Zero-gap semiconductors with magnetic impurities forming resonance donor states

I. M. Tsidil'kovskiĭ

Institute of Metal Physics, Ural Division of the Russian Academy of Sciences, Ekaterinburg (Submitted 24 April 1991; resubmitted after revision 18 September 1991) Usp. Fiz. Nauk **162**, 63–105 (February 1992)

We describe the anomalies in the electronic properties of zero-gap semiconductors doped with transition elements (iron, chromium) that form deep resonance donor states, i.e., states degenerate with the continuum of the conduction band. We present an analysis of the numerous studies that shows that the distinctiveness of the properties of the materials being discussed, in particular, such a marked anomaly as increased electron mobility with increasing concentration of the dopant, is due to the correlated distribution of the charged donors in the crystal. The study of resonance states in semiconductors is a new field in solid-state physics, which at the same time is of practical interest, since it enables one, for example, to obtain materials with maximal electron mobilities.

INTRODUCTION

Until relatively recently, studies of semimagnetic semiconductors were restricted mainly to materials doped with manganese. In the past 5–6 years zero-gap semimagnetic semiconductors in which the magnetic ion is iron have begun to be studied intensively. In contrast to manganese, which forms an impurity level in II–VI type crystals that lies deep in the valence band and hence does not influence the kinetic processes, ions of iron create in HgSe a donor level on the background of the continuous spectrum of the conduction band. This leads to greatly distinctive physical properties of the iron-doped zero-gap semiconductor HgSe.

The existence of the resonance donor level of iron has the result that, at a high enough content of iron atoms, the Fermi level is captured by the donor level and the electron concentration is stabilized. The most marked "anomaly" of the properties of HgSe: Fe crystals is a substantial decrease of electron scattering by the disordered system of impurity ions and a concomitant increase in the mobility of the electrons and a decrease in the Dingle temperature with increasing concentration of iron ions within certain limits. As the temperature decreases down to several tens of millikelvins, the electron mobility increases monotonically, whereas in HgSe specimens doped with shallow impurities, e.g., gallium, it approaches saturation. These "anomalies" of scattering involve the correlated distribution of charged iron donors in the crystal, which is a consequence of the Coulomb interaction among the donors.

Analogous anomalies, yet less marked, have been found in crystals of HgSe doped with chromium. Preliminary measurements show that doping with cobalt and nickel also forms resonance donor states in HgSe.

I. CRYSTALS OF HgSe:Fe

1. RESONANCE DONOR STATES OF IRON

1.1. Energy levels of transition elements in II–VI-type compounds

Impurity states in zero-gap semiconductors, as in metals, are resonance states. That is, they are degenerate with the continuum of the spectrum of the real crystal. Naturally, most of the electronic properties (including transport phenomena) depend substantially on the energy location of the impurity levels with respect to the band edges and the Fermi level.

For the resonance impurity states of transition metals in II-VI-type compounds that we are interested in, the spectrum of possible situations is very rich (Fig. 1). Thus, the state of the Mn^{2+} ion lies deep in the valence band, while the states of the ions Fe^{2+} , Cr^{2+} , Co^{2+} , and Ni^{2+} lie considerably higher in energy. Studies of HgMnTe crystals actually showed that the level of Mn^{2+} lies far from the edge of the band and the Fermi level, and does not contribute to transport phenomena. It was of interest to elucidate the region of the continuous spectrum of bands of the zero-gap semiconductor HgSe in which the levels of the other transition elements lie: Fe²⁺, Cr²⁺, Co²⁺, Ni²⁺, etc. An empirical rule was established, according to which the energy spacings between the levels of different transition elements are approximately the same for different II-VI-type crystals. Yet the first studies of HgSe:Fe crystals confirmed, in agreement with the empirical diagram of Fig. 1, that iron impurities form a resonance donor level degenerate with the conduction band.



FIG. 1. Arrangement of the energy levels of the transition metals in the 2^+ (1) and 1^+ (2) charge states with respect to the band edges of II-VI compounds (see, e.g., Ref. 31).

Compounds of II-VI-type containing iron are relatively new representatives of the class of semimagnetic semiconductors. They began to be intensively studied only in 1985-1986. The solubility of iron in HgSe reaches about 20%. Many experimental data indicate that the Fe^{2+} ions lie at the nodes of the regular HgSe lattice. That is, they are substitution impurities. They serve as neutral donors whose level lies in the conduction band at a distance of about 210 meV from its bottom. For HgFeSe zero-gap semiconductors measurements of optical absorption similar to those used for direct determination of the location of impurity levels in semiconductors having a gap (e.g., CdFeSe) cannot be performed owing to the strong interband absorption. Besides, photoemission measurements in the interval of photon energies up to 10 eV on specimens of HgSe and Hg_{1-x}Fe_xSe with $x \leq 0.12$ indicate the existence of a higher density of states near the Fermi level in HgFeSe as compared with HgSe, although they did not allow establishing the exact localization of the states of Fe^{2+} (3d⁶). The existence of the resonance donor level involving the Fe²⁺ ions has been confirmed by a number of experimental facts to be discussed below.

In studying resonance impurity states, we must take into account two competing processes:

1) delocalization of electrons owing to hybridization of the localized impurity states, both with band states and with other impurity states. In a mixed-valence system, which is usually taken to mean a set of ions of the same element existing at equivalent nodes of the crystal in at least two charge states, the electrons can tunnel among the partially occupied local states. Thus a system arises with variable valency. In the limiting case of strong interimpurity hybridization exceeding the Coulomb interaction, all the nodes of the lattice of impurities have the same fractional charge, and the spatial distribution of the impurity charges is homogeneous;

2) localization of the electrons (or holes) caused by their Coulomb repulsion, which tends to maintain the local character of the impurity states.

In metals the hybridization of resonance impurity states with band states, as a rule, leads to partial or complete delocalization of the impurity states, since the density of states of the band electrons ρ close to the Fermi level $\varepsilon_{\rm F}$ is high, while the natural broadening of the impurity level is $\Gamma \propto \rho(\varepsilon_{\rm F})$. In metals with resonance impurity levels formed by atoms of transition or rare-earth elements, one observes a decrease in the mobility $\mu_{\rm e}$ of the electrons with decreasing temperature in the low-temperature region. This effect can be caused by: 1) either spin fluctuations, i.e., antiferromagnetic exchange interaction of the conduction electrons of the metal with the magnetic ions, which have unfilled d- or f-electron shells; 2) or charge fluctuations, i.e., resonance electron scattering, when the Fermi level is captured by the impurity level ($\varepsilon_{\rm F} = \varepsilon_{\rm i}$).

In semiconductors with resonance impurity levels the behavior of the mobility of the electrons in the low-temperature region differs. Thus, in the compensated zero-gap semiconductors p-HgCdTe and p-HgMnTe, in which the Fermi level is captured by acceptor states ($\varepsilon_F \approx \varepsilon_A$) degenerate with the conduction band, the mobility μ_e of the electrons increases with decreasing temperature. The increase in μ_e results from formation of donor-acceptor pairs D⁺-A⁻

(dipoles): the negative charge of the acceptor A^- is compensated by the positive charge of the nearest donor D^+ .¹ Thus a certain correlated spatial distribution of the charged centers at which the electrons are scattered arises. The probability of scattering of an electron by an electric dipole under conditions in which the wavelength of the electron exceeds the separation of the dipole charges is less than that by two noninteracting point charges (ions). Upon a sufficient temperature increase, the dipoles break down, and scattering by the disordered system of impurity ions becomes predominant, and the mobility of the electrons decreases.

1.2. Spatial correlation of charged Fe³⁺ donors

In HgSe:Fe crystals, in which iron forms a resonance donor level, the mobility of the electrons also increases with decreasing temperature. It was proposed (I. Mycielski²)¹ that in HgFeSe, just as in HgMnTe, a correlated spatial distribution arises in the charged Fe³⁺ donors, which serve as the main scattering centers at low temperatures. Owing to the ordering of the charged impurity centers, the scattering of electrons by them is weakened. The correlation of the scattering centers in HgFeSe arises from the compensation of charges, which differs from the type of compensation that exists in HgMnTe; in HgFeSe the positive charge of the ionized Fe^{3+} donors is compensated uniformly by the distributed gas of free electrons. The interionic Coulomb repulsion tends to arrange the Fe^{3+} ions as far from each other as possible. In Mycielski's view, this leads to formation of a localized Wigner-like crystal (for a true Wigner crystal the charge of the ordered system of electrons is compensated by the aggregate positive charge of the ions).

The necessary conditions for appearance of spatial correlation of the charged impurities in HgFeSe consist in the following.

1) Not all the impurities should be ionized. That is, there must exist two charge states of iron— Fe^{2+} and Fe^{3+} . Such a situation can be realized when the impurity state is a resonance state, and the Fermi level is fixed at this resonance state. We shall present below experimental proofs of the existence in HgSe of two charge states of iron.

2) The Fe³⁺ impurity states must be long-lived. That is, the hybridization of the impurity states with one another and with the band states must be weak. Such a weak hybridization usually should occur in semiconductors, where the natural width Γ of the impurity level is small owing to the low density of band states at the Fermi level $\rho(\varepsilon_F)$. The hybridization is weakened even more if the symmetry of the impurity state differs from the symmetry of the band states, as occurs in the case of iron donors in HgSe. The interimpurity hybridization of iron are rather strongly localized.

Electron paramagnetic resonance (EPR) measurements have shown that the Fe³⁺ donor states in HgSe actually are long-lived. Hybridization of the donor and band states means that the probability of capture of a free electron by an ionized donor is finite. Such a capture is essentially a resonance scattering of the free electrons, i.e., a decrease in their relaxation time. We can describe the capture process in different words as a shortening of the lifetime of the Fe³⁺ ions, which can be established in EPR measurements. At temperature T = 0 this process is impossible, since the electron capture requires an activation energy equal to the difference of the Fermi energy and the energy of the state of a free donor (see below). At T > 0, a fraction of the electrons has a finite probability of being captured by Fe³⁺ ions. Then the lifetime of the Fe³⁺ donor states close in energy to the Fermi level is shortened, and the amplitude of the EPR signal decreases if, of course, the hybridization is not weak. However, the EPR measurements³ showed that the amplitude of the signal does not vary up to T = 30 K. An analysis⁴ of these data showed that the broadening of the level Γ owing to hybridization of impurity and band states is less than 0.01 meV. Consequently the lifetime of an Fe³⁺ ion $\tau_i \sim \hbar \Gamma^{-1}$ is greater than $\sim 10^{-10}$ s. An estimate of τ_i from the width of the EPR line, which equals ≈ 30 G, yields a lower bound of the lifetime of the Fe³⁺ state $\tau_i \sim 10^{-9}$ s.

1.3. Experimental proofs of the coexistence of two charge states of Fe in HgSe

One of the first proofs that HgFeSe crystals constitute systems of mixed valency was obtained in measurements of the Shubnikov-de Haas effect. As is known, in HgSe crystals the beats arise in the Shubnikov-de Haas oscillations owing to the absence of inversion symmetry in the sphalerite lattice. Taking account in the dispersion relationship $\varepsilon(\mathbf{k})$ of terms of the order of k^3 and k^4 (the terms $\sim k^3$ involve the inversion asymmetry, and the terms $\sim k^4$ the anisotropy of the Fermi surface) leads to the appearance of two dependences: $\varepsilon_1(\mathbf{k})$ and $\varepsilon_2(\mathbf{k})$. The extremal sections of the energy surfaces $\varepsilon_1(\mathbf{k}_F) = \text{const}$ and $\varepsilon_2(\mathbf{k}) = \text{const}$ by planes perpendicular to the direction of the magnetic field define two series of oscillations with close-lying frequencies, the superposition of which leads to beats in the amplitudes of the oscillations.

The study of the Shubnikov-de Haas effect in HgFeSe crystals showed that features appear in the beats of the amplitudes of the oscillations that involve the presence in the HgSe of Fe atoms.⁵ It turned out that, in crystals with an iron concentration $N_{\rm Fe} \approx 8.4 \times 10^{20}$ cm⁻³ and $N_{\rm Fe} \approx 1.2 \times 10^{21}$ cm⁻³, the location of the nodes of the beats shifts with the temperature (Fig. 2). One can explain this effect by the presence of exchange interaction between the

band p electrons and the d electrons of the iron ions. The exchange interaction shifts the spin levels and gives rise to a dependence of the effective Landé g^* factor on the temperature. Consequently the amplitude of the Shubnikov oscillations

$$A \propto \cos \frac{\pi g^* m}{2m_0} = \cos \left[\pi \left(\frac{gm}{2m_0} + \frac{\beta N_{\rm m}(S_z)}{\mu_{\rm B} H} \right) \right] \tag{1}$$

becomes a function of the temperature; here g is the Landé factor without allowance for the exchange interaction, m_0 is the mass of a free electron, H is the magnetic field intensity, $\mu_{\rm B}$ is the Bohr magneton, $N_{\rm m}$ is the concentration of transition-metal ions (Fe in this case), β is a parameter that characterizes the exchange interaction of the band p electrons with the d electrons of the magnetic ion, and $\langle \hat{S}_z \rangle$ is the thermodynamic mean projection on the z axis of the spin operator \hat{S} of the magnetic ion. In a magnetic field parallel to the z axis only the z component of the mean value of the spin operator $\langle \hat{S} \rangle$ remains:

$$\langle \hat{S}_{z} \rangle = -SB_{s} \left(\frac{\bar{g} u_{\rm B} SH}{k_{\rm B} T} \right). \tag{1'}$$

Here B_s is the Brillouin function, and $\overline{g} = 2$ is the Landé factor for d electrons of the magnetic ion.

As is evident from Eqs. (1) and (1'), the temperature shift of the nodes of the beats of the oscillations can seemingly be explained by the exchange interaction of the band electrons and the electrons localized on the Fe²⁺ ions. Yet here we must immediately bear in mind one essential fact. The ground state of the Fe²⁺ ions in the sphalerite crystal lattice (it is created as a result of splitting of the ground state of the individual Fe²⁺ ion by the tetrahedral crystal field and the spin-orbital interaction) is a singlet.^{2),6-10} Consequently, in the absence of a magnetic field the magnetic moment equals zero. The magnetization in the low-temperature region ($T \le 10-15$ K) does not depend on the temperature and increases linearly with the magnetic field of the Fe²⁺ ion in the ground state allows us to suppose that the temperature



FIG. 2. Temperature shift of the nodes of Shubnikov-de Haas oscillations of the transverse magnetoresistance $\Delta \rho_{xx}$ for a specimen of $Hg_{1-x}Fe_x$ Se with x = 0.05 [μ_e (4.2 K) = 1.5×10^4 cm²/(V·s)]. Magnetic field H|| [100].

shift of the nodes of the beats of the oscillations is due to the presence at the lattice nodes, besides the Fe^{2+} ions, of triply charged Fe^{3+} ions, which have a magnetic moment in the ground state. Then the exchange interaction of the band electrons with the 3d electrons of Fe^{3+} leads to the shift of the nodes of the beats.

The existence in HgFeSe crystals of Fe³⁺ ions was demonstrated by EPR measurements (see, e.g., Ref. 3). As we have already noted, in the region of concentrations $N_{\rm Fe} \gtrsim N_{\rm Fe}^*$, the width of the paramagnetic resonance lines is relatively narrow (30 G), and EPR can be detected up to a concentration $N_{\rm Fe} \lesssim 4 \times 10^{19}$ cm⁻³. This means that a fraction of the iron ions, namely the Fe³⁺ ions, which are responsible for the EPR signal, are long-lived and insignificantly subject to the influence of hybridization.

1.4. Anomalies of the properties of HgSe:Fe

A number of unusual physical properties, or "anomalies", have been found in crystals of HgSe containing iron. Let us list the major ones.

First "anomaly." At an iron content $N_{\rm Fe} < N_{\rm Fe}^* \approx 4.5 \times 10^{18}$ cm⁻³ the concentration *n* of electrons (just like the EPR amplitudes of the Fe³⁺ ions) increases proportionally to $N_{\rm Fe}$. Yet at concentrations $N_{\rm Fe} > N_{\rm Fe}^*$ the electron concentration ceases to increase and reaches saturation at the value $n \approx 4.5 \times 10^{18}$ cm⁻³.

Second "anomaly." In the low-temperature region the mobility μ_e of the electrons as a function of $N_{\rm Fe}$ varies nonmonotonically: 1) for $N_{\rm Fe} < N_{\rm Fe}^*$ the mobility declines approximately inversely proportionally to $N_{\rm Fe}$; 2) for $N_{\rm Fe}^* \leq N_{\rm Fe} \leq (1.5-2) \times 10^{19}$ cm⁻³, the mobility increases with increasing $N_{\rm Fe}$, and finally; 3) for $N_{\rm Fe} > 2 \times 10^{19}$ cm⁻³, $\mu_e(N_{\rm Fe})$ is a declining function. At temperatures T > 100 K the maximum on the $\mu_e(N_{\rm Fe})$ curve vanishes, and the mobility monotonically declines with increasing iron content.

Third "anomaly." In the concentration region $N_{\rm Fe}^* < N_{\rm Fe} \leq 1.5 \times 10^{20}$ cm⁻³, the electron mobility $\mu_{\rm e}$ monotonically increases with decreasing temperature. For T > 100 K the magnitude of the electron mobility in HgFeSe becomes the same as in specimens of HgSe with the corresponding concentration of shallow donors, say, Ga.

Fourth "anomaly." The Dingle temperatures T_D found in studies of quantum oscillations are small for $N_{Fe} \gtrsim N_{Fe}^*$ and reach a maximum at $N_{Fe} \approx 2 \times 10^{19}$ cm⁻³, i.e., at the same value of N_{Fe} at which $\mu_e(N_{Fe})$ has a maximum. All these "anomalies" will be discussed in greater detail below.

Now we shall present a number of experimental facts that confirm the existence of a resonance donor level of iron in HgSe and the fixation of the Fermi level at it for a sufficiently large iron content $(N_{Fe} \gtrsim N_{Fe}^*)$.

1.5. The Hall effect

Measurements of the Hall effect as a function of the concentration $N_{\rm Fe}$ of iron atoms in HgSe enable one to decide on the localization of the Fe level. Figure 3^{11} shows the dependence of the concentration of band electrons n on $N_{\rm Fe}$ for crystals of Hg_{1-x}Fe_xSe in the concentration range $1 \times 10^{18} \le N_{\rm Fe} \le 10^{21}$ cm⁻³. In the range $1 \times 10^{18} \le N_{\rm Fe} \le 5 \times 10^{18}$ cm⁻³, the concentration of electrons is $n \approx N_{\rm Fe}$, while in the interval $5 \times 10^{18} \le 1.5 \times 10^{21}$ cm⁻³ the



FIG. 3. The electron concentration *n* as a function of the iron concentration for HgSe:Fe at 4.2 K. Experimental data from: *1*—Ref. 16; 2—Ref. 14; 3—Ref. 5; 4–Ref. 25.

value of n is practically independent of $N_{\rm Fe}$. These experimental facts can be explained^{5,12} by assuming that the state of the Fe^{2+} ions is a resonance state and that the resonance level lies in the conduction band (Fig. 4). At iron concentrations $N_{\rm Fe} < N_{\rm Fe}^* \approx 4.5 \times 10^{18}$ cm⁻³, all the Fe²⁺ ions are autoionized. That is, they give up an electron to the conduction band (the Fermi level lies below the iron level), while being converted into Fe³⁺ ions. When $N_{\text{Fe}} = N_{\text{Fe}}^*$ the Fermi level reaches the resonance donor level and becomes fixed, so that further increase in the iron content $N_{\rm Fe}$ does not alter the electron concentration (continued ionization of Fe²⁺ donors when $N_{\rm Fe} > N_{\rm Fe}^*$ is energetically unfavorable). On the basis of these data and the known density of states in the conduction band of HgSe, we can estimate the location of the un-ionized Fe^{2+} level with respect to the bottom of the conduction band: $\varepsilon_{\rm Fe} \approx 210$ meV. Strictly speaking, one cannot rule out the possibility of formation of donors, not by the iron ions, but by other atoms, say, interstitial mercury atoms. However, we can state with assurance that the donors involve the presence in the crystal of iron atoms, as indicated by the proportionality between the quantities n and $N_{\rm Fe}$ for an iron content $N_{\rm Fe} < N_{\rm Fe}^*$.

For a concentration of iron atoms $N_{\rm Fe} > N_{\rm Fe}^*$ the Fermi level is "captured" by the donor states and only a fraction of the donors (namely, $N_{\rm Fe}^*$) is ionized—a mixed system arises of 3d⁵ and 3d⁶ states of iron (a system of ions of differing valencies Fe²⁺ and Fe³⁺).



FIG. 4. Schematic diagram of the conduction band of $Hg_{1-x}Fe_xSe$ with an iron donor level.

1.6. Stabilization of the Fermi level

A number of factors exist that indicate the fixation of the Fermi level at the resonance level of iron at concentrations $N_{\rm Fe} > N_{\rm Fe}^*$. If the magnitude of the Fermi energy $\varepsilon_{\rm F}$ is fixed, then in a quantizing magnetic field the electron concentration n will vary, rather than $\varepsilon_{\rm F}$, as is usual when the magnitude of *n* is constant. The discovery of the oscillations of n(H), such as were observed for resonance acceptor levels in HgCdTe, is a direct proof of the capture of the Fermi level by the resonance state. The oscillations of n(H) must give rise to oscillations of the plasma frequency $\omega_{\rm p} \propto n^{1/2}$. These expectations were confirmed by measurements of the reflection of infrared radiation in magnetic fields $H \leq 70$ kOe at $T \approx 10$ K in crystals of Hg_{1-x}Fe_xSe with $x \approx 1 \times 10^{-3}$ $(N_{\rm Fe} \approx 1.5 \times 10^{19} \text{ cm}^{-3}).^{13}$ In the measurements the Voigt configuration was used $(\mathbf{E} \| \mathbf{H})$,³⁾ since under such conditions the location of the plasma edge does not depend on the field H, but only on the plasma frequency $\omega_{\rm p}$. The oscillations of $\omega_{\rm p}(H)$ give rise to oscillations of the reflection coefficient for light (Fig. 5) that are periodic in 1/H. The Hall conductivity σ_{xy} also oscillates in the magnetic field. The magnitudes of the electron concentrations n found from the oscillation periods coincide with the values of n obtained from the Hall effect in weak magnetic fields $\mu_e H \ll 1$.

Studies of the influence of hydrostatic pressure on the Hall effect have yielded another confirmation of the fixation of the Fermi level at the resonance states of iron.^{14,25} Hvdrostatic pressure, by diminishing the gap between the s band of light holes and the p conduction band, leads to a decline in the density of states of the conduction band. This effect is compensated either by a displacement of the Fermi level, if $n = \text{const} (N_{\text{Fe}} \leq N_{\text{Fe}}^*)$, or by a decrease in the concentration *n*, if the Fermi energy $\varepsilon_{\rm F}$ is fixed $(N_{\rm Fe} > N_{\rm Fe}^*)$. Thus the pressure allows one to vary the ratio $N_{\text{Fe}^{3+}} / N_{\text{Fe}^{2+}}$ in a given specimen in a reversible fashion. For specimens with an elecconcentration $3.96 \cdot 10^{18} \le n \le 4.75 \cdot 10^{18}$ cm^{-3} tron $(4 \cdot 10^{18} \leq N_{\rm Fe} \leq 2 \cdot 10^{19} \text{ cm}^{-3})$, one observes a marked decline $n(\mathcal{P})$ (Fig. 6). For a specimen with $n = 3.14 \times 10^{18}$ cm⁻³ ($N_{\rm Fe} = 2 \times 10^{18}$ cm⁻³), a very slight variation of $n(\mathcal{P})$ begins above a certain pressure, while for a specimen with $n = 1.4 \times 10^{18}$ cm⁻³ ($N_{\rm Fe} = 1 \times 10^{18}$ cm⁻³), for which, as is known, $\varepsilon_{\rm F} < \varepsilon_{\rm Fe}$, the concentration



FIG. 5. Oscillations of the magnetoreflection in HgSe:Fe.¹³ $N_{\rm Fe} = 2 \times 10^{19}$ cm⁻³, $\hbar \omega = 87.2$ meV, $T \sim 10$ K. Inset—displacement of the plasma reflection minimum.



FIG. 6. Variation of the electron concentration in HgSe:Fe under hydrostatic pressure.^{14,25} $N_{\rm Fe}$ (10¹⁸ cm⁻³; at $\mathscr{P} = 0$ and 4.2 K) = 1, (1), 2.0 (2), 4.0 (3), 8.0 (4), and 20.0 (5).

 $n(\mathcal{P}) = \text{const.}$ The variation of $n(\mathcal{P})$ involves the exit of electrons from the conduction band owing to decrease in the density of states in it and the neutralization of the trivalent iron ions $\text{Fe}^{3+}:\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$.

1.7. Stabilization of the electron concentration in time

As is known, crystals of the mercury chalcogenides are very defect-rich: they contain rather many vacancies, while the mercury atoms move rather easily from nodes to interstices. It has been established that the concentration of free electrons *n* in HgSe involves intrinsic crystal-lattice defects: interstitial Hg atoms and Se vacancies supply electrons to the conduction band. In undoped HgSe crystals the concentration of electrons generated by defects is usually $n \sim 10^{17} - 10^{18}$ cm⁻³. The maximum values $n \simeq 5 \times 10^{18}$ cm⁻³ in undoped specimens are attained by annealing in mercury vapor. Doping, say, with gallium or indium enables one to bring the value of n up to $(3-4) \times 10^{19}$ cm⁻³. Annealing of HgSe specimens even at room temperature (passive annealing) can alter the number of intrinsic defects that supply free electrons, whereby the electron concentration n is controllable and varies reversibly in time. Thus, annealing of HgSe specimens at 50 °C leads to about a fivefold change in n.¹⁵

The study of the influence of doping of HgSe with iron on the variation of the electron concentration *n* upon annealing has shown that even relatively small admixtures of Fe sharply alter the instability of *n* in time.¹¹ For concentrations of iron $N_{\rm Fe} \gtrsim 5 \times 10^{19}$ cm⁻³, the value of *n* remains invariant even upon annealing near 200 °C in an atmosphere of excess mercury. What might cause this stabilization?

For specimens with $N_{\rm Fe} \gtrsim 4.5 \times 10^{18}$ cm⁻³, the value of n is determined by the number of charged Fe³⁺ ions, rather than by the intrinsic defects, which can generate no more than 5×10^{18} cm⁻³ free electrons. Owing to the fixation of the Fermi level at concentrations $N_{\rm Fe} \gtrsim 5 \times 10^{18}$ cm⁻³ at the donor level of iron, the electron concentration n becomes a weak function of the total number of lattice defects, and in particular, the number of iron atoms (see Fig. 3). On the other hand, introduction of iron into HgSe strengthens the interatomic bonds in the lattice and thus diminishes the variation in time of the number of defects. Actually, Fe²⁺ ions, having a smaller radius than Hg²⁺ ions (0.80 and 1.12 Å,

respectively), occupy lattice nodes of HgSe, and since the electronegativity of the Fe²⁺ ion is smaller than for the Hg²⁺ ion (1.7 and 1.8), the lattice becomes stronger. The introduction of a sufficiently large number of iron atoms decreases the number of vacancies, and hence decreases the variation in time of the number of defects. Their migration is diminished, and for an iron content $N_{\rm Fe} \gtrsim 5 \times 10^{19}$ cm⁻³, it apparently completely ceases.

1.8. Variation of the electron concentration with temperature

Another confirmation of the localization of the iron level in HgFeSe is the n(T) dependence. Figure 7 shows the n(T) dependence for single crystals of Hg_{1-x}Fe_xSe with $x = 3 \times 10^{-4}$, 1×10^{-3} , and 1×10^{-2} .¹⁶ The solid lines are the result of calculation for the band structure of HgSe with the resonance level of iron. The calculation of n(T) used the density of states in the nonparabolic conduction band (Kane model). The density of states of the Fe donors was given in the form of a delta function. The energy $\varepsilon_{\rm Fe}$ of the iron level was considered to be an adjustable parameter in comparing the calculated and measured values of the concentrations n. The calculation showed that one can obtain agreement of the calculated and measured values of n(T) if one assumes that the energy $\varepsilon_{\rm Fe}$ of the iron level varies with the temperature. The $\varepsilon_{\rm Fe}(T)$ relationship is not unexpected, since the energy $\varepsilon_{\rm Fe}$ is defined with respect to the degenerate edge of the band of p symmetry, with which the iron level is not genetically associated. The absolute location with respect to the vacuum of the donor level of iron actually does not depend on the temperature. But the edge of the p band shifts with the temperature, and consequently the energy $\varepsilon_{\rm Fe}$ becomes a function of T. Since it is difficult to distinguish the contributions to $\varepsilon_{\rm Fe}(T)$ from the temperature shift of the edge of the p band and from the variation of the gap $\varepsilon_{g}(T) = \varepsilon_{s}(T) - \varepsilon_{p}(T)$, to reconcile calculation with experiment we can use the empirical formula $\varepsilon_{\rm Fe}(T) = \varepsilon_{\rm Fe}(0) + \alpha(\varepsilon_{\rm g}(0) - \varepsilon_{\rm g}(T))$ with the new adjustment parameter α . As a result of this reconciliation for the temperature interval 4.2-300 K (see Fig. 7), it was found that, for values of x from 3×10^{-4} to 1×10^{-2} , the parameter α varies in the range from 0.24 to 0.16, while the energy $\varepsilon_{\rm Fe}(x)$ at 4.2 K is determined by the expression

 $\varepsilon_{\rm Fe}(x) = 0.21 + 0.52x$ eV. The values of $\varepsilon_{\rm Fe}$ at 4.2 K for $3 \times 10^{-4} \le x \le 5 \times 10^{-2}$ vary in the range from 0.192 $(x = 3 \times 10^{-4})$ to 0.233 eV $(x = 5 \times 10^{-2})$.

1.9. Variations of the Fermi level upon doping with cadmium and tellurium

Upon substituting part of the mercury atoms with cadmium atoms in HgFeSe, the spacing between the bands of s and p symmetry decreases and ultimately the inverted band structure is converted into a direct one (Fig. 8). One can easily understand that the electron concentration n in zerogap $Hg_{1-x-y}Fe_xCd_ySe$ crystals with a number of iron atoms sufficient to fix the Fermi level will be altered upon adding cadmium. Actually, when y increases, the density of states decreases in the conduction band owing to its increased curvature near the center of the Brillouin zone $\mathbf{k} = 0$. This leads to a decrease in the number of states under the Fermi level, which is fixed at the Fe^{2+} level, and hence, to a decrease in the value of n. Then, when y reaches a value at which the gap opens, the bottom of the conduction band begins to rise with respect to the Fermi level, which causes a further decrease in n. Finally, the bottom of the conduction band rises above the Fe^{2+} level, and the Fermi level enters the gap between the conduction band of s symmetry and the valence band of p symmetry. The situation that we have described differs from the case of the zero-gap crystals $Hg_{1-\nu}Cd_{\nu}Se$, where upon doping with cadmium the electron concentration n remains constant, while the Fermi energy $\varepsilon_{\rm F}$ varies in accord with the variation of the gap $\varepsilon_{\rm g}$ (and the effective mass of the electrons). Thus the system $Hg_{1-\nu}Cd_{\nu}Se$ doped with iron makes it possible to vary the magnitude of the gap ε_{g} without thereby influencing the position of the Fermi level.

One can vary the location of the iron donor level by replacing part of the Se ions with Te ions $(HgSe_{1-y}Te_y:Fe)$. This shift of the energy ε_{Fe} involves the fact that in HgTe:Fe crystals the iron level does not lie in the conduction band. Figure 9 shows the $n(N_{Fe})$ dependence obtained from measurements of the Hall effect at 4.2 K in specimens with y = 0, 0.04, and 0.05. The saturation value of the $n(N_{Fe})$ curves, which is associated with the fixation of the Fermi level in resonance states, varies with $y: \varepsilon_{Fe}(y) = 200-600y$ meV. The more tellurium the specimen has, the lower is the reso-



FIG. 7. Variation of the electron concentration with the temperature for three specimens of $Hg_{1-x}Fe_xSe$.¹⁶ Solid lines—result of calculation.



FIG. 8. Diagram of the band structure of $Hg_{1-x-y}Fe_xCd_ySe^{32}$



FIG. 9. The electron concentration as a function of the iron concentration in $HgSe_{1-y}Te_y$ at 4.2 K.¹⁴ y = 0 (1), 0.04 (2), and 0.05 (3).

nance level of iron. The temperature dependences n(T) for HgFeSe specimens with Te are analogous to the n(T) dependences for HgFeSe.

1.10. Quantum oscillations

We can draw certain conclusions on the influence of impurity iron atoms on the density of states of the conduction band on the basis of measurements of the Shubnikov-de Haas and de Haas-van Alfven effects.^{5,11,17} The study of these oscillations in HgFeSe crystals showed that the magnitudes of the effective masses m of the electrons agree reasonably with the values of m obtained for HgSe specimens having the same concentration of electrons. Therefore we can conclude that the presence of iron atoms in HgSe does not appreciably affect the density of states of the conduction band. An analogous conclusion arises from studies of the anisotropy of the angular dependence of the Shubnikov-de Haas oscillations, which allow one to determine the crosssectional area of the Fermi surface. The anisotropy of the angular dependence of the Shubnikov-de Haas oscillations in HgFeSe is very close to that for HgSe. This indicates a very weak perturbation of the form of the conduction band by the iron atoms. This is precisely why one can use the known band structure of HgSe to determine the location of the Fermi level, and hence the level $\varepsilon_{\rm Fe}$ of Fe²⁺ iron for $N_{\rm Fe} \gtrsim 4.5 \times 10^{18}$ cm⁻³. As we have already mentioned, the value of $\varepsilon_{\rm Fe}$ thus found is $\approx 210 \pm 10$ meV. The effective mass m lies within the range from $m \approx 0.066 m_0$ to $m \approx 0.07 m_0$ for $1 \times 10^{-3} \le x \le 3 \times 10^{-2}$.

2. SCATTERING OF ELECTRONS IN HgSe:Fe CRYSTALS 2.1. Anomalies of the electron mobility and the Dingle temperature

The most amazing property of HgFeSe crystals with an iron concentration $4.5 \times 10^{18} \leq N_{\rm Fe} \leq 1.5 \times 10^{20}$ cm⁻³ $(3 \times 10^{-4} \leq x \leq 1 \times 10^{-2})$ is the high mobility $\mu_{\rm e}$ of electrons at low temperatures, which appreciably exceeds the mobility in HgSe specimens having comparable concentrations of hydrogen-like small impurities, say gallium. For specimens with $N_{\rm Fe} \approx (1.5-5) \times 10^{20}$ cm⁻³ at the lowest temperatures, one also observes a certain increase of the electron mobility over the $\mu_{\rm e}$ values in HgSe. In the region of iron concentrations $4.5 \times 10^{18} \leq N_{\rm Fe} \leq (1.5-2) \times 10^{19}$ cm⁻³ the mobility μ_e at low temperatures increases with increasing $N_{\rm Fe}$ approximately fivefold (Fig. 10),⁵ while for $N_{\rm Fe} > (1.5 - 2) \times 10^{19}$ cm⁻³ the $\mu_e (N_{\rm Fe})$ relationship is a declining one. At T > 100 K the maximum on the $\mu_e (N_{\rm Fe})$ curve disappears.

The temperature dependences $\mu_e(T)$ for specimens with $N_{\rm Fe} \leq N_{\rm Fe}^* \approx 4.5 \times 10^{18}$ cm⁻³ in the interval $4.2 \leq T \leq 300$ K agree quite satisfactorily (at low temperatures to an accuracy as good as +10%) with those calculated for scattering by a disordered system of impurity ions (by the Brooks-Herring formula) of acoustic, polar and nonpolar optical phonons (see Fig. 11). This allows us to conclude that, at iron concentrations $N_{\rm Fe} \leq N_{\rm Fe}^*$, all the donors are actually ionized in the low-temperature region (the Fermi level lies below the iron level) and form a random aggregate charged centers. For of specimens with $4.5 \times 10^{18} \leq N_{\rm Fe} \leq 1.5 \times 10^{20}$ cm⁻³ an anomaly is observed in the $\mu_e(T)$ dependences: at low temperatures the measured values of μ_{a} are larger than those calculated by assuming a disordered distribution of donors throughout the crystal (Fig. 11–13). For specimens with $1.5 \times 10^{20} \le N_{\text{Fe}} \le 5 \times 10^{20}$ cm⁻³ the values of μ_{e} only somewhat exceed the theoretical values (see Fig. 13). But even with such a high iron content in the very lowest temperature region one observes a certain increase in μ_e with decreasing T characteristic of specimens with $4.5 \times 10^{18} \le N_{\rm Fe} \le 1.5 \times 10^{20}$ cm⁻³.

At high temperatures (T > 100 K) the magnitudes of the electron mobility are the same as in HgSe, and agree satisfactorily with the values of μ_e calculated for combined scattering by impurity ions and acoustic and optical phonons.

An experimental confirmation of the diminution of electron scattering in HgSe:Fe crystals as compared with the scattering in HgSe:Ga crystals at low temperatures is furnished by studies of the Shubnikov-de Haas and de Haas-van Alfven oscillations.^{5,11,17,18} The Dingle temperatures $T_{\rm D}$ found from these effects for HgSe:Fe specimens having an iron content $N_{\rm Fe} \gtrsim 4.5 \times 10^{18}$ cm⁻³ are anomalously



FIG. 10. Dependence of the electron mobility in HgSe:Fe on the iron concentration. T = 4.2 K. Experimental data from: *I*—Ref. 16; 2—Ref. 14; 3—Ref. 5; 4—Ref. 25. The dashed line is the result of calculation without allowance for interionic interaction, the solid line is the result of calculation in the model of short-range correlation,²³ and the dot-dash line is the result of numerical simulation with account taken of interionic interaction.²³



FIG. 11. Temperature dependences of the electron mobility in crystals of $Hg_{1-x}Fe_xSe$.¹⁶

small—about two to three times smaller than for HgSe:Ga specimens. The minimum temperature $T_{\rm D}$ was established for specimens with $N_{\rm Fe} \approx (1.5-2) \times 10^{19}$ cm⁻³, i.e., for those specimens whose electron mobility is a maximum. Thus, according to the measurements of the de Haas-van Alfven effect, at T = 0.55 K¹⁷ for specimens with $N_{\rm Fe} \approx 4.5 \times 10^{18} - 1 \times 10^{21}$ cm⁻³ we find $T_{\rm D} \approx 1-2$ K, whereas for scattering by impurity ions in an HgSe specimen with $n \approx 4 \times 10^{18}$ cm⁻³, the calculated value of $T_{\rm D}$ is ≈ 10 K.

Thus the increase in the electron mobility and decrease in the Dingle temperature in the region of iron concentrations $N_{\text{Fe}}^{\bullet} \leq N_{\text{Fe}} \leq 2 \times 10^{19} \text{ cm}^{-3}$ indicates a decreased efficiency of electron scattering by the disordered system of impurity ions in HgFeSe as compared with HgSe, where this



FIG. 12. Temperature dependences of the electron mobility in crystals of $Hg_{1-x}Fe_x$ Se.¹⁶



FIG. 13. Temperature dependences of the electron mobility in crystals of $Hg_{1-x}Fe_xSe$.¹⁶

scattering mechanism is predominant at low temperatures. As the concentration $N_{\rm Fe}$ increases from 1×10^{18} cm⁻³ to about 5×10^{18} cm⁻³, the electron mobility $\mu_{\rm e}$ decreases, while the Dingle temperature $T_{\rm D}$ increases in agreement with the theory of scattering by disordered ionized impurities.

One could try to explain the increased mobility and decreased Dingle temperature, as in the case of GaSb:Te, by screening of the impurity ions by the electrons of the side minima. In GaSb the L-minima with high effective mass (lying in the (111) directions) lie above the main Γ -minimum (which lies at the center of the Brillouin zone $\mathbf{k} = 0$) by ≈ 0.1 eV. Upon doping with tellurium the Fermi level reaches the L-minima, and the electrons of these minima, which make no substantial contribution to transport phenomena owing to their large mass, screen the impurity ions and weaken the scattering of Γ -electrons. In principle the same might occur also in HgSe:Fe. However, in HgSe the lowest side L-minimum lies above the Γ -minimum by ≈ 2.0 eV, while the Fermi energy in HgSe crystals doped with iron is $\varepsilon_{\rm F} \approx 0.21$ eV. Therefore the *L*-minima are not filled with electrons. One could also assume that the iron atoms lead to lowering of the L-minima or to formation in the band structure of HgSe of new minima whose electrons enhance the screening. Such changes must affect a number of measurable quantities. For example, in gray tin a sharp increase was noted in the effective mass of the Γ -electrons when the Fermi level reached a side minimum as their concentration n increases. However, the measurements of the quantum oscillations in HgFeSe crystals, as we have already mentioned, indicate that the form of the conduction band, and correspondingly the effective electron mass, do not vary upon introduction of iron into HgSe. Thus there are no grounds for assuming that the anomalies of mobility and Dingle temperature involve changes in the band structure of HgSe introduced by iron.

2.2. Resonance scattering of electrons

Thus the analysis of the studies of different phenomena in HgFeSe crystals shows that the Fermi level is fixed at the resonance level of iron and for concentrations $N_{\rm Fe} \ge N_{\rm Fe}^* \approx 4.5 \times 10^{18} \, {\rm cm}^{-3}$ two charge states of iron coexist (Fe²⁺ and Fe³⁺), the electron mobility μ_e increases, while the Dingle temperature $T_{\rm D}$ declines as the iron content $N_{\rm Fe}$ increases up to $\approx (1.5-2) \times 10^{19} \, {\rm cm}^{-3}$ in the temperature region $T \le 100 \, {\rm K}$. At present one can apparently consider it established that the increase in the mobility μ_e and the decrease in the Dingle temperature $T_{\rm D}$ —the principal features of the electronic properties of HgFeSe—are due to the interaction between the ionized Fe³⁺ donors, which lead to their correlated distribution. Before we discuss this idea and the interpretation of the principal experimental facts based on it, let us take up an effect that explicitly suggests itself, which under the described conditions can play an important role—the resonance scattering of electrons.

We must note that, for the discussed mixed-valence states in HgFeSe one should have expected not increases, but decreases in the electron mobility upon doping HgSe with iron, since, in addition to scattering by the $3d^5$ ions of iron, resonance scattering should be manifested—the iron level lies on the background of the continuous spectrum of the conduction band. However, one can point out at least two factors that sharply weaken the resonance scattering, i.e., transitions of electrons from the conduction band to the iron ions and vice versa from the iron atoms into the conduction band (charge fluctuations).

As is known, the Coulomb interaction of a localized electron with charged donors gives rise to a minimum in the single-particle density of states near the Fermi level—a Coulomb gap, which separates the filled from the empty impurity states. Under the conditions being discussed, in which transitions of electrons occur from the conduction band to donors and vice versa, a Coulomb gap is formed in HgFeSe near the Fermi level, which weakens the resonance scattering.¹⁹ This weakening will be substantial if the Coulomb gap is much larger than the natural broadening Γ of the d level of iron, which is the result of the hybridization of these d states and the band sp states:

$$\Gamma = \pi \rho(\epsilon_{\rm F}) |V_{\rm kd}|^2.$$
⁽²⁾

Here $\rho(\varepsilon_{\rm F})$ is the density of states at the Fermi level, and $|V_{\rm kd}|^2 = |\langle \psi_{\rm k} | \mathscr{H} | d \rangle|^2$. The broadening Γ must be relatively slight, since, first, the density of states $\rho(\varepsilon_{\rm F})$ is small in the conduction band of HgFeSe, and second, the d level being discussed has e-symmetry, whereas the Bloch components of the band wave function $\psi_{\rm k}$ have a_1 and t_2 symmetry (upon neglecting spin-orbital coupling). In this case the matrix element $V_{\rm kd} \rightarrow 0$ when $k_{\rm F} r_{\rm d} \rightarrow 0$, where $r_{\rm d}$ is the radius of localization of the d-function. Since under the conditions being discussed we have $k_{\rm F} r_{\rm d} \ll 1$, we can assume that $V_{\rm kd} \rightarrow 0$, and hence, the natural width of the d levels is small. Thus the weak sp-d hybridization and the appearance of a Coulomb gap should suppress resonance scattering. We can estimate the electron mobility for resonance scattering by using the Friedel formula

$$\mu_{\rm e} = ek_{\rm F}/8\pi\hbar N_{\rm Fe}.$$
(3)

For $N_{\rm Fe} = 1 \times 10^{19} \,{\rm cm}^{-3}$ and $n = 4.3 \times 10^{18} \,{\rm cm}^{-3}$ we obtain from (3) $\mu_e \approx 30 \,{\rm cm}^2/(V \cdot s)$ (experimental value $\mu_e \approx 10^5 \,{\rm cm}^2/(V \cdot s)$). The estimate of the mobility μ_e by the Friedel formula is valid when $k_{\rm B}T$ is smaller than the width of the resonance band. Measurements of the conductivity in a specimen having an iron content $N_{\rm Fe} = 1 \times 10^{19}$ cm⁻³ showed²⁰ that one can detect no influence of resonance scattering up to T = 40 mK.

A numerical calculation of the width of the Coulomb gap for a randomly distributed system of donors in HgFeSe with a content of iron of $N_{\rm Fe} = 8.8 \times 10^{18}$ cm⁻³ and of electrons $n = 4.3 \times 10^{18}$ while neglecting the hybridization of band and resonance states showed²¹ that, for a value of the dielectric constant $\varkappa = 29.7$,⁴⁾ the gap width is ≈ 4.5 meV, the maximum width of the band of filled donor states ≈ 22 meV, and the width of the empty donor band ≈ 14 meV. The presence of a gap must substantially impede the charge fluctuations between the conduction band and the d states of iron, or in other words, weaken or totally suppress resonance scattering. The calculation also showed that, for a relatively small concentration of iron $N_{\rm Fe} = 8.8 \times 10^{18}$ cm⁻³, the configuration of the ionized donors is far from ideal periodicity.

2.3. The Mycielski model of ordering

To explain the effect of weakening of electron scattering discussed above, I. Mycielski proposed an interesting idea.² He suggested that the distribution of donors among the nodes of the metallic sublattice is random, while, owing to the Coulomb interaction among the charged donors, the fraction $N_{\text{Fe}^{3+}}/N_{\text{Fe}}$ of which is small, a correlation arises in their spatial distribution: positive charges appear on the donors that are farthest from one another. In the limit $N_{\rm Fe} \gg N_{\rm Fe}^* \approx n$, and at low temperatures, the ionized donors form an ordered structure (superlattice)-a localized Wigner crystal of charged donors. Of course, if all the randomly distributed donors are ionized, then ordering does not arise, since the positions of the donors are fixed. In his calculation Mycielski proposed that the resonance level of iron is very narrow, and one can neglect the resonance scattering of free electrons. As we saw above, this assumption is quite warranted. Moreover, it was assumed in the calculation that the resonance state of iron is sufficiently localized that an impurity band is not formed. This assumption seems reasonable since, as we have already noted, the radius of a wave function of d-symmetry of iron atoms is small-of the order of several lattice constants.

The energy of the screened Coulomb interaction between the ionized donors as calculated per donor is

$$=\frac{e^2n^{1/3}}{2\varkappa}A,\tag{4}$$

where we have

ε

4

$$A = \frac{1}{n\Omega} \sum_{l \neq m} \frac{\exp(-C|\mathbf{r}_l - \mathbf{r}_m|)}{|\mathbf{r}_l - \mathbf{r}_m|},$$
(5)

 $n = N_{Fe^{3+}}$, Ω is the volume of the crystal, $C = n^{-1/3}/r_0 = r_i/r_0$, r_i is the mean distance between the charged donors, r_0 is the screening radius, \varkappa is the dielectric constant, $\mathbf{r}_i = \mathbf{R}_i/r_i$, where the \mathbf{R}_i are the coordinates of the charged donors. The energy difference between the ordered and disordered states of the system of ionized donors is determined by the difference between the dimensionless quantities A, which depend on the spatial distribution of these donors. For a random distribution we can average in (5) over \mathbf{r}_m and for the given \mathbf{r}_l and obtain

$$A_{\rm rd} = \int \frac{\exp(-Cr)}{r} {\rm d}^3 r = \frac{4\pi}{C^2}.$$
 (6)

For an ordered arrangement of the ionized donors in the form of a Bravais lattice we obtain from (5):

$$A_{\text{latt}} = \sum_{n \neq 0} \frac{\exp(-Cr_n)}{r_n},$$
(7)

Here \mathbf{r}_n is a translation vector of the Bravais lattice. The difference $A_{rd} - A_{latt}$ was calculated in Ref. 2 numerically for several types of Bravais lattices. The lowest energy corresponds to the bcc lattice, but the difference of energies for the different lattices is much smaller than the mean difference $\varepsilon_{rd} - \varepsilon_{latt}$, which amounts to $\approx 12.5 \text{ meV} \approx 145 \text{ K}$ as calculated per Fe³⁺ ion for $n = 5 \times 10^{18} \text{ cm}^{-3}$, $\kappa = 20$, $m = 7 \times 10^{-2} m_0$ ($C = r_i/r_0 \approx 1.27$).

The temperature T_0 at which the system of ionized donors becomes correlated can be estimated by comparing the free energies for a regular lattice $n\Omega\varepsilon_{\text{latt}}$ and for a disordered structure $n\Omega[\varepsilon_{rd} - k_{\text{B}}T\ln(N_{\text{Fe}}/n)]$ (in the latter, as we see, an entropy term is taken into account):

$$T_{0} \approx \frac{1}{k_{\rm B}} \left(\varepsilon_{\rm rd} - \varepsilon_{\rm latt} \right) \left(\ln \frac{N_{\rm Fe}}{n} \right)^{-1}$$
$$= \frac{e^{2} n^{1/3}}{2k_{\rm B}^{\varkappa}} \left(A_{\rm rd} - A_{\rm latt} \right) \left(\ln \frac{N_{\rm Fe}}{n} \right)^{-1}. \tag{8}$$

Calculation² shows that the typical values are $A_{rd} - A_{latt} = 1-3$. For the parameters x = 20, $m = 0.07m_0$, $n = 6 \times 10^{18}$ cm⁻³, and $N_{Fe} = 1.5 \times 10^{20}$ cm⁻³ ($x \approx 0.01$), the screening radius is $r_0 = 4.6 \times 10^{-7}$ cm, C = 1.2, and according to (8), we have $T_0 \approx 45$ K.

An important consequence of the ordering of charged impurities should be to reduce their electron scattering, and hence, to increase the mobility of electrons and decrease the Dingle temperature. This must occur because the scattering event in an ordered system of impurity centers is coherent in character, whereas only incoherent scattering contributes to the relaxation of the momentum. Coherent (Bragg) scattering by a strictly periodic lattice must be absent, since the wave vector of the scattered electron $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ must equal one of the reciprocal-lattice vectors \mathbf{g}_m . This rules out processes of elastic scattering of electrons having small Fermi momenta $|\mathbf{k}_F| < |\mathbf{g}_m|$ (it was shown in Ref. 2 that $2|\mathbf{k}_F|$ is smaller than the shortest of the vectors $|\mathbf{g}_m|$). And it is precisely these processes that are most important for scattering by the Coulomb potential.

The diminished scattering for an ordered system of Fe^{3+} impurity ions must occur only at low temperatures when: 1) the thermal fluctuations are not capable of destroying the order; 2) scattering by the impurity ions dominates, and moreover, 3) the concentration of iron atoms satisfies $N_{\mathrm{Fe}} > N_{\mathrm{Fe}}^{*}$, since at smaller concentrations N_{Fe} all the donors are ionized, and hence are randomly distributed.

2.4. Analysis of the Mycielski ordering model

The idea of I. Mycielski² that the formation of a periodic structure of charged Fe^{3+} donors can serve as the cause of the diminished electron scattering upon doping HgSe with iron is per se elegant and highly attractive. However, one must establish how close this idea of formation of a strictly periodic lattice of impurities is to the conditions of experiment. We shall present a number of considerations that demonstrate that the model proposed by Mycielski amounts to an idealization of a real crystal containing defects, and cannot be directly used for interpretation (especially quantitative) of the experimental data.

We shall begin with the fact that, even as $T \rightarrow 0$, i.e., in the absence of thermal disorder, a lattice of ionized donors must be, as a rule, defective owing to the presence in the specimen of a certain number of shallow donors, which in a zero-gap semiconductor are all ionized and randomly distributed.

Further, we should pay attention to one important fact that compels us to view the appearance in HgSe:Fe of a strictly periodic Wigner structure of charged Fe³⁺ donors as not very probable. Let us estimate the ratio of the mean distance between charged donors $r_i \approx n^{-1/3}$ to the screening radius r_0 . For values of the parameters $m = 0.07m_0$, $\kappa = 20$, and $n = 4.5 \times 10^{18}$ cm⁻³, we find $r_i/r_0 \approx 1/3$. In such a situation, when $r_0 \leq r_i$ and screening weakens the Coulomb interaction between the Fe³⁺ ions, it is difficult to expect the formation of a strictly regular lattice of charged donors. We can speak only of a greater or lesser degree of ordering of the Fe³⁺ ions, say, of formation of islands of regular lattice with close-range order, or in other words, of a certain correlation in the spatial distribution of the Fe³⁺ ions.

We can point out a very cogent argument indicating that the model of Mycielski does not fit the experimental data. Actually, one of the fundamental anomalies of the properties of HgSe:Fe, namely, the increase in electron mobility μ_e with increasing iron content in HgSe in the lowtemperature region, begins already at concentrations $N_{\rm Fe} \approx N_{\rm Fe}^*$ (see Fig. 10), whereas, according to Mycielski, the strict periodicity in the system of Fe³⁺ ions, which leads to the increase in μ_e , can arise only as $N_{\rm Fe}/N_{\rm Fe^{3+}} \rightarrow \infty$. (As we have already noted in another limit, when all the atoms of iron in the crystal are triply charged, the aggregate of Fe³⁺ ions will be completely disordered.)

We should add to what we have said that the actual realization by Mycielski of his idea is not irreproachable. Let us turn to estimating one of the fundamental characteristics of the Mycielski model-the ordering temperature T_0 . This estimate (8) cannot claim great accuracy. Thus, in particular, it is assumed in deriving (8) that the free energy $\varepsilon_{\text{latt}}$ of the regular lattice of Fe³⁺ ions is the same at all temperatures and equal to the energy at T = 0. Thus in calculating $\varepsilon_{\text{latt}}$ one ignores the contribution of transitions of the Fe³⁺ ions at finite temperature from positions of the regular lattice to randomly distributed nodes of the rest of the crystal, i.e., the contribution of migration of "holes" through the crystal at $T \neq 0$.

Moreover, we note that the expression (8) for T_0 was derived in the approximation of the strong inequality $N_{\rm Fe} \ge n$. If the condition $N_{\rm Fe} \ge n$ is not satisfied, then the expression for the entropy $S = -k_{\rm B}n \ln(N_{\rm Fe}/n)$ used by Mycielski must be replaced with the following:

$$S = -k_{\rm B} \left[(N_{\rm Fe} - n) \ln \left(1 - \frac{n}{N_{\rm Fe}} \right) + n \ln \frac{n}{N_{\rm Fe}} \right]$$

Here the entropy is defined in the usual way as the logarithm of the number of distinguishable permutations n of the ions over the N_{Fe} nodes:

$$S = k_{\rm B} \ln \left[N_{\rm Fe}! / (N_{\rm Fe} - n)! n! \right].$$

Then we have

$$T_{0} = -\frac{1}{k_{\rm B}} \frac{n(\varepsilon_{\rm rd} - \varepsilon_{\rm latt})}{(N_{\rm Fe} - n)\ln[1 - (n/N_{\rm Fe})] + n\ln(n/N_{\rm Fe})}.$$
 (9)

(This expression goes over into (8) in the limit $N_{\rm Fe} \ge n$.)

Table I compares the values of T_0 calculated for several iron concentrations $N_{\rm Fe}$ by Eqs. (8) and (9) with the values of the temperatures T^* at which the experimental curves $\mu_e(T)$ for each concentration $N_{\rm Fe}$ merge (intersect) with the curve of $\mu_e(T)$ for $N_{\rm Fe}^* \approx 4.5 \times 10^{18}$ cm⁻³ (the values of T^* were determined from the experimental graphs of $\mu_e(T)$ from the work of Pool *et al.*¹⁶ with an accuracy of 5–10 K. Table I gives also the calculated values for T_0^* (see Fig. 15 below).

For a concentration of iron $N_{\rm Fe} = 6 \times 10^{18}$ cm⁻³ $(x \approx 4 \times 10^{-4})$ (at this concentration $N_{\rm Fe}$ the mobility $\mu_{\rm e}$ is appreciably higher than for $N_{\rm Fe}^* \approx n \approx 4.5 \times 10^{18}$ cm⁻³ (see Fig. 10), i.e., the mobility anomaly is already manifested), according to Eq. (8) we have $T_0 \approx 795$ K, while according to Eq. (9) $T_0 \approx 270$ K. Interpolation of the curves $\mu_{\rm e}(T)$ (see Fig. 11) for $N_{\rm Fe} \approx 8 \times 10^{18}$ cm⁻³ and $\approx 5 \times 10^{18}$ cm⁻³ shows that $T^* \sim 100$ K for $N_{\rm Fe} = 6 \times 10^{18}$ cm⁻³, i.e., appreciably smaller than the calculated values of T_0 .

As we see from Table I, on the whole we can speak of qualitative agreement between the calculated values of the temperatures T_0 of ordering of the Fe³⁺ ions and the experimental values of T^* . The appreciable discrepancy between the values of T_0 and T^* for low concentrations $N_{\rm Fe} \leq 8 \times 10^{18} \, {\rm cm}^{-3}$ can be primarily due to the fact that the degree of order in the system of Fe³⁺ ions must keep on decreasing with decrease in the ratio $N_{\rm Fe^{2+}}/N_{\rm Fe^{3+}}$: for small values of $N_{\rm Fe^{2+}}/N_{\rm Fe^{3+}}$ one can speak only of close-range order in the system of Fe³⁺ ions.

We note that, if the quantity T^* is actually determined by the ordering of the system of Fe³⁺ ions, then the role of this ordering affects the electron scattering up to concentrations $N_{\rm Fe} \approx 5 \times 10^{20}$ cm⁻³, since only at $N_{\rm Fe} > 5 \times 10^{20}$ cm⁻³ does the mobility $\mu_{\rm e}$ in HgFeSe at 4.2 K become less than in HgSe (see Fig. 10). The decrease in mobility in the concentration region $N_{\rm Fe} > 2 \times 10^{19}$ cm⁻³ (see Fig. 10) most likely is due to alloy scattering, while for sufficiently large values of $N_{\rm Fe}$ —due also to the increase in the number of interstitial atoms (see below for a discussion of possible reasons for the decline in $\mu_{\rm e}$ ($N_{\rm Fe}$).

Thus the analysis of the known experimental data and, in particular, the comparison of the calculated temperatures T_0 for breakdown of order in the distribution of Fe³⁺ ions with the experimental values of T^* at which the mobility anomaly vanishes, allows us to consider that the idea of formation of an ordered system of charged iron donors in HgFeSe crystals is fruitful: it makes it possible to explain this anomaly qualitatively.

Evidently a satisfactory interpretation of the anomalous $\mu_e(N_{Fe})$ dependence demands a further development of the theory. First, one should examine the influence on the mobility of the deviation of the system from periodicity, and second, a quantitative analysis is needed (i.e., a direct calculation) of the electron mobility μ_e as a function of the iron concentration N_{Fe} . In doing this it is important to take into account in the calculation the close-range interionic $(Fe^{3+}-Fe^{3+})$ correlations, since strict long-range order in the system of Fe³⁺ ions evidently does not exist. The following sections are devoted to describing the realization of this program of quantitative analysis.

2.5. Taking into account the disorder in the system of \mbox{Fe}^{3+} ions

According to the estimate given above, the gain in energy per ion upon ordering the system of Fe³⁺ ions, which is $\approx 12.5 \text{ meV}$, suffices for formation of a Wigner-like lattice at T = 0. However, in a real crystal, even at T = 0, the lattice of charged donors, as we have already noted, cannot be ideal. A lattice of Fe³⁺ ions close to regular might be formed only under the condition $N_{\text{Fe}^{2+}}/N_{\text{Fe}^{3+}} \rightarrow \infty$. However, in experiment the maximum mobility μ_e of electrons is observed in HgFeSe crystals in which the concentration $N_{\text{Fe}^{3+}}$ of ions is only severalfold smaller than the total concentration of iron atoms N_{Fe} (see Fig. 10).

Pool *et al.*¹⁶ proposed a more realistic model based on the same idea of a regular lattice of impurities. They introduced a random displacement of the lattice node of ionized donors from the position in an ideal lattice. The degree of disorder is described by the variance σ (mean deviation) of a

TABLE I.

$N_{\rm Fe}$, cm ⁻³	x	Т ₀ , К		<i>Τ</i> ₀ , K	Т, К
		(8)	(9)		
$\approx 8 \cdot 10^{18}$	5.10-4	≈ 308	≈ 135	~ 160	~ 100 - 105
≈ 1,5·10 ¹⁹	I · 10 ⁻³	≈ 132	≈ 76	≈ 100	≈ 80 − 90
≈ 5·10 ¹⁹	3·10 ⁻³	≈ 63	≈ 45	≈ 35	≈ 65 ~ 75
$\approx 8 \cdot 10^{19}$	5·10 ⁻³	≈ 52	≈ 40	≈ 10	~ 60 - 65
$\approx 1,5 \cdot 10^{20}$	1.10-2	≈ 43	≈ 33	0	≈ 35 - 40
$\approx 5 \cdot 10^{20}$	3.10-2	≈ 31	≈ 26	*)	

*) The $\mu_e(T)$ curves for $x \ge 3 \times 10^{-2}$ lie below the curve for $x = 3 \times 10^{-4}$ throughout the interval $4.2 \le T \le 300$ K.

Gaussian distribution, with σ being treated as an adjustment parameter that varies with the composition (x) of the crystals $Hg_{1-x}Fe_xSe$ and the temperature. In such a phenomenological model one calculates the relaxation time τ of the electrons for scattering by the ions of the impurity, and then calculates the mobility μ_e with allowance for scattering by phonons.

The relaxation time of the momentum of an electron, which is described by the wave function $\psi_k(\mathbf{r}) = \Omega^{-1/2} \exp(i\mathbf{kr})$, for scattering by a system of N impurity centers with coordinates \mathbf{r}_i can be written in the form

$$\frac{1}{\tau} = \frac{1}{4\pi^2 \hbar} \int |V(\mathbf{q})|^2 (1 - \cos\theta) S(q) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) \, \mathrm{d}\mathbf{k}'. \tag{10}$$

Here we have $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, θ is the angle between the vectors \mathbf{k} and \mathbf{k}' corresponding to the initial and final states (i.e., before and after scattering), $V(\mathbf{q})$ is the Fourier transform of the scattering potential, and $S(\mathbf{q})$ is the structure factor, which takes into account the spatial distribution of the scattering centers:

$$S(\mathbf{q}) = \frac{1}{\Omega} \langle \sum_{l,l'}^{N} \exp[i\mathbf{q}(\mathbf{r}_{l'} - \mathbf{r}_{l})] \rangle_{imp}, \qquad (11)$$

and Ω is the volume of the crystal. The double summation in (11) averaged over the coordinates of the impurity atoms is equal to the number of scattering centers N for a completely random system of these centers. But if the centers are arranged strictly periodically and Bragg scattering takes place, this double summation is proportional to $\Sigma \delta(\mathbf{q} - \mathbf{g}_m)$.

Now let the system of charged donors form an imperfect lattice in which the coordinates of the donors are $\mathbf{r}_{l} = \mathbf{R}_{l} + \Delta \mathbf{r}_{l}$; here the $\Delta \mathbf{r}_{l}$ are random deviations of the nodes of the impurity lattice from the strictly periodic positions \mathbf{R}_{l} . Then the double summation in (11) acquires the form

$$\langle \sum_{l,l'}^{N} \exp[iq(\mathbf{r}_{l'} - \mathbf{r}_{l})] \rangle_{imp} = N[1 - (\langle \exp(iq\Delta \mathbf{r}) \rangle_{imp})^{2}] + (\langle \exp(iq\Delta \mathbf{r}) \rangle_{imp})^{2} \frac{(2\pi)^{3}}{\Omega_{0}} \sum_{g_{m}} \delta(q - g_{m}).$$
(12)

Here Ω_0 is the volume of the unit cell of the regular lattice of ions having the coordinates \mathbf{R}_i .

The first term in (12) describes the incoherent scattering, i.e., the scattering by the randomly distributed ionized donors. The second term, which characterizes the coherent scattering of electrons by the regular lattice, equals zero since, as we have already noted, the Fermi wave vector $|\mathbf{k}_{\rm F}|$ is more than twofold shorter than the smallest reciprocallattice vector $|\mathbf{g}_{\rm m}|$, and processes of electron scattering with small wave vectors $|\mathbf{k}_{\rm F}| < |\mathbf{g}_{\rm m}|$ are ruled out.

It was proposed further that the lengths of the vectors $\Delta \mathbf{r}$ are described by the Gaussian distribution $P(\Delta r) = (1/\sqrt{2\pi}\sigma)\exp(-\Delta r^2/2\sigma^2)$, where the parameter σ is the displacement of the charged iron donor from its ideal position in the hypothetical strictly periodic lattice. Uncomplicated calculations show that

$$\langle \exp(iq\Delta r) \rangle_{imp} = \exp(-q^2 \delta^2/2).$$
 (13)

By using (11)-(13) we can derive from (10) an expression for the relaxation time of the momentum of an electron of the isotropic parabolic band in scattering by the screened Coulomb potential of the ions, which form a regular lattice with Gaussian disorder:

$$\frac{1}{\tau} = \frac{4me^4}{2\pi\kappa^2\hbar^3} \int_0^{2k_p} [1 - \exp(-q^2\sigma^2)] \frac{q^3 \mathrm{d}q}{(q^2 + r_0^{-2})^2}.$$
 (14)

Here r_0 is the screening radius and \varkappa is the permittivity.

The quantity σ is treated as a phenomenological parameter in terms of which the mobility is expressed. Equation (14) implies that, if $\sigma \rightarrow 0$, then $\tau^{-1} \rightarrow 0$. That is, the electrons do not undergo scattering in the case of a strictly periodic system of ionized donors. In the opposite limit of a completely random aggregate of impurities, i.e., for $\sigma \to \infty$, one can derive from (14) the ordinary Brooks and Herring expression for the relaxation of momentum. Upon using (14) and the relaxation times for scattering by acoustic, polar and nonpolar optical phonons, one can adjust the values of σ at each temperature in such a way that the calculated and measured values of the electron mobility coincide. An example of calculated variation of $\sigma(T)$ for a crystal having $x = 5 \times 10^{-4}$ is shown in Fig. 14. The dashed line corresponds to the mean distance $\langle r_{\rm Fe} \rangle$ between the donors. We see that σ is smaller than $\langle r_{\rm Fe} \rangle$ only when T < 150 K, while the values of σ at low temperatures are comparable to $\langle r_{\rm Fe} \rangle$ (at 4.2 K we have $\sigma/\langle r_{\rm Fe}\rangle \approx 0.5$, just as in a crystal having $x = 1 \times 10^{-3}$). This indicates that the order in the lattice of Fe^{3+} ions is far from ideal.

According to Pool *et al.*,¹⁶ we can treat the temperature T_0^* at which $\sigma = \langle r_{\rm Fe} \rangle$ as the temperature of ordering of the system of ionized donors. The basis of this conclusion is the dependence of T_0^* on $[\ln(N_{\rm Fe}/n)]^{-1}$ as constructed for specimens of varying iron content (Fig. 15). This variation is approximately linear, in agreement with Eq. (8), which was derived by Mycielski for the ordering temperature T_0 of the system of charged iron atoms Fe³⁺.



FIG. 14. Mean displacement of a Fe³⁺ ion as a function of the temperature for a crystal of Hg_{1-x}Fe_xSe with x = 0.0005.¹⁶



FIG. 15. Dependence of T_0^{\pm} on the ratio between the concentrations of electrons and of iron atoms.¹⁶

2.6. Influence of vibrations and nonideality of the Wigner lattice of charges on the temperature dependence of the electron mobility

The interpretation of the anomaly in the temperature dependence of the electron mobility in HgFeSe proposed by Ablyazov and Éfros²² merits attention. They propose that at high enough temperatures the electron mobility is restricted by the vibrations of the Wigner lattice of charges, while at low temperatures it is restricted by the nonideality of this lattice caused by the random distribution of the iron atoms.

Three temperature regions are studied. At temperatures exceeding the energy of Coulomb interaction of the charges (at their mean distance) $e^2(N_{Fe^2+})^{1/3}/\kappa$, the concentration of the charged Fe³⁺ centers at each point fluctuates in time, since the electrons, while undergoing thermal motion, pass from node to node. The probability of providing all donors with electrons is approximately the same. That is, it depends weakly on the surroundings, and is close to 1 - c, where $c = N_{Fe^{3+}}/N_{Fe}$. The correlation of charge in this case recalls the correlation in a weakly nonideal plasma. The electrons are scattered by the Gaussian fluctuations of the concentration of Fe³⁺ charges, whose size exceeds the mean distance between the charges. By using the calculated correlator of the fluctuations of the Fe³⁺ charges, the authors of Ref. 22 found the electron mobility

$$\mu_e = \mu_0 [\ln(1+b) - cb(1+b)^{-1}]^{-1}.$$
(15)

Here we have

$$\mu_{0} = \frac{3\pi}{2} \frac{\hbar}{z_{e}^{3}}^{3}, b = 4k_{F}^{2}r_{0}^{\prime 2} = \frac{T}{T_{k}}(1-c),$$

$$T_{k} = (9\pi)^{-1/3} \frac{e^{2}n^{1/3}}{x}.$$
(16)

The correlation radius $r'_0 = \left[\kappa k_B T / 4\pi e^2 n(1-c) \right]^{1/2}$ for $k_B T < \varepsilon_F$ is smaller than the electronic screening radius r_0 . The factor 1 - c in the expression for r'_0 describes the fact that, at small c, the concentration of screening charge carriers equals n, while as $c \rightarrow 1$ it amounts to (1 - c)n. For $\kappa = 20$ we have $T_k \approx 47$ K, and for $\kappa = 29.7$ we have $T_k \approx 32$ K. Thus the mobility increases logarithmically with decreasing temperature owing to the decrease in the correlation radius r'_0 . The fundamental difference between Eq. (15) and the Brooks-Herring formula for the scattering by randomly distributed impurities in a crystal

$$\mu_{\rm e} = \mu_0 [\ln(1+b_0) - b_0(1+b_0)^{-1}]^{-1} \quad (b_0 = 4k_{\rm F}^2 r_0^2)$$

consists in the fact that the correlation radius r'_0 enters instead of the screening radius r_0 in (15). Equation (15) is valid when $T \gg T_k$.

In the region $T \ll T_k$ the system of Fe³⁺ ions amounts to a strongly correlated Wigner liquid. At no temperature does the liquid transform to a crystal, owing to the random distribution of the donors throughout the crystal. However, we can assume that, when $T \ll T_k$ and $N_{\rm Fe} \gg N_{\rm Fe}^*$, the closerange order in the distribution of Fe³⁺ charges differs little from a crystalline distribution. When $T \ll T_k$ the amplitude of the thermal migration of charge over the iron atoms in the neighborhood of a given node, which is fixed by the arrangement of the neighboring charges, is small in comparison with the mean distance between charges. Under these conditions we can assume that the electrons are scattered mainly by dipoles. The negative pole of each dipole corresponds to a node of the ideal Wigner lattice, and the positive pole to a Fe^{3+} charge that is migrating in the vicinity of the given node. The mobility, which is limited by the scattering by the system of dipoles with randomly oriented moments (we assume that the moments of adjacent dipoles are not correlated with one another) is determined by the expression

$$\mu_{\rm e} = \mu_0 (4Dk_{\rm F}^2 r^{\rm T}(T))^{-1}.$$
 (17)

Here D is a numerical coefficient (for a parabolic band D = 1/3), and $\overline{r^2(T)}$ is the mean square of the separation of the dipole charges.

One must perform the calculations of $\overline{r^2(T)}$ in two temperature intervals in the region $T \ll T_k$. At relatively high temperatures $(r^2)^{1/2}$ considerably exceeds the mean distance between the impurity centers. This allows us to neglect the discreteness in the distribution of positive charge over the donors, and to assume that the Fe^{3+} ions form a Wigner lattice without long-range order on the background of the negative charge of the electrons, which is uniformly distributed in space. In this lattice no acoustic vibrations exist with frequencies exceeding Γ/\hbar (Γ is the width of the level), since \hbar/Γ is the time for transfer of charge from one node to another. For a narrow level $\Gamma \ll k_{\rm B}T$ the acoustic branches need not be considered at all, and one can assume in calculating $r^{2}(T)$ that the positive charge migrates in the statistical potential of the remaining charges forming the Wigner lattice. As a result we obtain the following expression for $\overline{r^2(T)}$ (see Ref. 22):

$$\overline{r^2(T)} = \frac{3}{4\pi} \left(\frac{3}{\pi}\right)^{1/3} \frac{T}{T_k} n^{-2/3}.$$
(18)

It is noteworthy that $\overline{r^2} = 9r_0^{\prime 2}$ as $c \to 0$.

We have the following expression for the mobility in the interval of relatively high temperatures in the region $T \ll T_k$:

$$\mu_{\rm e} = \mu_0 \left[D\left(\frac{3}{\pi}\right)^{4/3} \frac{T}{T_{\rm k}} n^{-2/3} \right]^{-1}.$$
 (19)

We see from (18) that $(\overline{r^2})^{1/2}$ is comparable to the mean distance between donors $N_{\text{Fe}}^{-1/3}$ for $T \sim T_k c^{2/3} \equiv T'_k$.

In the interval of lower temperatures, i.e., for $T \leq T'_k$, the spatial distribution of Fe³⁺ ions corresponds to minimum energy. For small c and $T \leq T'_k$ we have

$$\overline{r^{2}} = \left(\frac{3}{4\pi}\right)^{2/3} \Gamma\left(\frac{5}{3}\right) N_{\rm Fe}^{-2/3}.$$
 (20)

Upon substituting (20) into (17), we obtain the following expression for the region $T \leq T'_k$:

$$\mu_{\rm e} = \mu_0 \left[4D \left(\frac{3}{4\pi} \right)^{2/3} \Gamma \left(\frac{5}{3} \right) N_{\rm Fe}^{-2/3} \right]^{-1}.$$
 (21)

Thus, in the region $T < T'_{k}$ the electron mobility μ_{e} in crystals of $Hg_{1-x}Fe_{x}$ Se need not depend on T, and must be proportional to $x^{2/3}$. Due to the reduction of the role of the occasional distribution of the iron impurity atoms asN_{Fe} . concentration is increasing.

To compare the results of calculation with the experimental data for HgFeSe crystals having a nonquadratic dispersion law for electrons, one should take into account the nonparabolicity of the conduction band. Without reproducing the intermediate stages of the calculation,²² we shall give its results. An interpolation formula was devised for the electron mobility that merges at $T \sim T_k$ the formulas for the temperature regions $T \gg T_k$ and $T \ll T_k$. Here it was necessary to introduce a certain adjustment parameter β . Another adjustment parameter μ^* was introduced to take into account the temperature-independent scattering by neutral centers, which competes with the scattering by charged impurities. The dependence of the mobility for scattering by neutral centers on the iron content has the form

$$\mu_{\rm N}(x) = \frac{\mu^*}{x(1-x)}.$$
 (22)

The experimental values of the electron mobility are compared with the interpolation quantities

$$\mu_{\rm int}(x, T) = (\mu_{\rm e}^{-1}(T, \beta) + \mu_{\rm N}^{-1}(x))^{-1}.$$
(23)

Here $\mu_e(T,\beta)$ is the mobility in the case of scattering by the system of Fe^{3+} ions that becomes ordered with the temperature (for a parabolic band the formula for $\mu_e(T,\beta)$ has the form (15), where b must be replaced by an expression containing the temperature T and the parameter β). Analysis shows that the parameter μ^* varies from 8×10^2 cm²/(V·s) for $c = 6 \times 10^{-3}$ to $60 \text{ cm}^2 / (\text{V} \cdot \text{s})$ for $c = 10 \times 10^{-1}$. Comparison of the results of calculation with the measurements of Pool et al.¹⁶ of the temperature dependences of the electron mobility for seven specimens of $Hg_{1-x}Fe_xSe$ having $5 \times 10^{-4} \le x \le 5 \times 10^{-2}$ (here one subtracts from the experimental values of μ_e the calculated contribution of phonon scattering) showed that satisfactory agreement of theory with experiment is obtained with a value of the parameter $\beta = 0.02$ and with the variation of the value of μ^* given above as a function of the variation of c.

The idea of Ablyazov and Éfros²² of explaining the anomaly of the temperature dependence of the electron mobility $\mu_e(T)$ in HgFeSe by the idea that the magnitude of μ_e is limited at sufficiently high temperatures by the thermal vibrations of the regular lattice of charges, and at low temperatures by the nonideality of this lattice caused by the random distribution of the impurity atoms, is interesting *per se*. Unfortunately the quantitative interpretation of the experimental $\mu_e(T)$ dependences cannot claim great cogency, since here one must use two adjustment parameters: μ^* and β .

2.7. Quantitative analysis of the variation of the electron mobility upon doping HgSe with iron

Thus we have seen that the model of Mycielski,² which is based on the idea of strict ordering of the charges on the iron donors in HgSe:Fe, is not adequate to the situation in real crystals and therefore cannot be used for a quantitative explanation of the experimentally observed anomalous behavior of the electron mobility and other electronic characteristics. Within the framework of this model it was possible to obtain only qualitative agreement between the estimated ordering temperature T_0 and the temperature T^* at which the mobility anomaly vanishes (see Table I). Yet the magnitudes of the mobility and the Dingle temperature were not calculated. The mobility calculations of Pool et al.¹⁶ and of Ablyazov and Éfros²² for more realistic models than the Mycielski model do not seem satisfactory enough, in particular because free adjustment parameters are used in them for the quantitative description of the experimental data.

One important question has remained outside the framework of the qualitative treatment of Mycielski,² and which was not explained in the studies of Pool *et al.*¹⁶ and of Ablyazov and Éfros:²² why does the mobility increase $\mu_e(N_{\rm Fe})$ begin already at a low iron content in HgSe, when the concentrations $N_{\rm Fe^{3+}}$ and $N_{\rm Fe^{2+}}$ are comparable, which according to the Mycielski model should occur only as $N_{\rm Fe^{2+}}/N_{\rm Fe^{3+}} \rightarrow \infty$? Evidently here we need a quantitative treatment that takes into account the presence of correlations of the spatial distribution of the charged donors caused by the ordering of the closest environment of a given ion. The ordering arises from the Coulomb interaction between the charges.

Such calculations have been recently performed by Wilamowski *et al.*²³ Their idea is rather simple: one takes into account the interaction between closest charged donors. In essence this idea goes back to the studies of Arapov *et al.*^{1a} and Brandt *et al.*,^{1b} who studied the interaction of closelying charged donors and acceptors, whereby donor-acceptor pairs (dipoles) are formed. Such a correlated distribution of scattering centers leads to an increase in the electron mobility. The authors of Ref. 23 used two methods of calculations: 1) one treats a simple analytical model that takes into account only pair interactions between closest charges, and 2) one performs a numerical simulation of the system of donors. Let us describe briefly the results of this study.

Let us study a system of randomly distributed iron donors at T = 0, part of which are occupied by electrons (Fe^{2+}) , and part are ionized (Fe^{3+}) . Owing to the Coulomb repulsion of the charges on the ionized donors, a region exists around each Fe⁺³ ion depleted in other Fe³⁺ ions (the electrons will first of all populate the Fe³⁺ ions close to which other ionized donors exist). It is reasonable to assume for T = 0 that within such a region of volume $\Omega_c = 4\pi r_c^3/3$ (we assume that the region is spherical) there are no other ionized donors at all. The degree of ordering of the system of ionized donors can be described by using the pair correlation function g(r)—a function well known in statistical physics, which characterizes the deviation from real spatial disorder in the distribution of ions. For small distances $r < r_c$ between ions we have g(r) = 0, which implies the absence for a given Fe³⁺ ion of another ionized neighbor within a correlation sphere of radius r_c . For $r \ge r_c$ the function is g(r) = 1, which corresponds to a random distribution of ionized donors outside the correlation sphere. To make it possible to solve the problem analytically, one approximates the pair correlation function g(r), which describes the probability of finding an ionized donor at the distance r from a given ionized donor, by the step function

$$g(r) = \theta(r - r_{\rm c}) = \begin{cases} 0 & \text{for } r < r_{\rm c}, \\ 1 & \text{for } r \ge r_{\rm c}. \end{cases}$$
(24)

When we choose the correlation function in this form, we neglect the correlations in the distribution of charged donors that are separated from one another by distances exceeding r_c , and treat only the short-range correlations. It is pertinent to recall again that the correlations being discussed arise from the redistribution of donor electrons over the possible donor nodes, rather than from displacement of the iron impurity atoms themselves. It is easy to write an equation that allows us to express the correlation radius r_c in terms of the concentrations $N_{\rm Fe^{3+}} = n$ and $N_{\rm Fe}$. Upon noting that the volume Ω_c equals the mean volume per ionized donor $(1/N_{\rm Fe^{3+}})$ decreased by a factor that describes the probability $1 - P(\Omega_c)$ that at least one iron atom lies inside the volume Ω_c , we have

$$N_{\rm Fe^{3+}}\Omega_{\rm c} = 1 - P(\Omega_{\rm c}). \tag{25}$$

Thus, upon neglecting the overlap of correlation spheres, i.e., assuming that the concentration of Fe³⁺ ions is sufficiently small and the correlation radius r_c is relatively small, we obtain the following equation for the Poisson distribution of donors $P = \exp(-\Omega_c N_{\rm Fe})$, which enables us to find r_c :

$$\frac{4}{3}\pi r_{\rm c}^3 N_{\rm Fe^{3+}} = 1 - \exp\left(-\frac{4}{3}\pi r_{\rm c}^3 N_{\rm Fe}\right). \tag{26}$$

Upon defining in this way the pair correlation function g(r), we can calculate the electron mobility. By using the Fourier transform of g(r), $g(\mathbf{q}) = 1/\Omega_c \int g(\mathbf{r}) \times \exp(-i\mathbf{q}\mathbf{r}) d\mathbf{r}$, which takes into account the distribution of the scattering centers, and performing relatively uncomplicated transformations (one must transform from Cartesian to spherical coordinates), we find the structure factor [see (11)]:

$$S(q) = 1 + 4\pi N_{\text{Fe}^{3+}} \int (g(r) - 1) \frac{r \sin(qr)}{q} dr.$$
 (27)

By using S(q) we can calculate the relaxation time τ of the momentum for scattering by the ionized impurities [see (10)]:

$$\frac{1}{\tau} = \frac{m(\varepsilon_{\rm F})}{6\pi\hbar^2} \int_0^{2k_{\rm F}} |V(q)|^2 S(q) q^3 \,\mathrm{d}q;$$
(28)

Here V(q) is the matrix element of the screened Coulomb potential. The results of calculating the mobility as a function of the iron concentration are shown in Fig. 10 by the solid line. We see that the $\mu_e(N_{Fe})$ curve agrees quite satisfactorily with the experimental data up to concentrations $N_{Fe} \approx 2 \times 10^{19}$ cm⁻³, where the measured mobility values begin to decline upon further increase in N_{Fe} . The described theoretical model, which takes into account the short-range correlations, predicts a considerable increase in the mobility $\mu_e(N_{Fe})$ even in the region $0 < N_{Fe} - N_{Fe^{3+}} \ll N_{Fe}$, where the formation of a strictly periodic structure of charged donors with long-range order is unlikely in practice. The saturation of the calculated $\mu_e(N_{Fe})$ curve in the region of high iron concentrations involves taking into account only shortrange correlations in the calculation.

The calculations of the electron mobility μ_e in the model of short-range correlations enabled a quantitative explanation of the results of measuring the mobility in specimens of HgFeSe subjected to hydrostatic pressure. Figure 16 shows the experimentally found $\mu_e(\mathcal{P})$ relationships for five specimens of HgSe:Fe, whose fundamental parameters are given in Table II.²⁵

We see from Fig. 16 that, for specimens 1 and 2, for which $N_{\rm Fe} < N_{\rm Fe}^*$, the $\mu_e(\mathcal{P})$ relationships agree with the results of calculation¹⁵ (solid lines) based on the assumption that the predominant mechanism of electron scattering is scattering by the randomly distributed ionized donors. The weak dependence of the calculated values of μ_e on the pressure \mathcal{P} involves the decrease in the effective mass *m* of the electrons caused by the decrease in the energy gap $|\varepsilon_g|$ between the s and p bands. Yet for specimens 3–5, for which $N_{\rm Fe} \gtrsim N_{\rm Fe}^*$, the $\mu_e(\mathcal{P})$ curves calculated according to Ref. 15 are very far from the experimental points.

Figure 17 shows the results of measuring the mobility $\mu_e(\mathscr{P})$ for specimen 4 having $N_{\rm Fe} > N *_{\rm Fe}$ and the theoretical curves calculated with (solid curve) and without (dashed curve) taking into account the interionic interactions.²⁴ We see that the solid curve, which was obtained on the basis of the model of short-range correlations, agrees



FIG. 16. Electron mobility as a function of the hydrostatic pressure at 4.2 K for five specimens of HgSe:Fe.²⁵ Numbers on the curves are the numbers of the specimens, whose parameters are given in Table II. Solid curves—results of calculation for scattering of electrons by the disordered system of impurity ions.

TABLE II.

Specimen number	$\frac{N_{\rm Fe}}{10^{18} {\rm cm}^{-3}}$	$p \cdot 10^{-18}, \mathrm{cm}^{-3}$ $\mathcal{P} = 0, T = 4.2 \mathrm{K}$	$\mathcal{P}_{e}, cm^{2}/(V \cdot s)$ $\mathcal{P} = 0, T = 4.2K$
1	1	1,40	58 000
2	2	3,14	35 600
3	4	3,96	38 000
4	8	4,70	56 300
5	20	4,75	88 000

well with the experimental data. What is the reason for the increase in mobility of electrons in HgFeSe specimens with $N_{\rm Fe} > N_{\rm Fe}^*$ subjected to hydrostatic pressure?

A quite evident reason for the increase in mobility as a function of the pressure is the decrease in the effective mass $m(\mathscr{P})$ in zero-gap semiconductors having $\varepsilon_g < 0$: $(dm/d\mathscr{P}) < 0$. This is reflected by the dashed line in Fig. 17. However, the influence of the hydrostatic pressure on the concentration of band electrons is more substantial. As we have already noted, under the action of pressure in HgFeSe, the number of band states below the resonance level of iron decreases. If $N_{\rm Fe} \gtrsim N_{\rm Fe}^*$ and the Fermi level is fixed, the concentration *n* of electrons decreases (see Fig. 6). Since the system of ionized Fe³⁺ donors is not strictly periodic, a certain contribution to the electron scattering is introduced by the Fe³⁺ ions distributed in disorder, and the decrease in the concentration of these scattering centers $n = N_{\rm Fe^{3+}}$ leads to an increase in mobility.

A more important factor that influences the magnitude of the electron mobility under the action of pressure is the increase in the degree of ordering of the Fe³⁺ ions (more exactly, their correlated distribution) owing to the enhanced role of the interionic Coulomb interaction as the ratio $N_{\rm Fe^{3+}}/N_{\rm Fe^{2+}}$ decreases. It is precisely taking account of the correlated spatial distribution of the Fe³⁺ ions that leads to good agreement of calculation with experiment for concentrations $N_{\rm Fe} > N_{\rm Fe}^{*}$ (solid line in Fig. 17). In the language of the model of short-range correlations, the increase in mobility with the pressure $\mu_{e}(\mathscr{P})$ can be interpreted as resulting from a decrease in the overlap of the adjacent correlation spheres upon decrease in concentration of Fe^{3+} ions, which improves the conditions of applicability of the model. Therefore the theory describes better the mobility in specimens of HgFeSe subjected to pressure than in specimens at atmospheric pressure $\mathcal{P} = 0$ (cf. Figs. 17 and 10).



FIG. 17. Variation of the electron mobility under pressure for a specimen of HgSe:Fe with $N_{Fe} = 8 \times 10^{18}$ cm⁻³ at 4.2 K.²⁴ Dashed line—result of calculation without allowance for interionic interaction; solid line—result of calculation with allowance for interionic interaction in the model of short-range correlations.

We can easily convince ourselves that the increase in mobility with the pressure $\mu_e(\mathscr{P})$ is directly implied by the expression for the relaxation time τ in (28). Actually, when $N_{\rm Fe} > N_{\rm Fe}^*$, the Fermi energy $\varepsilon_{\rm F}(\mathscr{P})$ is constant. Since a zero-gap semiconductor has $dm/d\mathscr{P} < 0$, then for a quadratic dispersion law $\varepsilon_{\rm F} \propto k_{\rm F}^2/2m$ (for a nonquadratic isotropic dispersion law of the Kane type, the conclusion following below is also valid), we find that the derivative $dk_{\rm F}/d\mathscr{P} < 0$. Then it is evident from (28) that $d\tau^{-1}/d\mathscr{P} < 0$. That is, the mobility $\mu_e = e\tau/m$ increases as a function of the pressure.

It is of interest to compare the results of calculating the Dingle temperature $T_{\rm D}$ with the experimental data. Figure 18 shows the values of $T_{\rm D}$ for a crystal of Hg_{1-x} Mn_xSe:Fe with x = 0.0025 as found from the dependence of the amplitudes of Shubnikov-de Haas oscillations on the magnetic field and the calculated values of $T_{\rm D}$ for disordered and correlated (i.e., with account taken of the interionic interaction) systems of ionized Fe³⁺ donors.²⁷ We see that the anomalously small values of $T_{\rm D}$ at $N_{\rm Fe} \sim 10^{19}$ cm⁻³ can be explained by taking into account the interaction between the Fe³⁺ ions.

By using the pair correlation function, the gain in energy per ion $\varepsilon_{rd} - \varepsilon_{latt}$ was calculated²³ for formation of a correlated configuration of Fe^{3+} ions [cf. (6) and (7)]. Figure 19 shows the results of calculation for three concentrations of iron. We see that this gain is maximal at $N_{\rm Fe} = 2 \times 10^{19}$ cm^{-3} . The relatively small difference between the curve for $N_{\rm Fe} = 2 \times 10^{19}$ cm⁻³ calculated in the model of short-range correlations and the dashed curve found in the Mycielski model for an ideally periodic system of ionized donors in a fcc lattice $(N_{\rm Fe}/N_{\rm Fe^{3+}} \rightarrow \infty)$ proved to be unexpected. In the model of short-range correlations also the concentration of band electrons n was calculated²³ as a function of $N_{\rm Fe}$ (from the minimum of the total energy of the system of band and impurity electrons $d\varepsilon_{tot}/dn = 0$). The calculated $n(N_{Fe})$ relationship agrees well with the experimental data shown in Fig. 3.

In addition to the relatively simple model of shortrange correlations, the authors of Ref. 23 used the method of numerical simulation of the system of donors to calculate the



FIG. 18. The Dingle temperature for $Hg_{1-x}Mn_x$ Se:Fe (x = 0.0025) as a function of the iron concentration at 4.2 K.²⁷ The solid line " T_D , disorder" was calculated without taking account of interionic interactions; the line " T_D , order" was calculated with account taken of these interactions.



FIG. 19. Energy gain upon formation of a correlated system of Fe^{3+} ions in HgSe:Fe.²³ The solid lines were calculated using the model of shortrange correlations; the points are the results of numerical simulation; the dashed line was calculated under the assumption of a regular fcc lattice of ionized donors (model of Mycielski²).

electron mobility and other characteristics, taking into account the Coulomb interaction between the Fe^{3+} ions. In a cube of finite dimensions a random distribution of donors was assigned, part of them ionized. The number of donors was varied from 300 to 1000 (320 for $N_{\rm Fe} = 5 \times 10^{18}$ cm $^{-3}$ and 900 for $N_{\rm Fe} = 5 \times 10^{19}$ cm⁻³). This ensures the absence of an influence of the finite dimensions of the system. Further, a minimum was sought of the energy of Coulomb interaction of the system of donors [see (4)] by simulating the charge transfer among the donors (electron migration) that yields the energy gain $\varepsilon_{rd} - \varepsilon_{latt}$. The points in Fig. 19 show the results of the numerical calculations of $\varepsilon_{rd} - \varepsilon_{latt}$. We see that they either fully coincide or are very close to the solid curves calculated in the model of short-range correlations. This allows us to conclude that the model of shortrange correlations constitutes a simple and sufficiently reliable method of calculating the energy gain $\varepsilon_{rd} - \varepsilon_{latt}$ in the presence of interionic correlations.

If one knows the energy of the ground state of the system of donors and averages over many specimens (this was done for 32 specimens), one can determine the pair correlation function g(r) and use it to calculate the electron mobility. The calculated function g(r) is shown in Fig. 20,²⁷ where the step function (24) is drawn for comparison. The results of calculating the mobility are shown by the dot-dash line in Fig. 10. The mobility found in this way is larger than the values of μ_e obtained by using the step function g(r). Apparently this difference reflects the lack of account taken in the short-range-correlation model of correlations of charges separated from one another by distances exceeding r_e .

Also the single-particle density of impurity states was calculated by the method of numerical simulation. It was established that the populated and free states are separated by a Coulomb gap (near the Fermi level), which becomes more distinctly marked upon increasing the iron concentration $N_{\rm Fe}$.

Thus the correlation model allows one to describe quantitatively the fundamental features of the electronic properties of the HgSe:Fe system-the variation of the concentration of electrons, their mobility, and the Dingle temperature as functions of the iron content in HgSe, the temperature,



FIG. 20. Pair correlation function in the model of short-range correlations (dotted line) and as found by numerical simulation (solid line).²⁷ $N_{\rm Fe^{3.+}} = 4.3 \times 10^{18} \, {\rm cm}^{-3}$, $N_{\rm Fe} = 8.8 \times 10^{18} \, {\rm cm}^{-3}$.

and the hydrostatic pressure. All these features stem from the appearance of close-range order in the system of partially ionized iron impurities. However, within the framework of the model being discussed, one cannot understand the reason for the decline in mobility at iron concentrations exceeding $N_{\rm Fe} \approx 2 \times 10^{19}$ cm⁻³. According to this model one should rather expect that, as the total iron concentration increases, the ordering of the Fe³⁺ ions should improve and the system should approach ever closer to a regular Wignerlike lattice, and hence, the electron scattering should decline.

The decline in electron mobility in HgFeSe crystals having a high iron content can be explained either by hybridization effects or by a contribution from other scattering mechanisms. If the hybridization of donor states with band states or with other donor states were substantial, this would be a system of variable valency (the distribution of point charges would vary with time), in which the interionic interaction would play a weaker role and the degree of ordering of the ions would be smaller. Yet if any other scattering mechanism is responsible for the decline in mobility with increasing $N_{\rm Fe}$, we can expect that the ordering of the system of ionized Fe³⁺ donors should be maintained.

We have already said above that the effects of hybridization in HgFeSe are very weak. The broadening Γ of the level owing to p-d hybridization should be less than 0.01 meV according to EPR measurements. On the other hand, to explain the decline in the mobility μ_e with increasing N_{Fe} , one must adopt as the broadening parameter the value 0.1 meV, which exceeds by an order of magnitude the value found by EPR measurements. Since the natural broadening Γ of the level is at least three orders of magnitude smaller than the energy of interionic Coulomb interaction (which is ~10 meV), p-d hybridization cannot cause a breakdown in the correlated distribution of the ionized donors, and hence cannot be the reason for the decline in mobility.

Interdonor hybridization also cannot cause the decline in mobility because it is small owing to the rather strong localization of the d-state of iron. Qualitative analysis of the amplitude of the EPR signal and its variation with the iron concentration showed²⁶ that, for $N_{\rm Fe} = 4 \times 10^{19}$ cm⁻³ the natural broadening of the level owing to interaction among the donors is $\Gamma \approx 3 \times 10^{-4}$ meV. That is, it is approximately five orders of magnitude smaller than the energy of interionic interaction. This implies that the state of iron is rather strongly localized and interdonor hybridization is practically absent. Therefore we are left to assume that certain additional mechanisms of electron scattering are responsible for the decline in μ_e ($N_{\rm Fe}$) for $N_{\rm Fe} > 2 \times 10^{19}$ cm⁻³.

We can point out two very substantial scattering mechanisms that can generally play a role in HgSe:Fe crystals with increasing iron content: scattering by spin disorder and alloy scattering. Scattering by spin disorder is due to the exchange coupling of the spin of a band electron and the localized spin of an iron ion. As we have already noted above, the experimental data of measurements of the magnetic susceptibility^{3,6-10} indicate that the ground state of the Fe^{2+} ion in a tetrahedral crystal field is a magnetic singlet (the first excited configuration amounts to a triplet⁷). In this case electron scattering with spin reversal should play no role.

As regards the Fe³⁺ ions, the EPR measurements⁴ showed that the ground state amounts to an orbital singlet with sixfold spin degeneracy. The local symmetry is cubic, and the spin splittings are distinctly marked. Analysis of the temperature dependence of the width of the EPR lines allows us to conclude that, in weakly doped specimens of HgSe: Fe and at high enough temperatures (T > 20 K), the EPR line due to Fe^{3+} ions is broadened by spin-flip collisions with band electrons. An estimate of the relaxation time of spin-flip scattering $au_{
m sf}$ for a specimen with $N_{
m Fe}^{3\,+}$ $= 4.5 \times 10^{18}$ cm⁻³ and for a width of EPR line of 30 G yielded $\tau_{\rm sf} = 2 \times 10^{-11}$ s, which is only severalfold greater than the relaxation time of the momentum $\tau = 4 \times 10^{-12}$ s found from the mobility $\mu_e = 10^5 \text{ cm}^2/(\text{V}\cdot\text{s})$. On these very shaky grounds (i.e., on the basis of the closeness of the values of τ_{sf} and τ), Wilamowski²⁶ concluded that spin-flip scattering of band electrons by Fe³⁺ ions plays a substantial role in HgSe:Fe. However, it is fully evident that this process cannot be responsible for the decline in mobility μ_e with increasing concentration $N_{\rm Fe}$, since the value of $N_{{\rm Fe}^{3\,+}}$ in the region $N_{\rm Fe} > N_{\rm Fe}^*$ remains invariant. There are also no grounds for assuming, as the author of Ref. 26 does, that in specimens of HgSe strongly doped with iron the spin-flip scattering of band electrons by Fe^{2+} ions is perhaps dominant, since, as we have already said, according to the known experimental data the ground state of neutral Fe^{2+} ions is a magnetic singlet.

Now we shall take up the question of another possible mechanism of electron scattering in HgSe crystals having a high iron content, involving the nonideality (defect content) of the lattice. Studies of the Mössbauer effect by ⁵⁷Fe atoms in HgSe²⁸ confirmed that most of the iron ions are divalent and serve as neutral donors, while only a small fraction [(6 \pm 1) \times 10 $^{18}\,$ cm $^{-3}$] of these ions are trivalent, independently of the total iron concentration $N_{\rm Fe}$. It was shown that the local cubic symmetry of the iron ions is distorted either by static axial deformations or by dynamic Jahn-Teller deformation. The degree of deformation increases with increasing iron content in the specimen. With such a lowering of the local symmetry, the alloy scattering is caused not only by the difference in potentials of the ion cores of Hg^{2+} and Fe^{2+} , but also by local stresses in the neighborhood of an Fe^{2+} ion.

We also cannot rule out the possibility of appearance of interstitial atoms at high iron concentrations $(\gtrsim 10^{20} \text{ cm}^{-3})$, which can serve as additional sources of electron scattering. The situation at present is that the most likely mechanisms of electron scattering that diminish the mobility are alloy scattering, acted on by local deformations, and perhaps, scattering by interstitial iron atoms. In contrast to resonance scattering, these two mechanisms do not violate the order in the spatial distribution of triply charged iron ions, and hence do not influence the increase in mobility of electrons in HgSe:Fe crystals as compared with HgSe:Ga. As we see from Fig. 10, the electron mobility in HgSe:Fe crystals exceeds the theoretically calculated values of μ_e [which coincide with the mobilities in HgSe with shallow impurities (Ga, In) up to their solubility limit] up to iron concentrations $N_{\rm Fe} \approx 5 \times 10^{20}$ cm⁻³.

To summarize the analysis of the electronic properties of zero-gap HgSe:Fe crystals, we can state with assurance that the interaction between the charged Fe^{3+} donors plays a very important role. Precisely because of this interaction, the spatial distribution of Fe^{3+} ions is correlated, which in turn substantially influences a number of electronic characteristics—electron mobility, Dingle temperature, etc.

II. HgSe:Cr CRYSTALS

The question is of undoubted interest of whether other transition elements form resonance donor levels in HgSe. According to Fig. 1 the location of the energy levels of Cr, Co, and Ni should be high enough, just like the location of the iron level. Gluzman et al.29 studied the fundamental kinetic characteristics of crystals of HgSe:Cr. For chromium $(3d^{5}4s^{1})$ the ionic radii of Cr^{2+} and Cr^{3+} are 0.83 Å and 0.64 Å, i.e., about the same as for Fe^{2+} (0.80 Å) and Fe^{3+} (0.67 Å). The electronegativities of the ions Cu²⁺ (1.4) and Cu^{3+} (1.5) are also close to the corresponding values for Fe^{2+} and Fe^{3+} . Therefore we can suppose that chromium atoms, just like iron atoms, can be substitution impurities in HgSe. From the data of resistance measurements, the Hall effect, and the Shubnikov-de Haas oscillations of the transverse magnetoresistance of crystals of $Hg_{1-x}Cr_xSe$ $(5 \times 10^{-5} \le x \le 3 \times 10^{-2})$, the temperature dependences of the concentration and mobility of electrons, their effective masses, and the Dingle temperatures were determined.

Figure 21 shows the dependence of the electron concentration *n* on the concentration of chromium atoms $N_{\rm Cr}$. Despite a certain scatter in the values of *n*, we can state that the electron concentration stabilizes at the level of $n \approx 2.5 \times 10^{18}$ cm⁻³. The independence of the electron concentration *n* of the concentration of chromium atoms $N_{\rm Cr}$ when $N_{\rm Cr} \gtrsim 5 \times 10^{18}$ cm⁻³ warrants concluding that, just as in HgSe:Fe, the Fermi level ε_F is fixed at the donor level of chromium.

The effective masses of the electrons determined from the temperature dependences of the amplitudes of the Shubnikov oscillations differ somewhat for specimens of differing chromium content, and lie in the range $(0.05-0.07) m_0$. If one knows the effective mass and concentration of the electrons and assumes, as for HgSe:Fe, that the conduction band near the Fermi level is weakly perturbed by the chromium atoms, i.e., that the form of the band is the same as in HgSe,



FIG. 21. Electron concentration as a function of the concentration of chromium atoms in HgSe:Cr at 4.2 K. 29

one can find $\varepsilon_{\rm F}$, and this means, also the position of the chromium level $\varepsilon_{\rm Cr}$ with respect to the edge of the band. An estimate shows that $\varepsilon_{\rm F} \approx 0.16$ eV. That is, the chromium level $\varepsilon_{\rm Cr} \approx \varepsilon_{\rm F}$ lies closer to the edge of the band than the iron level. This agrees with the location of the donor levels of chromium and iron shown in Fig. 1.

For all the studied specimens of HgSe:Cr a certain decrease in the electron concentration n was observed upon increasing the temperature from 4.2 to 300 K. The greatest decrease in n(T) occurs in a specimen having a chromium content $N_{\rm Cr} = 5 \times 10^{18}$ cm⁻³. Such a n(T) relationship can be associated, as in the case of HgSe:Fe crystals, with a change in the distance of the d-level of chromium, which is not genetically associated with either the conduction band or the valence band, from the edge of the band of p symmetry, which shifts with the temperature (cf. Fig. 7). This is precisely why the energy $\varepsilon_{\rm Cr}$ becomes a function of the temperature.

Figure 22 shows the experimentally found dependence of the electron mobility μ_e on the chromium concentration $N_{\rm Cr}$ at 4.2 K. For two specimens with $N_{\rm Cr} \approx 5 \times 10^{18}$ cm⁻³ the mobility reaches values of 4.5×10^4 and 5.3×10^4 cm²/(V·s), which appreciably exceed the value $\mu_e \approx 2.5 \times 10^4$ cm²/(V·s) for specimens of HgSe:Ga having about the same concentration of electrons. The magnitudes of the mobility for specimens of HgSe:Ga are rather close to the values of μ_e calculated under the assumption of scattering by the disordered system of impurity ions. For a specimen of HgSe:Cr with $N_{\rm Cr} = 1 \times 10^{18}$ cm⁻² the measured mobility $\mu_e \approx 4 \times 10^4$ cm²/(V·s) differs insignificantly from either the magnitude of μ_e for HgSe:Ga or the calculated value $\mu_e = 4.6 \times 10^4$ cm²/(V·s).

The experimentally established increase in the electron mobility upon doping HgSe with chromium serves as evidence that, first, the chromium atoms, like iron, form a donor level in HgSe on the background of the conduction band and exist in two states: Cr^{2+} and Cr^{3+} . Second, the Coulomb interaction between the Cr^{3+} ions leads to a correlated spatial distribution of them, and hence diminishes the electron scattering.

Figure 23 shows the temperature dependences of the electron mobility for several specimens of HgSe:Cr. For specimens having a chromium content $N_{\rm Cr} \approx 5 \times 10^{18}$ cm⁻³,



FIG. 22. Electron mobility as a function of the concentration of chromium ions in HgSe:Cr at 4.2 K.²⁹ Dashed line—result of calculation for scattering by a disordered system of impurity ions.

for which the values of the mobility μ_e at 4.2 K appreciably exceed the values of μ_e for specimens with other concentrations of chromium (see Fig. 22), the mobility increases monotonically with decreasing temperature to 4.2 K, as for the corresponding specimens of HgSe:Fe (cf. Figs. 11–13). This fact also evidences the appearance of spatial ordering in the system of ionized Cr³⁺ donors.

The Dingle temperature determined for the studied specimens of HgSe:Cr from the Shubnikov-de Haas oscillations has a minimal value at the concentration $N_{\rm Cr} \approx 5 \times 10^{18}$ cm⁻³, i.e., at the value of $N_{\rm Cr}$ at which the mobility is a maximum.

Thus the features of the $n(N_{\rm Cr})$, $\mu_e(N_{\rm Cr})$, $T_D(N_{\rm Cr})$, $\mu_e(T)$ and n(T) dependences are analogous in general outline to the corresponding dependences established for HgSe:Fe crystals. The weaker increase in the mobility upon varying the concentration $N_{\rm Cr}$ from 1×10^{18} to 5×10^{18} cm⁻³ than the corresponding increase in $\mu_e(N_{\rm Fe})$ in HgSe:Fe at 4.2 K and the somewhat greater spread in the magnitudes of the electron concentrations and mobilities in



FIG. 23. Temperature dependence of the electron mobility for specimens of HgSe:Cr with $N_{\rm Cr}$ (10¹⁸ cm⁻³) = 1; 5; 10; 50; and 500, respectively.

the region of large values of $N_{\rm Cr}$ than in HgSe:Fe can arise from a number of factors. In particular, possibly this involves the fact that the solubility of chromium in HgSe is smaller than the concentration of iron and that interstitial chromium atoms create local inhomogeneities in the specimen. Such imperfections of the crystals can give rise to variation of the concentration and mobility of electrons from specimen to specimen. We can suppose that the smaller values of the electron mobility at a chromium concentration $N_{\rm Cr} > 1 \times 10^{19}$ cm⁻³ as compared with the calculated values for scattering by impurity ions (see Fig. 22) also arise from local imperfections of the specimens. Of course, in HgSe:Cr crystals, just as in HgSe:Fe, the decline in the mobility μ_e with increasing concentration of chromium atoms above $\approx 5 \times 10^{18}$ cm⁻³ can arise from alloy scattering.

We can point out another reason for the greater spread of values of *n* for specimens of HgSe:Cr in the saturation region of the $n(N_{\rm Cr})$ curve at 4.2 K than for HgSe:Fe specimens. In contrast to Fe²⁺ ions, Cr²⁺ ions in the ground state have a magnetic moment. Therefore the interaction between the magnetic moments of the Cr²⁺ ions can lead to broadening of the donor level of chromium. And in turn, the broadening of the chromium level can be the reason for the greater spread in values of *n* than in HgSe:Fe specimens. Actually, owing to the random distribution of Cr²⁺ ions through the specimen, the width of the level, which is determined by the interaction among these ions, can vary from specimen to specimen, whereby the Fermi level can be fixed at somewhat differing energy values.

CONCLUSION

Thus the doping of the zero-gap semiconductor HgSe with the transition elements-iron and chromium-leads to formation of a resonance donor level lying in the region of the continuous spectrum of the conduction band. Above a certain level of doping the aggregate of donors is only partially populated by electrons. That is, two charge states coexist in it (Fe³⁺ and Fe²⁺, or Cr³⁺ and Cr²⁺)—a mixedvalency system arises. The Coulomb repulsion between the charges of the donors, which tries to separate them as far apart from one another as possible, leads to correlation in the spatial location of the charged donors. The spatially correlated charged impurities are less effective scatterers of electrons than randomly distributed impurity centers are. For this reason an anomalous increase arises in the electron mobility and a corresponding decrease in the Dingle temperature. Thus impurity doping, which forms rather well localized resonance states, can serve as a method for attaining higher electron mobilities in strongly doped semiconductors than the mobility in such semiconductors having shallow hydrogen-like impurities.

The problem seems highly interesting and important of seeking other semiconductor materials in which the electron mobility is increased by the presence in them of resonance impurity states and spatial correlation of charged impurities existing in at least two charge states.

One of the materials in which the mechanism of increased mobility being discussed can occur is GaAs containing DX-centers. The microscopical nature of DX-centers has not yet been completely elucidated. According to one hypothesis (see the review of Ref. 30) a DX-center amounts to a complex consisting of a substitution donor atom (D) and an unknown lattice defect (X), perhaps an As vacancy. DX-centers form deep donor levels degenerate with the continuous spectrum of the conduction band. The capture or emission of an electron by a donor is accompanied by a multiphonon process in which the crystal lattice in the neighborhood of the donor strongly relaxes, which is the reason for the appearance of non-decaying photoconductivity. The hypothesis has also been advanced that the level formed by the DX-center is a deep state of a substitution donor atom firmly bound to the L-minimum of the conduction band. In this model the capture and emission of an electron are allowed by the selection rules only via the L-minimum. And yet, despite intensive studies performed in the past decade, the microstructure of this deep donor state, the mechanism of capture and emission of electrons, as well as the magnitude of the lattice relaxation, remain topics for discussion.

One of the unsolved problems concerning the nature of DX-centers is the question of their charge state: has the DX-center captured one electron, i.e., exists in the neutral state DX^{0} (which corresponds to a positive energy U of the electron at the impurity), or has it bound two electrons, i.e., exists in the charged state DX^{-} (U<0) (see Refs. 24, 27, and 30).

DX-centers arise in the doping of GaAs with impurities of Si, Sn, and Te, and form deep resonance donor levels, like iron and chromium in HgSe. If the DX-center is occupied by a single electron, then the situation is fully analogous to that occurring in HgSe:Fe. But if two electrons are bound to the DX-center, a tendency arises toward forming pairs of positively charged DX⁺ centers and negatively charged (populated) DX^- centers. Besides this Coulomb attraction in the system of impurities, repulsive forces also act between charged centers of the same sign. Therefore, in analyzing the electron mobility one must study the three correlation functions $g_{-+}(r)$, $g_{++}(r)$ and $g_{--}(r)$, which are not independent, since the donors generally are randomly distributed in the lattice. It was assumed in the calculation based on the model of short-range correlations²⁴ that all three correlation functions have the same step-like form as the function g(r) [see Eq. (24) and Fig. 20]. By using an equation analogous to Eq. (25), one determines the correlation radius for which in the DX⁻ model one can take the maximum charge separation distance of the dipole $DX^+ - DX^-$. When the wavelength of an electron exceeds the charge separation distance of the dipole, the scattering of such an electron by the dipoles is considerably weaker than that by two independently acting point charges. Thus, also in the case of DXcenters, the spatial correlation of charges involving their interaction decreases the probability of electrons being scattered, i.e., increases their mobility. The dependence of the electron mobility on the hydrostatic pressure for DX^{0} centers calculated²⁴ within the framework of the model of short-range correlations agrees satisfactorily with the experimental data for a specimen of GaAs:Si $(N_{\rm Si} = 6.8 \times 10^{18} \text{ cm}^{-3})$ up to a pressure $\mathscr{P} \approx 12 \text{ kbar, just}$ as for HgSe:Fe (see Fig. 17). The values of the mobility calculated without taking into account the interaction between the charged centers disagrees substantially with the results of measurement. The model of spatial correlations used in Ref. 24 practically coincides with the model of pair correlations proposed by Arapov et al.^{1a} and by Brandt et al.^{1b} to explain the anomalous increase in electron mobility with decreasing temperature in the zero-gap crystals p-HgCdTe and p-HgMnTe, in which the Fermi level is captured by a resonance acceptor state.

- ²⁾ Kramers' theorem is not valid here, since the number of d electrons is even.
- ³⁾ The magnetic field **H** is parallel to the electric vector **E** of the electromagnetic wave (perpendicular to the direction of propagation of the wave).
- ⁴⁾ The total energy of the system consists of: 1) the kinetic energy of the electrons of the conduction band $\varepsilon_k(n)$; 2) the energy of the electrons in the d-level formed by the iron atoms $\varepsilon_d(n) = (N_{Fe} - n)\varepsilon_d$ where ε_d is the energy of the level formed by a single iron atom; 3) the energy $\varepsilon_c(n)$ of interaction between the ionized Fe³⁺ donors as determined by the screened Coulomb potential, which contains the dielectric constant \varkappa .
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Translated by M. V. King

¹⁾ A separate section is devoted below to the Mycielski model.