Inelastic electron scattering in HgSe:Fe crystals

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We present the results of measurements of the electrical conductivity and the longitudinal Nernst–Ettingshausen (NE) thermomagnetic effect in eight HgSe:Fe crystals with an iron content as high as 4×10^{20} cm^{-3}. The data are used to find the dependence of the effective Lorenz number on the temperature and on the iron-impurity concentration. These are found to be "anomalous." We develop a theory that provides a qualitative interpretation of these anomalies. We also propose a new mechanism for the inelastic electron scattering on static defects, the bivalent iron ions substituting for mercury ions in the HgSe lattice. We show that the anomalous decrease in the Lorenz number as the temperature increases is caused primarily by just this inelastic scattering of the band electrons accompanied by a charge transfer involving bivalent and trivalent iron ions, i.e., a change in their configuration inside a short-range order cluster in the system of trivalent iron ions. © *1994 American Institute of Physics.*

1. INTRODUCTION

Gapless HgSe crystals alloyed with iron exhibit several remarkable electronic properties, which it has been possible to explain by the short-range correlation model.[1–4] It has been shown that the experimentally observed "anomalous" dependence of some electronic characteristics (the concentration and mobility of band electrons, the Dingle temperature, etc.) on the concentration of iron substitution impurities and the sample temperature are caused by the ordering of the charged donors Fe^{3+} due to their Coulomb repulsion. The repulsion tends to arrange the positive charges on those iron atoms that are farthest from one another. As a result electron scattering on these charges weakens, leading to an increase in electron mobility. Our analysis[4] showed that at low temperatures and low iron concentrations, $(N_{\mathrm{Fe}}-N_{\mathrm{Fe}^3})N_{\mathrm{Fe}}\ll 1$, when the ion–ion correlations are weak, the system of Fe^{3+} ions resembles a low-density gas. For higher ion concentrations there remains a rather large space for electron redistribution in the Fe^{2+}–Fe^{3+} system of ions, and Coulomb repulsion between the charged donors Fe^{3+} leads to strong correlations in their positions. Thus, when the iron concentration N_{Fe} is high, the system of Fe^{3+} ions resembles a Coulomb liquid in its properties.

Analysis of thermomagnetic phenomena suggests that in a system of charged impurities the Coulomb correlations greatly affect the scattering of the band charge carriers. It has been established that as the Coulomb correlations become stronger, the dependence of the electron relaxation time τ on the energy ε changes. Such behavior of τ as a function of ε in the vicinity of the Fermi level strongly affects the concentration dependence of the thermomagnetic coefficients: the Nernst–Ettingshausen (NE) effects change sign.

Thus, according to the correlation model, as the concentration of iron substitution impurities increases, we must expect the electron scattering on these impurities to weaken and, as a result, the electron mobility μ to increase. In experiments, however, a mobility μ increasing with N_{Fe} in the concentration range $N_{\mathrm{Fe}}\leqslant 2\times10^{19}\,\mathrm{cm}^{-3}$ is replaced by a decreasing μ as the iron concentration grows up to roughly 10^{21} cm^{-3}. In Ref. 3 we showed that the decrease in mobility in HgSe:Fe crystals as the iron content grows is due to alloy scattering caused by the difference between the potentials of the Hg^{2+} and Fe^{2+} ions. The model proposed in Refs. 2–4 seemed able to describe all the features of the kinetic coefficients related to the presence of impurities with mixed valence in the HgSe:Fe system. But analysis of the temperature and concentration dependence of the thermomagnetic effects has shown that the short-range correlations model can explain neither the experimentally observed behavior of the longitudinal NE coefficient $\Delta\alpha=|\alpha(\alpha)|-|\alpha(0)|$ nor the change in the Wiedemann–Franz law $L=\lambda/\sigma T$, where λ and σ are the electron thermal and electrical conductivities, respectively. The quantity L, the Lorenz number, depends on many factors: temperature, charge carrier concentration, nature and mechanism of carrier scattering, etc. It is known that by studying the changes in the Lorenz number we can extract information about several physical characteristics of the crystal under investigation and, what is especially important, about the mechanism of scattering of the charge carriers.

Below we show that the observed features of the dependence of L on the substitution-impurity content in HgSe:Fe crystals and on the crystal temperature are due to the channel of inelastic band electron scattering, which, we believe, has never been considered by researchers. This new scattering mechanism operates only in a system of impurities with different valences (in our case iron in HgSe). Inelastic scattering of band electrons on iron impurities (note that the scattering is on impurities and not on phonons!) can be pictured as follows.

Let us examine a finite cluster, i.e., a region of short-range order containing donors of two types: Fe^{2+}, which are neutral in the lattice, and Fe^{3+}, which are charged. When a band electron collides with a neutral ion, it can transfer to the latter an amount of energy sufficient for the transition of a d-electron from an Fe^{2+} ion to an Fe^{3+} ion, whose energy is higher. This charge exchange between Fe^{2+} and Fe^{3+} ions is

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TABLE I.

Sample	$N_{Fe}\times10^{-19}$, cm^{-3}	$n\times10^{-18}$, cm^{-3}	$\mu\times10^{-4}$, cm^2 V^{-1} s^{-1}	H, kOe	$\omega\tau$
1	0	2.4	2.25	7.6	1.7
2	0	4.7	1.60	–	–
3	0.3	4.0	2.90	–	–
4	0.1	3.0	2.80	4.5	1.3
5	0.5	4.8	5.10	4.5	1.8
6	1.0	4.64	9.90	3.6	1.2
7	5.0	4.81	5.95	3.6	1.3
8	40.0	6.2	2.50	3.6	0.7

obviously a consequence of a band electron scattering inelastically on a neutral Fe^{2+} center. This, naturally, violates the short-range order in the arrangement of charged Fe^{3+} donors. We repeat that such a mechanism for the inelastic scattering of electrons on static defects has been overlooked before not only in gapless semiconductors but in other semiconducting compounds as well.

Inelastic electron scattering in HgSe:Fe crystals may also occur in another way: the scattered electron transfers to a d-electron sufficient energy for the d-electron to climb to a higher level. Such intracenter transitions were observed in II–VI semiconductors with wide energy gaps within which the levels of the transition elements lie. For instance, for an iron impurity in CdTe the intracenter transitions correspond to temperatures of 11, 21, and 42 K (see Ref. 5). This inelastic scattering mechanism differs from the one described above in that the d-electron remains inside the given impurity atom, i.e., does not go to another impurity atom; hence, the short-range order in the system of Fe^{3+} donors is not violated.

2. RESULTS OF MEASUREMENTS

We measured the electrical conductivity and the longitudinal NE effect in eight HgSe:Fe crystals with iron content ranging from 0 to 4×10^{20} cm^{-3} in a temperature interval from 4.2 to 100 K. Table I lists the main characteristics of the samples: the iron content N_{Fe} and the electron number density n and the electron mobility μ at 4.2 K, and the parameter $\omega\tau$, where ω is the cyclotron frequency.

The temperature dependence of the coefficient of the longitudinal NE effect, $\Delta\alpha$, for the HgSe:Fe and HgSe samples studied is depicted in Fig. 1. Clearly, introducing iron impurities into HgSe causes a marked change in the temperature dependence of $\Delta\alpha$. First, the effect proves to be positive at low temperatures, which, as shown in Ref. 6, is due to electron scattering on the correlated system of charged Fe^{3+} centers. Second, the $\Delta\alpha$ vs T curves exhibit a peak at 30 K, whose height depends to a large extent on the iron content in the sample. The nonmonotone nature of the temperature dependence was found to be the most pronounced in sample 6, in which the system of Fe^{3+} ions was the most ordered. As the temperature grows from 30 K to roughly 100 K, the value of the longitudinal NE effect in HgSe:Fe monotonically decreases, in contrast to its behavior with HgSe samples.

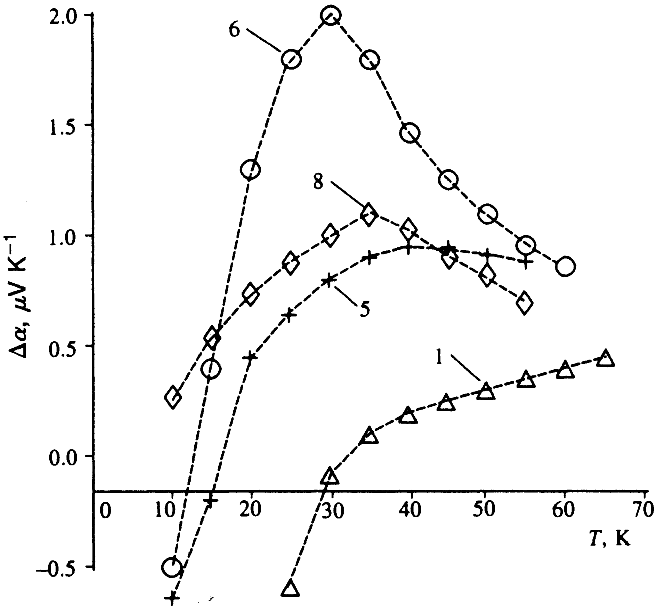

FIG. 1. Temperature dependence of the longitudinal NE effect $\Delta\alpha(H)$. The samples are numbered 1, 5, 6, and 8.

Figure 2 depicts the magnetic field dependence of the dimensionless field of the longitudinal NE effect in the samples, $\varepsilon_x = e\Delta\alpha/k_0$, where k_0 is the Boltzmann constant. As is well known, the thermoelectric power of a degenerate electron gas in a classically strong magnetic field becomes saturated and independent of the mechanism of scattering of the band carriers. However, the experimental data suggest that only the most heavily iron-alloyed sample 8 can guarantee that $|\alpha(H)|$ becomes saturated. For samples with lower iron content the cures of ε_x vs H exhibit a peak at a certain field strength $H = H_{\max}$. Such nonmonotone behavior of the dimensionless NE field ε_x as a function of the magnetic field strength is unexpected and requires additional study. Here we

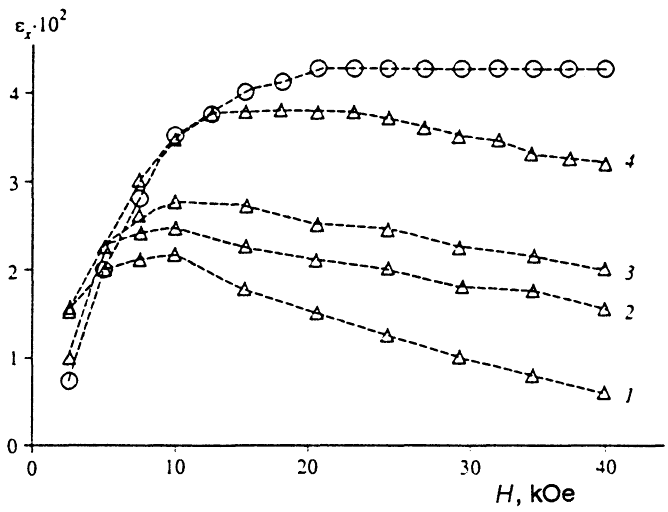

FIG. 2. The dimensionless field of the longitudinal NE effect as a function of the magnetic field strength for sample 8 (○) at T=58 K, and sample 6 (△) at 18 K (curve *1*), 25 K (curve *2*), 42 K (curve *3*), and 64 K (curve *4*).

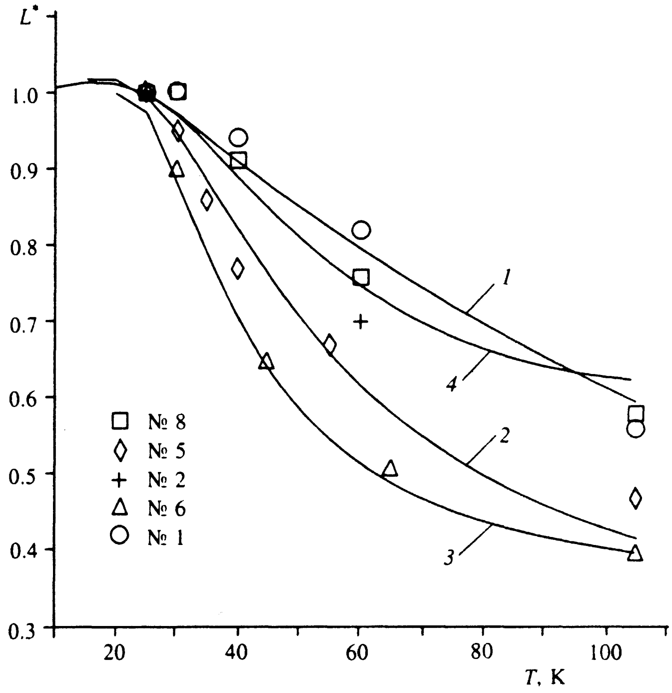

FIG. 3. Temperature dependence of the reduced Lorenz number L^* for HgSe and HgSe:Fe samples. The samples are numbered 1, 2, 5, 6, and 8. The solid curves correspond to the results of calculations: curve *1*, $N_{\text{Fe}}=0$; curve *2*, $N_{\text{Fe}}<4.5\times10^{18}$ cm^{-3}; curve *3*, $N_{\text{Fe}}=10^{19}$ cm^{-3}; and curve *4*, $N_{\text{Fe}}=4\times10^{20}$ cm^{-3}.

only note that in our samples $\varepsilon_x(H)$ was found to decrease only slightly for $H>H_{\max}$ in the range of fairly high temperatures. Hence, in weak magnetic fields, $H<H_{\max}$, the negative contribution to the longitudinal NE effect can be ignored. Further analysis of the experimental data on the longitudinal NE effect is done with a formula for $\Delta\alpha(H)$ valid for a degenerate electron gas and an arbitrary inelastic scattering mechanism:[5,7]

$$\Delta\alpha(H)=\left(\frac{\mu L}{cL_0}\right)^2\Delta\alpha_\infty H^2\left[1+\left(\frac{\mu L}{cL_0}\right)^2\right]^{-1}, \tag{1}$$

where $L_0=\frac{1}{3}\pi^2(k_0/e)^2$ is the Lorenz number for elastic electron scattering, L is the Lorenz number in the presence of inelastic scattering mechanisms ($L\leqslant L_0$), and $\Delta\alpha_\infty=(|\alpha_\infty|-|\alpha_0|)$ is the change in the thermoelectric power brought on by a strong magnetic field.

Equation (1) implies that $H^2/\Delta\alpha(H)$ is a linear function of H^2,

$$\frac{H^2}{\Delta\alpha(H)}=\frac{1}{A}+\frac{B}{A}H^2, \tag{2}$$

with a slope of $(\Delta\alpha_\infty)^{-1}=B/A$, where $A^{-1}=[(\mu L/cL_0)^2\Delta\alpha_\infty]^{-1}$ is the intercept of the straight line (2) on the ordinate. Analyzing Eq. (2), we find the value of the reduced Lorenz number:

$$L^*\equiv\frac{L}{L_0}=\frac{c}{\mu}\left(\frac{A}{\Delta\alpha_\infty}\right)^{1/2}. \tag{3}$$

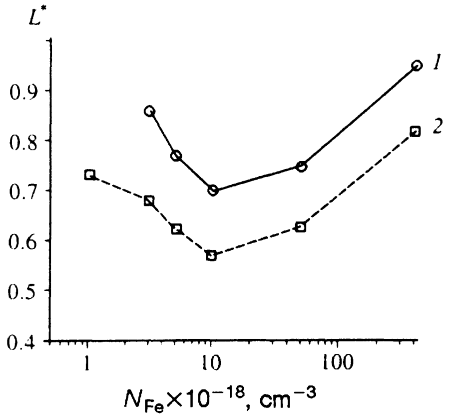

FIG. 4. The reduced Lorenz number L^* for HgSe:Fe as a function of iron-impurity concentration at a fixed temperature: curve *1*, $T=40$ K; and curve *2*, $T=60$ K.

The temperature curves of the reduced Lorenz number for HgSe and HgSe:Fe crystals are shown in Fig 3. Clearly, L^* is a nonmonotone function of the iron content in HgSe. An increase in the iron-impurity concentration up to $N_{\text{Fe}}<1.10^{19}$ cm^{-3} at a fixed temperature reduces the Lorenz number. However, with a further increase in iron content in HgSe:Fe the Lorenz number begins to grow, approaching the value of L^* for the HgSe sample. This is vividly shown in Fig. 4, which illustrates the N_{Fe}-dependence of the reduced Lorenz number L^* at $T=40$ K and 60 K. Note that the Lorenz number varies with temperature at values of $N_{\text{Fe}}<N^*_{\text{Fe}}\approx4.5\times10^{18}$ cm^{-3} such that the iron ions are only in one charge state, Fe^{3+}.

This behavior of L^* is unexpected, Indeed, the deviation of L^* from unity (more precisely, the decrease in L^*) usually indicates that the inelastic scattering of band electrons is beginning to play a more prominent role. But in our case the decrease in L^* occurs not as the temperature rises, when the importance of scattering on phonons increases, but as iron content rises. Thus, we are prompted to believe that the possible cause of inelastic electron scattering is iron ions, which are in different charge states, depending on their concentration in HgSe:Fe: for $N_{\text{Fe}}<N^*_{\text{Fe}}$ there are only Fe^{3+} ions, while for $N_{\text{Fe}}>N^*_{\text{Fe}}$ the system consists of Fe^{2+} and Fe^{3+} ions.

Below we analyze quantitatively the temperature dependence of the Lorenz number L^* for HgSe:Fe crystals with different iron content. In our calculations we allow for elastic electron scattering on the correlated system of iron ions Fe^{3+}, acoustic phonons, and the alloy potential and also for inelastic scattering on iron impurities with mixed valence, which proved to be important.

3. ELECTRON RELAXATION TIME IN HgSe:Fe

According to the model suggested in Ref. 2, the system of ions in HgSe:Fe can be considered a binary alloy consisting of charged Fe^{3+} centers and Fe^{2+} centers neutral in the lattice. The longitudinal momentum of the electrons changes owing to their interaction with these centers. If we operate in the Born approximation, among the factors that contribute to the reciprocal relaxation time τ_p^{-1} of the electrons is the scattering on correlated Fe^{3+} centers (τ_c^{-1}) and on disordered Fe^{2+}–Fe^{3+} and Fe^{2+}–Fe^{2+} pairs (τ_a^{-1}). In addition to these mechanisms of relaxation of the electron longitudinal momentum, we consider the inelastic scattering of band electrons on neutral centers, in which a d-electron goes from a Fe^{2+} ion to a Fe^{3+} ion (charge exchange between ions), and intracenter transitions from the d-level of a Fe^{3+} ion to higher energy levels (τ_d^{-1}). Thus, the total relaxation time τ_p^{-1} for the combined scattering can be written as

$$\tau_p^{-1}=\tau_c^{-1}+\tau_a^{-1}+\tau_d^{-1}. \tag{4}$$

Let us examine each contribution to (4) separately. In our calculations we allow for the fact that the conduction band of HgSe is not parabolic. According to Ref. 3, for $\tau_{ca}^{-1}=\tau_c^{-1}+\tau_a^{-1}$ we have

$$\tau_{ca}^{-1}=\frac{4\varepsilon_B(\varepsilon_g+2\varepsilon_F)}{3\pi\varepsilon_g\hbar}\left\{\Phi_c+\Lambda\left[\left(\frac{N_0}{N_+}\right)^{1/2}\Phi_{+0}+\frac{\Lambda N_0}{2N_+}\right]\right\}. \tag{5}$$

Here ε_B is the Bohr energy, N_0 and N_+ are the concentrations of the neutral Fe^{2+} and charged Fe^{3+} impurity centers, ε_F is the Fermi energy, ε_g is the energy gap between the Γ_6 and Γ_8 states, and

$$\Phi_c(k_F)=2\int_0^1\frac{x^3S(2k_Fx)}{x^2+b_s^{-2}}dx,\quad \Phi_{+0}(k_F)=1-\frac{\ln(1+b_s^2)}{b_s^2}, \tag{6}$$

with $b_s=2k_Fr_s$, and r_s the screening radius. The dimensionless parameter Λ is the ratio of the coupling constants for the interaction of conduction electrons with neutral Fe^{2+} and charged Fe^{3+} centers. According to our estimate,[3] $\Lambda\simeq0.1$–0.2, which corresponds to a value of $\Delta U=(0.32$–$0.35)$ eV of the potential on which alloy scattering occurs.

The structure factor $S(q)$ in (6) describes Coulomb correlations in the system of charged impurities. If the set of scattering centers is completely disordered, $S=1$. Since the structure and properties of the system considered are determined primarily by the rapidly varying repulsive part of the ion–ion interaction potential, we can approximate it with sufficient accuracy by the hard-sphere potential.[2] Here the packing factor, which determines the degree of correlation in the arrangement of the hard spheres, can be expressed in terms of the diameter d of a hard sphere as

$$\eta=\tfrac{1}{6}\pi d^3N_+. \tag{7}$$

For a strongly correlated liquid, $\eta=0.45$, while a weakly correlated gas corresponds to the inequality $\eta\ll1$.

In the hard-sphere approximation, the distribution function describing the spatial arrangement of particles with potential $U(r)$ depends only on the particle number density in the system and does not explicitly contain the temperature. When analyzing the temperature dependence of the kinetic coefficients, we must in some manner allow for the temperature variations in the correlations in the system of charged Fe^{3+} centers. There are several ways to do this. For instance, when the system is moderately dense, the total distribution function characterizing the correlations between two atoms can be represented in the form of the Mayer function, which depends explicitly on temperature.[2] This approach, however, proves to be too difficult when thermomagnetic coefficients must be calculated. The alternative and simpler method of calculation consists in using the soft-sphere approximation, which enables the temperature variation of the diameter of the correlation sphere to be taken into account.[4] Within this approximation scheme the temperature variation of the diameter d of the sphere can be obtained by expanding the potential $U(r)$ responsible for the correlation properties of the system of Fe^{3+} ions near the point r_{cr} at which the potential vanishes. Using the condition $\Delta U(r)\leq\frac{3}{2}k_0T$ and limiting our expansion to terms quadratic in the displacement Δr, we can express the temperature dependence of d as follows:

$$d(T)=d_0[1-\beta_1(\sqrt{1+\beta_2T}-1)], \tag{8}$$

where d_0 is the hard-sphere diameter at $T=0$, and β_1 and β_2 are parameters generally depending on the concentration of Fe^{3+} ions and the screening radius.

We consider β_1 and β_2 parameters of the theory. Their values can be found by comparing the experimental data with the theoretically calculated temperature dependence of the electron mobility for samples with different iron content. This was the procedure in Ref. 3, where we found $\beta_1=0.02$ and $\beta_2=3$. Using the above approximation to interpret the temperature dependence of μ considerably simplifies the analysis of experimentally established temperature curves for the thermomagnetic coefficients of HgSe:Fe crystals.

Let us now turn to calculation of the relaxation time τ_d^{-1} For an electron scattering from state k into state k' as it collides with a d-electron, which goes from state j into state j', we have [** widetext **]

$$\begin{aligned}\tau_d^{-1}=\frac{2\pi\hbar}{3mnT}\sum_{kk'jj'}&|V(kj,k'j')|^2(k-k')^2\{f(\varepsilon_k)\\&\times[1-f(\varepsilon_{k'})]F_{dj}[1-F_{dj'}]\delta(\varepsilon_k-\varepsilon_{k'}-\Delta_{jj'})\\&+f(\varepsilon_{k'})[1-f(\varepsilon_k)]F_{dj'}\\&\times[1-F_{dj}]\delta(\varepsilon_k-\varepsilon_{k'}+\Delta_{jj'})\}.\end{aligned} \tag{9}$$

Here $f(\varepsilon_k)$ and F_{dj} are the distribution functions for the band and d electrons, $\Delta_{jj'}$ the energy lost by the band electrons in the scattering act, and $V(kj,k'j')$ the matrix element describing scattering processes, whose explicit form is determined by the wave functions and the interaction potential of the electrons. Generally the matrix element has the form

$$V(kj,k'j')\approx V(k-k')D_{jj'}(k-k'), \tag{10}$$

where

$$D_{jj'}(k-k')=\int\psi_j^*e^{i(k-k')\cdot\mathbf{r}}\psi_{j'}(r)\,d^3r,$$

with the $\psi_j(r)$ the wave functions of d-electrons. To find the explicit form of the reciprocal relaxation time τ_d^{-1} we must know the wave functions of the localized d-electrons.

If we introduce the notation

$$\sum_k |V(kj,k'j')|^2(k-k')\delta(\varepsilon_k-(\varepsilon_{k'}-\Delta_{jj'}))$$

$$=g(\varepsilon_k-\Delta)J^-_{kk'}, \tag{11}$$

$$J^-_{kk'}=\frac{1}{2}\int_{-\pi}^{\pi}|V(kj,k'j')|^2(k-k')^2\sin\Theta\, d\Theta,$$

and go from summation to integration in (9), we get

$$\tau_d^{-1}=\frac{\pi}{\hbar k^2_{\mathrm{F}}}\sum_{jj'}\frac{y_{jj'}}{e^{y_{jj'}}-1}F_{dj}(1-F_{dj'})J^-_{jj'}g(\varepsilon_{\mathrm{F}}), \tag{12}$$

with $y_{jj'}\equiv\Delta_{jj'}/k_0T$. In calculating (12) we have allowed for the fact that $\Delta_{jj'}\ll\varepsilon_{\mathrm{F}}$.

Reasoning along similar lines, for the relaxation time τ_λ, which enters into the expression for the thermal conductivity λ, we obtain

$$\tau_\lambda^{-1}=\frac{3\hbar}{\pi mn(k_0T)^3}\sum_{kk'jj'}|V(kj,k'j')|^2J^\lambda_{kk'}\{f(\varepsilon_k)[1$$

$$-f(\varepsilon_{k'})]F_j[1-F_{j'}]\delta(\varepsilon_k-\varepsilon_{k'}-\Delta_{jj'})$$

$$+f(\varepsilon_k)[1-f(\varepsilon_{k'})]F_{j'}[1-F_j]\delta(\varepsilon_k$$

$$-\varepsilon_{k'}+\Delta_{jj'})\}. \tag{13}$$

Here

$$J^\lambda_{kk'}=(\varepsilon_k-\zeta)^2(\mathbf{k}-\mathbf{k}')^2$$

$$-\Delta(\varepsilon_k-\zeta)[(\mathbf{k}-\mathbf{k}')^2+k^2-k'^2]$$

$$+\tfrac{1}{4}\Delta^2[(\mathbf{k}+\mathbf{k}')^2+2(\mathbf{k}^2-\mathbf{k}'^2)], \tag{13a}$$

where ζ is the chemical potential of the band electrons. Here we have ignored the spread in the energy lost by band electrons in inelastic scattering, which is related to the spread in the impurity levels, i.e., we put $\Delta\approx\Delta$.

For further calculations it is convenient to first consider summation over k'. In this case we can represent $\mathfrak{R}^\pm\equiv\Sigma_{k'}|V(kj,k'j')|^2J^\lambda_{kk'}\delta(\varepsilon_k-\varepsilon_{k'}\pm\Delta)$ as

$$\mathfrak{R}^\pm=\tfrac{1}{3}g(\varepsilon_k\mp\Delta)\{(\varepsilon_k-\zeta)^2J^-\mp\Delta(\varepsilon_k-\zeta)[J^-+(k'^2-k^2)J^0]$$

$$+\tfrac{1}{4}\Delta^2[J^++J^-+2(k'^2-k^2)J^0]\}, \tag{14}$$

where

$$J^\pm=\int_{-\pi}^{\pi}|V(kj,k'j')|^2(k'\pm k)^2\sin\Theta\, d\Theta,$$

$$J^0=\int_{-\pi}^{\pi}|V(kj,k'j')|^2\sin\Theta\, d\Theta, \tag{15}$$

$$J^-+J^+=2(k'-k)^2J^0,$$

and $g(\varepsilon)$ is the density of states. In what follows we ignore the difference in the density of states related to the change in energy in inelastic scattering, i.e., we put $g(\varepsilon\pm\Delta)\approx g(\varepsilon)$.

To sum over k' we write (13a) in the form $\varphi(\varepsilon-\zeta)=A(\varepsilon-\zeta)^2+B(\varepsilon-\zeta)+C$. Then

$$\mp\sum_{\mathbf{k}_1}\varphi(\varepsilon)[f(\varepsilon_1\pm\Delta)-f(f(\varepsilon_1))]=\mp\frac{m_{\mathrm{F}}k_{\mathrm{F}}}{2\pi^2\hbar^2}$$

$$\times\int d\varepsilon\,[f(\varepsilon\pm\Delta)-f(\varepsilon)]\varphi(\varepsilon)$$

$$=A\frac{\Delta^3}{3}\mp B\frac{\Delta^2}{2}+C\Delta+\frac{\pi^3}{3}(k_0T)^2A\Delta. \tag{16}$$

Here $m_{\mathrm{F}}=m_n(1+2\varepsilon_{\mathrm{F}}/\varepsilon_g)$ is the electron mass at the Fermi level, where m_n is the mass at the bottom of the band. In calculating (16) we allowed for the fact that both $g(\varepsilon)$ and $J(k)$ are smooth functions in the vicinity of the Fermi energy; this allows them to be taken outside the integral sign at $\varepsilon=\varepsilon_{\mathrm{F}}$ and $k=k_{\mathrm{F}}$.

Combining this with Eqs. (12) and (13) yields

$$\tau_\lambda^{-1}=\frac{\pi}{\hbar k^2_{\mathrm{F}}}\sum_{jj'}\frac{yF_{dj}(1-F_{dj'})}{e^y-1}J^-\{1+Z_0y^2\}, \tag{17}$$

where

$$Z_0=\frac{3}{(2\pi)^2}\left[\frac{1}{3}+\frac{J^+}{J^-}\right]\approx0.1, \quad y=\frac{\Delta}{k_0T}.$$

Formulas (12) and (17) determine the electrical and thermal conductivities due to electrons in their inelastic scattering. Let us examine these formulas for different types of interaction.

1. For a point interaction, $|V(kj,k'j')|^2=V_0^2\tilde{D}^2_{jj'}$. Evaluating the integrals in (15), we find

$$\tau_i^{-1}=\frac{2\pi V_0^2g(\varepsilon_{\mathrm{F}})}{\hbar}\sum_{jj'}\frac{\tilde{D}^2_{jj'}yF_{dj}(1-F_{dj'})}{e^y-1}K_i, \tag{18}$$

where $i=d$ or λ, $K_d=1$, and $K_\lambda=1+(y/\pi)^2$.

2. For inelastic scattering in which a d-electron hops between iron ions of different valences, the interaction $V(kj,k'j')$ has the form

$$|V(kj,k'j')|^2=\frac{4\pi e^2}{\chi}\frac{V_0}{(k-k')^2+r_s^{-2}}\tilde{D}^2_{jj'}, \tag{19}$$

where χ is the dielectric constant. Evaluating the integrals in (15), we get

$$J^-=1-\frac{r_s^2}{4kk'}P, \quad J^+=\frac{2k^2+k'^2+r_s^{-2}}{4kk'}P-1, \tag{20}$$

$$J^0=\frac{1}{4kk'}P,$$

where

$$P=\ln\frac{(k+k')^2+r_s^{-2}}{(k-k')^2+r_s^{-2}}.$$

Introducing (20) into the formulas determining the reciprocal relaxation times, we get

$$\tau_i^{-1}=\frac{(2\pi e)^2V_0g(\varepsilon_{\mathrm{F}})}{\hbar k^2_{\mathrm{F}}\chi}\sum_{jj'}\frac{\tilde{D}^2_{jj'}yF_{dj}(1-F_{dj'})}{e^y-1}$$

$$\times\left\{1-\frac{\ln(1+b_s^{-2})}{b_s^2}\right\}K_i, \tag{21}$$

where $i=d$ or λ, $K_d=1$, and $K_\lambda=1+Z_1y^2$, with

$$Z_1\approx\frac{3}{2\pi^3}\left\{\frac{1}{3}+\frac{(1+b_s^{-2})\ln(1+b_s^{-2})}{1-b_s^{-2}\ln(1+b_s^{-2})}\right\}\approx 0.23. \tag{22}$$

3. Now let us turn to the inelastic scattering of a band electron as a result of which a d-electron is excited to a higher energy level. Obviously, in this case we have

$$|V(kj,k'j')|^2=\left(\frac{4\pi e^2}{\chi}\right)^2\left[\frac{1}{(k-k')^2+r_s^{-2}}\right]^2\tilde{D}_{jj'}^2. \tag{23}$$

Evaluating the integrals in (15) yields

$$J^{\mp}=\left(\frac{2\pi e^2}{\chi k_F^2}\right)^2\tilde{D}_{jj'}^2k_F^2\{\pm\ln(1+b_s^2)\mp 4b_s^2\}I^{\mp}, \tag{24}$$

where $I^-=(1+b_s^2)^{-1}$, and $I^+=1$. Then the formula for the reciprocal relaxation time becomes

$$\tau_\lambda^{-1}=\frac{4\varepsilon_B}{3\pi\hbar}\Phi_{BH}\tilde{D}_{jj'}^2\frac{y}{\mathrm{sh}(y)}(1+Z_2y^2), \tag{25}$$

where

$$\Phi_{BH}=\ln(1+b_s^2)-\frac{b_s^2}{1+b_s^2},\quad Z_2=\frac{3}{8\pi^3}\left(\tfrac{1}{3}+\frac{J^+}{J^-}\right)\approx 0.71, \tag{26}$$

and $\tilde{D}_{jj'}^2(2k_F)$ is the square of the overlap integral averaged over the Fermi surface.

4. TEMPERATURE DEPENDENCE OF THE LORENZ NUMBER

Let us now examine the temperature dependence of

$$L^*\equiv\frac{L}{L_0}=\sum_i\tau_{pi}^{-1}\sum_i\tau_{\lambda i}^{-1}, \tag{27}$$

where τ_{pi} and $\tau_{\lambda i}$ are the relaxation times determining the electrical and thermal conductivities in the scattering of electrons on centers of species i.

We start our discussion of the temperature dependence of the Lorenz number with HgSe. It was established that the main inelastic mechanisms of scattering of band electrons that determine the temperature variation of L at low temperatures are the scattering of electrons on optical phonons and electron–electron scattering. Of course, when calculating the L^* vs T dependence for HgSe one should also allow for elastic electron scattering on impurities and lattice vibrations. The results of numerical calculations (for an optical phonon energy $\hbar\Omega$ of 200 K and a deformation potential constant E_1 of 10 eV) are represented by curve *1* in Fig. 3.

Now about the temperature dependence of L^* for HgSe:Fe crystals. As already noted, for iron-impurity concentrations $N_{Fe}<4.5\times10^{18}$ cm^{-3} the correlation effects do not noticeably affect the scattering of electrons. We could, therefore, expect the variations of the Lorenz number with temperature to be the same as for HgSe. Experiments, however, show that the value of L^* for HgSe:Fe noticeably decreases compared to that for HgSe even when the iron content is low (Fig. 3). This unexpected behavior of L^* requires thorough analysis. The first explanation that comes to mind is that an electron scattered by an Fe^{3+} ion uses a fraction of its energy to excite a d-electron of iron to a higher energy level. Such intracenter scattering is described by Eq. (25). The typical values of the inelasticity energy $\Delta_{dd'}$ for intracenter transitions are of the order of 100 K (see Ref. 8), owing to the splitting of the ground state of unfilled d-shells by the crystalline field. Obviously, as the iron content in HgSe:Fe grows, the contribution to the thermal conductivity from intracenter transitions increases and reaches saturation at $N_{Fe^{3+}}=N_{Fe}^*$ The results of numerical calculations of the temperature dependence of L^* for HgSe:Fe with an iron-impurity concentration $N_{Fe}<4.5\times10^{18}$ cm^{-3} are indicated by curve *2* in Fig. 3. The values of the variable parameters were found to be $\Delta_{dd'}\sim 30$ meV, $Z_{dd'}\approx 5$, and $\tau_{ph}^{-1}\tau_{BH}^{-1}\approx 0.01$.

An increase in iron content in the range $N_{Fe}>N_{Fe}^*$ in HgSe:Fe samples leads to a further decrease in the Lorenz number, as Fig. 3 clearly shows. Such a decrease in L^* cannot be described solely by intracenter electron scattering, which reaches saturation at N_{Fe}^* as noted earlier. There must be another relaxation mechanism contributing substantially to inelastic electron scattering. Analysis shows that this mechanism could be the scattering of band electrons on Fe^{2+} ions neutral in the lattice, accompanied by charge exchange between Fe^{2+} and Fe^{3+} iron ions. A band electron scattered by an Fe^{2+} ion transfers sufficient energy to a d-electron of the Fe^{2+} ion for the electron to hop to an Fe^{3+} ion. As a result of such a charge exchange in the given Fe^{2+}–Fe^{3+} cluster, the short-range order in the system of charged ions is violated, i.e., the configuration of the Fe^{3+} ions in the cluster is altered. This process of charge exchange involving ions and, hence, the change of correlation between the ions can be described using the language of energy diagrams.

Indeed, in the presence of ion–ion correlations caused by the Coulomb interaction between Fe^{3+} ions, the density of states $g(\varepsilon)$ near the iron level has two peaks separated by a Coulomb gap. The band of unfilled states of Fe^{3+} lies above the Fermi level, while the filled states of Fe^{2+} are below it.[9] The distance between the peaks in the density of states depends on the iron-impurity concentration and temperature and can be represented in the form

$$\Delta_{+0}=\varepsilon_{d+}-\varepsilon_{d0}=\langle V(R_{ij})[g(R_{ij})-1]\rangle, \tag{28}$$

where $\varepsilon_{d0}=210$ meV is the energy of the unperturbed d state, and $V(R_{ij})$ the potential of the interaction between impurities i and j separated by a distance of R_{ij}. For weak Coulomb correlations,[10] the splitting Δ_{+0} is roughly 15 meV. Estimates done in the strong-correlations approximation[2] lead to a value $\Delta_{+0}\sim 20$ meV

Since in the inelastic scattering act a Fermi electron can transfer an energy of the order of k_0T, transitions between filled and vacant states in the temperature interval of interest to us, $T<50$ K, are, obviously, possible only for electrons

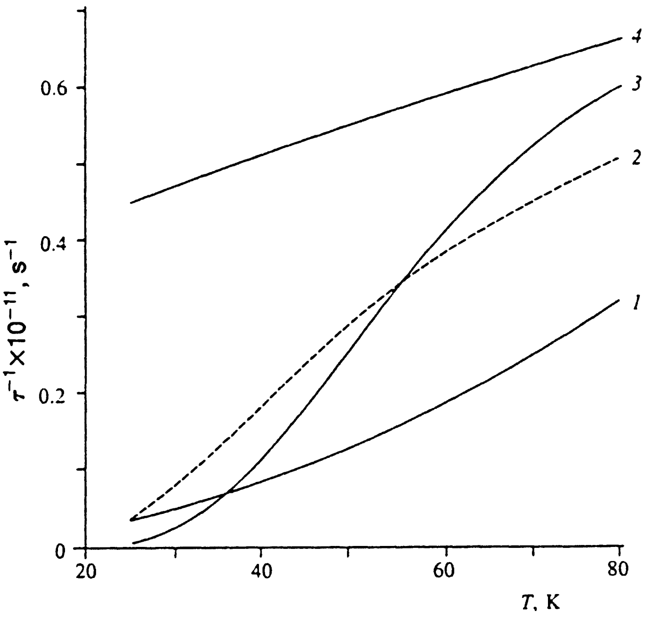

FIG. 5. Temperature dependence of the reciprocal relaxation time for the various mechanisms of inelastic electron scattering in HgSe:Fe with $N_{\rm Fe}=10^{19}$ cm^{-3}: curve *1*, electron–electron scattering; curve *2*, scattering on optical phonons; curve *3*, intracenter scattering; and curve *4*, scattering related to charge exchange between iron ions.

near the minimum in the density of states, at the Fermi level. We allow for these processes phenomenologically via the temperature dependence of η. Electron transitions near the peaks in the density of states are effective only at high temperatures, $T>200$ K. Hence, their contribution to the charge exchange between ions at $T<200$ K is negligible.

The results of calculating the temperature dependence of L^* for the high iron-impurity concentration of $N_{\rm Fe}=10^{19}$ cm^{-3} are represented by curve *3* in Fig. 3. Clearly, in this case, too, good agreement has been achieved between the observed and calculated values of L^*. The values of the variable parameters were found to be $\Delta_{+0}\approx 20$ meV, $Z_{dd'}\approx 3$, and $\tau_{+0}^{-1}\tau_{\rm BH}^{-1}\approx 0.01$.

Figure 5 illustrates the effectiveness of the different inelastic scattering mechanisms examined above for band electrons in HgSe:Fe with $N_{\rm Fe}=10^{19}$ cm^{-3}. We see that for $T>30$ K the main contribution to inelastic electron scattering is provided by the scattering on the correlated system of charged Fe^{3+} ions.

Now let us see whether intracenter transitions related to the excitation of d-electrons in iron ions Fe^{2+} contribute to L^*. When $N_{\rm Fe}$ increases in the region where $N_{\rm Fe}>N_{\rm Fe}^*$ the concentration of neutral impurity centers Fe^{2+} increases too. This should obviously be accompanied by an increase in the contribution of intracenter scattering processes to the Lorenz number L^*. There is experimental evidence, however, that an increase in iron content in HgSe:Fe leads to an increase in L^* rather than a decrease, with L^* approaching its value for HgSe. Such behavior of L^* suggests that the contribution of intracenter transitions in Fe^{2+} ions is negligible. It is easy to see that the observed rise in the Lorenz number with iron-impurity concentration is caused by the increasing role of alloy scattering, related to the difference in the potentials of the matrix and the substitution atoms. The results of calculations of the temperature dependence of L^* for $N_{\rm Fe}=4\times10^{20}$ cm^{-3} done with the same values of the parameters as for the sample with $N_{\rm Fe}=10^{19}$ cm^{-3} are presented by curve *4* in Fig. 3. Clearly, in this case, too, good agreement has been achieved between theory and experiment.

5. CONCLUSION

We have interpreted the experimentally discovered anomalous behavior of the Lorenz number L^* on iron content and temperature for HgSe:Fe crystals in the low-temperature range. We have demonstrated that the nonmonotone variation of the Lorenz number L^* with temperature is caused by the presence in HgSe crystals of iron impurities with mixed valence. A new channel of inelastic scattering of band electrons on these impurities opens in such crystals. Loss of energy by the band electrons in inelastic scattering events for $N_{\rm Fe}>N_{\rm Fe}^*$ is caused principally by scattering related to charge exchange between iron ions Fe^{2+} and Fe^{3+}. For $N_{\rm Fe}<N_{\rm Fe}^*$ the excitation of localized d-electrons to higher energy levels inside Fe^{3+} ions contributes significantly to inelastic scattering.

Satisfactory agreement of the results of calculations and the experimental data suggests that the new mechanism of electron scattering, related to charge exchange between impurity states, is the main reason for the experimentally discovered features in the behavior of the Lorenz number in HgSe:Fe crystals.

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