma_d/\gamma_b)}{(E'-\Omega)^2+\xi}. \quad (16)$$

It is clear from Fig. 2 (curves 3) that $\Gamma_M(E')>\gamma_b$ throughout the investigated range and it has a maximum at $E'=\Omega$. However, if $\gamma_d>\gamma_b$, then $\Gamma(E')$ has a resonance peak at $E'=\Omega$ (curve 2 in Fig. 2), but the value of the amplitude of the peak differs from that calculated using the Matthiessen rule.

We have thus demonstrated that both the Matthiessen rule and the approach based on the use of the Breit–Wigner formula are unsuitable for the calculation of the transport relaxation time of carriers if one of the scattering mechanisms is of resonant nature. It should be noted that actually the dependence $\Gamma(E)$ in the vicinity of a d resonance is more complex: for example, if we allow for the electron correlations (Kondo effect), we find that $\Omega=\Omega_0+\Delta_d(E,:\Gamma,:T)$ is a function of the electron energy, of $\Gamma(E)$, and of temperature. However, an analysis of this effect together with an allowance for the expressions in Eq. (13) in the solution of Eq. (12) should be investigated independently.

Using Eq. (9), we obtain the density of states of the conduction electrons $g(E)$;

$$g(E)=\frac{1}{V}\sum_{\mathbf{k}}S(E,\varepsilon_{\mathbf{k}})=\frac{Qm_e^{3/2}}{2^{1/2}\pi^2\hbar^3},$$
$$S(E,\varepsilon_{\mathbf{k}})=\frac{1}{2\pi i}[G_{\mathbf{kk}}^-(E)-G_{\mathbf{kk}}^+(E)], \qquad (17)$$
$$Q=\{{}^1/_2[\tilde{E}+(\tilde{E}^2+(\Gamma/2)^2)^{1/2}]\}^{1/2},$$

where

$$\tilde{E}=E-\Delta_b(E)-\xi(E-\Omega)[(E-\Omega)^2+(\gamma_d/2)^2]^{-1}.$$

The dependence $g(E)$ is shown in Fig. 3. A maximum of $g(E)$ occurs at $E=\Omega-\gamma_d/2$ and its amplitude is

$$g_m\approx g_0(\Omega)[1+N_d/3\pi g_0(\Omega)\Omega]^{1/2},$$

whereas the width of the maximum is of the order of γ_d. We shall now estimate the number of "excess" electrons which can be placed in the region where states are pumped at $T=0$

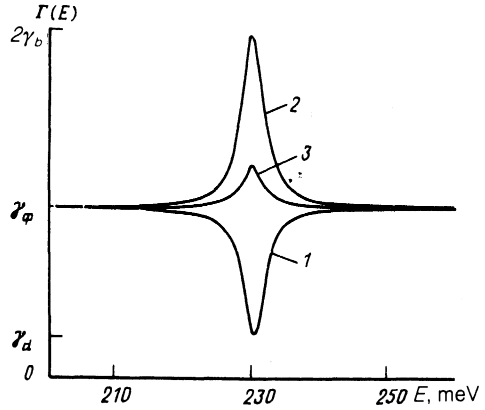

FIG. 2. Energy dependences of the collisional broadening of the electron states $\Gamma(E)$: 1) $\gamma_b=0.56$ meV, $\gamma_d=0.14$ meV; 2) $\gamma_b=0.56$ meV, $\gamma_d=0.14$ meV; 3) $\gamma_b=0.56$ meV, $\gamma_d=1.1$ meV ($N_d=10^{19}$ cm^{-3}).

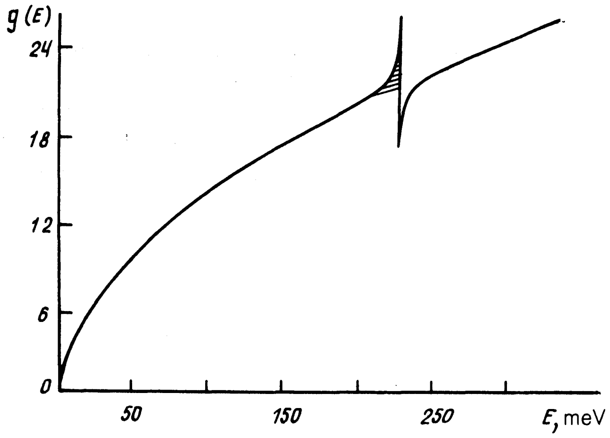

FIG. 3. Density of states in the conduction band (plotted for the same parameters as in Fig. 1).

(shown shaded in Fig. 3). We shall do this by representing n_e in the form

$$n_e=\int dE\, f(E)N(E)$$

$$=n_e^0+\Delta n_e=2\left\{\int_0^\Omega dE\, g_0(E)+\int_0^\Omega dE[g(E)-g_0(E)]\right\}. \quad (18)$$

If $N_d\sim 10^{19}$ cm^{-3} and $\gamma_d\sim 0.1$ meV, we find that $\Delta n_e\sim 2[g_m-g_0(\Omega)]\gamma_d\sim 10^{15}$ cm^{-3}. Since $n_e\sim 5\times 10^{18}$ cm^{-3}, it follows that $\Delta n_e/n_e \ll 1$ applies throughout the full range of the concentrations N_d and the expression

$$n_e\approx N_d^*(\zeta_F/\Omega)^{3/2} \quad (19)$$

determines the relationship between the electron density n_e and the Fermi energy ζ_F for all the values of N_d.

5. CALCULATION OF THE ELECTRICAL CONDUCTIVITY OF Hg-Fe-Se

We shall calculate the electrical conductivity of the investigated system of compounds by applying the Kubo formula[16]

$$\sigma_{zz}=-\frac{\pi\hbar e^2}{V}\int dE\frac{\partial f}{\partial E}J_{zz},$$

$$J_{zz}=\mathrm{Tr}\,\langle v_z\delta(E-H)v_z\delta(E-H)\rangle_{sc}. \quad (20)$$

Using the approximation[17,16]

$$J_{zz}=\mathrm{Tr}\, v_z\langle\delta(E-H)\rangle_{sc}v_z\langle\delta(E-H)\rangle_{sc}$$

$$=\frac{2}{3m_e}\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}\{S(E,\varepsilon_{\mathbf{k}})\}^2, \quad (21)$$

we find that

$$\sigma_{zz}=-\frac{4e^2}{3m_e}\int dE\frac{\partial f}{\partial E}\tau(E)g(E)[\tilde{E}^2+(\Gamma/2)^2]^{1/2}. \quad (22)$$

Here,

$$\tau(E)=\frac{\hbar}{\Gamma(E)}\left\{1-\frac{\Gamma^2}{16[\tilde{E}^2+(\Gamma/2)^2]^{1/2}Q^2}\right\}.$$

The expression (22) allows not only for the change in the spectrum and the density of states of the conduction electrons because of the s–d hybridization, but also for collisional broadening of the electron states due to the background scattering mechanisms and due to the interaction with the d-electron iron impurities. The second term in the braces in the above expression for $\tau(E)$ is usually small; it must be allowed for if the Fermi level lies in the region of "exhaustion" of the states and $\tilde{E}\leqslant\Gamma(E)$ is obeyed.

In an analysis of the change in the mobility $\mu(N_d)=\sigma_{zz}/|e|n_e$, considered as a function of the iron impurity concentration, we shall determine $\zeta_F(N_d)$ from the electrical neutrality equation

$$n_e=\int dE\, f(E)N(E)=N_{\mathrm{Fe}^{3+}}=2n_1N_d, \qquad N_d=N_{\mathrm{Fe}^{3+}}+N_{\mathrm{Fe}^{2+}}. \quad (23)$$

Here,

$$n_1=\langle X_j^{--}\rangle=\langle X_j^{++}\rangle, \quad n_2=\langle X_j^{22}\rangle, \quad n_1+n_2=1. \quad (24)$$

The quantity n_2 is found in the usual way:[12]

$$n_2=\langle X_j^{2-}X_j^{-2}\rangle$$

$$=\frac{1}{2\pi i}\int dE\, f(E)\{\langle\langle X_j^{-2}|X_j^{2-}\rangle\rangle_{E^-}-\langle\langle X_j^{-2}|X_j^{2-}\rangle\rangle_{E^+}\}. \quad (25)$$

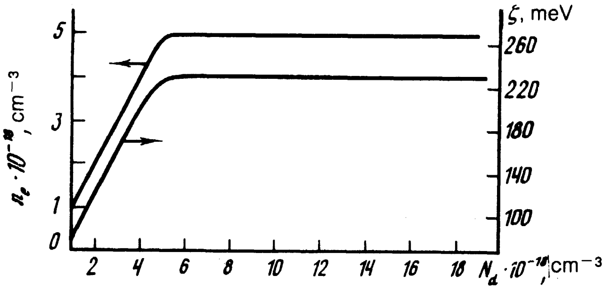

FIG. 4. Dependences of the conduction electron density and of the Fermi energy on the concentration of iron in Hg-Fe-Se (T = 4.2 K).

Decoupling the system of equations for the Green functions $\langle\langle X_j^{-2}|X_j^{2-}\rangle\rangle$, we find that in the second order in the s–d hybridization constant, the result is

$$\langle\langle X_j^{-2}|X_j^{2-}\rangle\rangle_E$$

$$=\frac{\langle X^{--}+X^{22}\rangle}{E-\Omega_0-\Sigma_d(E)}\left\{1-\frac{V_0}{V^{1/2}}\sum_{\mathbf{k}}\frac{\langle X_j^{2+}a_{\mathbf{k}\downarrow}\rangle\exp(-i\mathbf{k}\mathbf{R}_j)}{(E-\varepsilon_{\mathbf{k}})\langle X_j^{--}+X_j^{22}\rangle}\right.$$

$$\left.+[E-\Omega_0-\Sigma_d(E)]^{-1}\frac{V_0^2}{V}\sum_{\mathbf{k}}G_{\mathbf{k}\mathbf{k}}(E)\right\}. \quad (26)$$

In view of the smallness of V_0, we shall neglect the second and third terms in the braces in Eq. (26). This approximation is equivalent to an allowance solely for the broadening of the d level because of hybridization with the conduction band. Substituting Eq. (26) into Eq. (25) and allowing for Eq. (19), we obtain

$$N_d\approx N_d^*(\zeta_F/\hbar\Omega)^{3/2}\{1+{}^1/_2\exp[\beta(\zeta_F-\Omega)]\}, \quad T\gg\gamma_d.$$

$$N_d\approx N_d^*(\zeta_F/\hbar\Omega)^{3/2}\frac{{}^3/_2-(1/\pi)\,\mathrm{arctg}[2(\zeta_F-\Omega)/\gamma_d]}{1-(2/\pi)\,\mathrm{arctg}[2(\zeta_F-\Omega)/\gamma_d]}, \quad T\ll\gamma_d. \quad (27)$$

The dependences of the Fermi energy $\zeta_F(N_d)$ and of the conduction electron density on the iron concentration (Fig. 4) demonstrate stabilization of the Fermi level ζ_F and of the conduction electron density $n_e(N_d)$ in the vicinity of a resonant donor level if $N_d>N_d^*$, in accordance with Refs. 1, 3, and 4.

It is clear from Fig. 5 that at iron concentrations N_d well below N_d^* the conduction electron mobility is governed

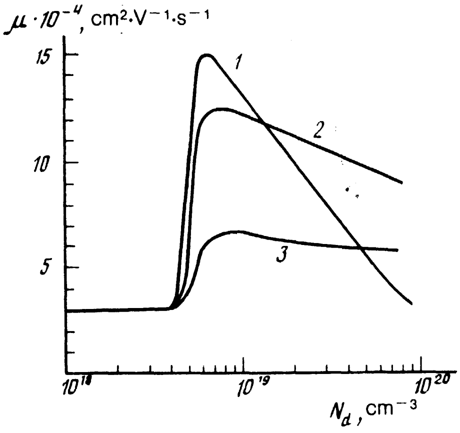

FIG. 5. Dependences of the conduction electron mobility on the concentration of iron (γ_b = 0.64 meV, γ_d = 0.31 meV), plotted for different temperatures: 1) T = 1 K; 2) T = 4 K; 3) T = 25 K.

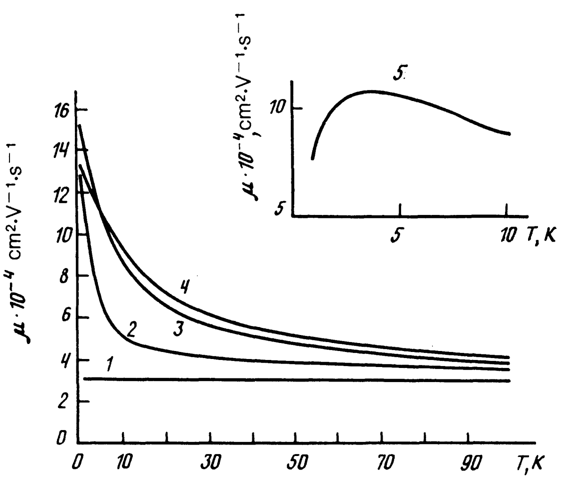

FIG. 6. Temperature dependences of the conduction electron mobility plotted for different values of the impurity concentration: 1) $N_d = 3\times10^{18}$ cm^{-3}; 2) 5×10^{18} cm^{-3}; 3) 6×10^{18} cm^{-3}; 4) 13×10^{18} cm^{-3}; 5) 3×10^{19} cm^{-3}.

by the background scattering mechanisms. If $N_d > N_d^*$, the maximum mobility is given by $\mu_{\max}(N_d) = \mu_b\gamma_b/\gamma_d$. An increase in the temperature reduces the mobility $\mu_{\max}(N_d)$ because of an increase in the number of electrons which contribute to the conductivity and whose transport relaxation time is governed by the background scattering mechanisms. This factor is also responsible for the reduction in the electron mobility on increase in temperature observed for different values of N_d. The temperature dependences of the mobility $\mu(T)$ (for N_d = const) are nonmonotonic (inset in Fig. 6). The presence of a maximum of the dependence $\mu(T)$ is in this case due to the fact that if $\zeta_F > \Omega$, we reach the region of "exhaustion" of the states (i.e., the region of a minimum of the density of states). An increase in temperature increases the contribution to the mobility made by those electrons whose transport relaxation time is governed by the d-level width, so that the mobility rises; a further increase in temperature results in predominance of those electrons whose mobility is determined by the background scattering mechanisms, which reduces the carrier mobility.

The model based on the hypothesis of the formation of a Wigner crystal from the Fe^{3+} ions can predict only a monotonic rise of the mobility as a result of cooling with saturation in the limit $T\to0$. On the other hand, an allowance for the valence fluctuations in the hybridized Anderson model yields a nonmonotonic temperature dependence $\mu(T)$, which is generally speaking observed when the mobility is measured at low temperatures such as $T = 0.04$ K, 1.5 K (Ref. 18), or $T = 4.2$ K (Ref. 1).

It follows from our model that we can explain the experimentally observed dependences $\mu(N_d)$, $\zeta(N_d)$, and $n_e(N_d)$, and predict a new "anomaly" in the dependence $\mu(T)$. However, the final conclusion in favor of one of the models can be made only after additional low-temperature measurements of $\mu(T)$ at $T\sim0.1$–10 K for $N_d \sim (2–10)\times10^{19}$ cm^{-3}.

CONCLUSIONS

Calculations of the energy spectrum and damping and of the conduction electrons, and a self-consistent calculation of the transport relaxation time of these electrons, carried out using the Anderson model for mixed-valence impurities, provide a satisfactory explanation of the "anomalous" behavior of the electron mobility in Hg–Fe–Se without invoking the hypothesis of formation of a Wigner crystal from the Fe^{3+} ions at low temperatures.

It should be stressed that the Hg–Fe–Se compounds represent a unique object for the investigation of the influence of the correlation effects in the scattering of the conduction electrons by the d-electron iron impurities (Kondo effect) on the kinetic and thermodynamic characteristics of these compounds under conditions when the Fermi level crosses a resonant level. A radical change in the energy spectrum of the band carriers at energies close to the d-level energy, and also interference between a d resonance with a Suhl–Abrikosov resonance, can give rise to a wide range of interesting physical characteristics of the low-temperature transport and thermodynamic properties of these compounds.

We ignored the influence of the correlation effects in calculation of the physical quantities because of the smallness of the constant V_0 and because the density of states is much lower in Hg–Fe–Se than in metals. However, it is obvious that this approximation may be insufficient at temperatures $T < 1$ K. Since

$$\Delta_d(\zeta_F) \sim -\frac{2}{3}\gamma_d/\pi[\ln(T/\zeta_F - 1)],$$

it follows that if the temperature is $T \leqslant 1$ K, we have $\gamma_d < \Delta_d$ and, consequently, we can expect the characteristics associated with the Kondo effect to be manifested in the transport coefficients of Hg–Fe–Se at temperatures $T < 1$ K. We shall therefore assume that above all it is necessary to investigate the structure of a d resonance under the conditions when the Fermi level crosses a resonant level and to allow for the energy dependences of the parameters $\gamma_b(E)$, $\gamma_d(E)$, and $\Delta_d(E)$ in calculation of both the energy spectrum and of the damping of the branches of the spectrum.

1) A different selection, Fe$^{1+}\to d^2$, Fe$^{2+}\to d^1$, Fe$^{3+}\to d^0$, gives rise to the same physical results in the calculations.

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