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Peculiarities of magnetic oscillations in HgSe monocrystal with Co impurities of low concentration (< 1 at%)

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The results of experimental studies of magnetoresistance oscillations are described for a HgSe monocrystal with Co impurities of low concentration (< 1 at%). It has been discovered that at such impurity concentrations ($\sim 10^{18}$ cm^{-3}) there exists two types of magnetic oscillations: Shubnikov de Haas oscillations at low temperatures ($T < 10$ K) and magnetophonon oscillations at higher temperatures ($T > 10$ K). The first ones are caused by the interaction of electrons with magnetic fieled inside of a Landau sublevel and the latter — by the interaction with longitudinal optical phonons. The differences of these oscillations are characterized. A hypothesis of a nature of magnetophonon oscillations in such structures is proposed.

Keywords: 3*d*-impurities of low concentration, zero-gap semiconductors, magnetophonon oscillations, SdH oscillations, optical and acoustic phonons.

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1. Introduction

The interest to studying the HgSe semiconductor with 3*d*-impurities is defined by the possibility of its usage as a detector, operating in IR range, as well as in various spintronics devices. From fundamental point of view these crystals also attract large attention of researchers, because they possess a whole range of interesting physical properties, which studying allows to better understand their behavior at various external events. One of such events is a crystal reaction to external magnetic field, that changes trajectory of electrons, moved freely along the crystal. This results in appearance of such classical effects as Hall effect, Shubnikov–de-Haas (SdH) effect and others. Analysis of these effects allows to define the main parameters of the semiconductor crystal charge: concentration, compensation, mobility, relaxation time, lifetime, effective mass, *g*-factor, etc. Review of oscillation events in metals and degenerated semiconductors is presented in detail in Schoenberg monography [1]. Detailed discussion of SdH oscillations in HgSe crystals is presented in the article of Whitsetta [2]. Application of microwave absorption for registration of this effect in InAs is described in the study of Veinger et al. [3], while the direct registration of oscillating magnetoresistance in microwave range in HgSe crystal with impurities of Fe of low concentration (< 1 at%) is presented in the article [4].

This study is dedicated to experimental study of the Shubnikov–de-Haas effect in HgSe monocrystal with impurities of Co of low concentration (< 1 at%) and detailed analysis of the observed results, that will allow to define the values of parameters of the examined system and compare them with the results, observed earlier for HgSe monocrystal with impurities of Fe of low concentration. Impurity atoms of Fe and Co in metal state possess the ferromagnetic properties, therefore it is interesting to compare the behavior of these impurities (*d*-electrons) in diluted state, when they act as impurities in the main lattice.

When doping HgSe with impurities of transition metals of Fe or Co the oscillation picture includes peculiarities, primarily related to the fact, that these impurities create resonance levels in the crystal conductivity band [5]. As a result, Fermi level is captured by the impurity level and within the wide range of its concentration it ceases to depend on this parameter. Study of this effect influence on electrons concentration, mobility and Dingle temperature is presented in study [6], while the results of qualitative interpretation, developed under the theory of resonance scattering based on Friedel approach, are presented in study [7]. Thus, the interesting peculiarity of impurities of transition metals of low concentration (less than 1 at%) in HgSe semiconductor is their capability to appear in two effect simultaneously: from one side, they create the spontaneous magnetization caused by the presence of spin polarization [8,9], and from another side, they replace Hg atoms and act as donors, supplying the additional electrons to conductivity band, which states hybridize with conductivity electrons states [10].

Technique of electron paramagnetic resonance (EPR), described in studies [3,4], allows to increase the accuracy of measurement of magnetic field intensity and to detect the quantum oscillations of kinetic and thermodynamic coefficients in weaker fields. Physics of this event assumes that microwave magnetic field excites the circular currents in a sample, and these currents value is defined by the sample resistance. Therefore, the EPR spectrometer is capable to register not only the microwave absorption change, related to spin flip, but also the microwave absorption change, related to sample resistance change, for instance, semiconductor [11,12] or superconductor [13,14]. We examined the peculiarities of the positive microwave absorption in HgSe monocrystal with impurities of Fe of low concentration in weak fields in study [15], while in SdH oscillations appearing area ($H > 10$ kOe) — in study [4]. Results of the study of the microwave absorption in HgSe monocrystal with impurities of Co of low concentration in weak fields are described in article [16].

The purpose of this study is to perform the comparative analysis of SdH oscillations picture in HgSe crystals, doped with ferromagnetic impurities of Fe and Co of low concentration (< 1 at%), and to define their common properties and peculiarities, specific for each impurity.

2. Samples and measurement procedure

The studies were performed on crystallographic-oriented samples of HgSe with impurities of Fe and Co of low concentration (< 1 at%). It should be noted that Fe impurity is dissolved significantly better in this material (solubility of Fe in HgSe — $\sim 20\%$) compared to Co impurity (solubility of Co in HgSe — $\sim 10\%$). Therefore, HgSe monocrystals with close impurity concentration, but not maximum for Fe impurity, was used for comparison: $N_{Fe} \approx 7 \cdot 10^{18}\,cm^{-3}$; $N_{Co} \approx 7 \cdot 10^{18}\,cm^{-3}$.

While both impurities are ferromagnetic, their properties as of impurities are significantly different. Fe atom on outer shell has two electrons in s-state and six electrons in d-state. When it is included in HgSe matrix lattice, two s-electrons bond with s-electrons of surrounding lattice atoms, five d-electrons create a deep impurity band, and one d-electron becomes weakly bond with the lattice, transfers to degenerated conductivity band and has a resonance energy level $E_C \sim 0.2$ eV [6]. Thus, Fe ion on the outer shell has five d-electrons, that give the typical EPR spectrum, described in several studies [17,18].

Co atom on the outer shall has nine electrons, two of which are in s-state, as in Fe atom, while the other seven are in d-state. The first ones create bonds with the surrounding lattice atoms, one d-electron transfers to degenerated conductivity band, while six electrons create deep impurity band, that gives the EPR spectrum, typical for that impurity [19]. It contains only one line, that in some directions is weakly split by the crystal field. Electron in the degenerated conductivity band has the resonance energy level $E_C \sim 0.09$ eV [20].

For study we also used the samples of HgSe:Co, grown in the Chernivtsi National University (Ukraine), with concentration Co: $N_{Co} = 6 \cdot 10^{17}$, $4 \cdot 10^{18}$ and $7 \cdot 10^{18}\,cm^{-3}$.

Experiments were performed using EPR spectrometer E-112 made by „VARIAN“ with continuous-flow cryostat „Oxford Instruments ESR-910“, that is capable to maintain the sample temperature within wide ranges of $(2-300)$ K. Peculiarities of the experimental results interpretation in microwave range are described in detail in study [4].

3. Experimental results

3.1. SdH effect manifestation

First of all, we compared the SdH oscillations type for samples doped with Fe and Co at close concentrations. They are shown in Fig. 1. Concentration $N_{Fe} = 7 \cdot 10^{18}\,cm^{-3}$, $N_{Co} = 7 \cdot 10^{18}\,cm^{-3}$. Classical magnetoresistance is excluded from the measured dependencies. As seen from Fig. 1, the oscillations, at doping with Co ions, have a significantly bigger period compared with oscillations at doping with Fe ions. This difference is caused by the fact that Fermi level is located significantly lower in the first case than in the second, that corresponds with the results of the referenced studies [6,17,18,20].

Since the solubility limit of Co impurities in HgSe matrix is 2 times lower than solubility limit of Fe, only relatively small area of Co concentrations is available for studying the SdH oscillations. At the same time, at concentration $N_{Co} = 6 \cdot 10^{17}\,cm^{-3}$ the oscillations were not observed. Figure 2 shows the type of SdH oscillations at two concentrations: $N_{Co} = 4 \cdot 10^{18}$ and $7 \cdot 10^{18}\,cm^{-3}$. It seems, at concentration Co $\sim 10^{18}$ the degeneration is strong enough for the oscillations appearing. As seen in this figure, at lower concentrations of impurity the low-frequency magnetophonon oscillations, that are described in several monographies [21,22], are overlaid on high-frequency SdH oscillations in the area of strong fields. This oscillations peculiarity will be discussed in detail further.

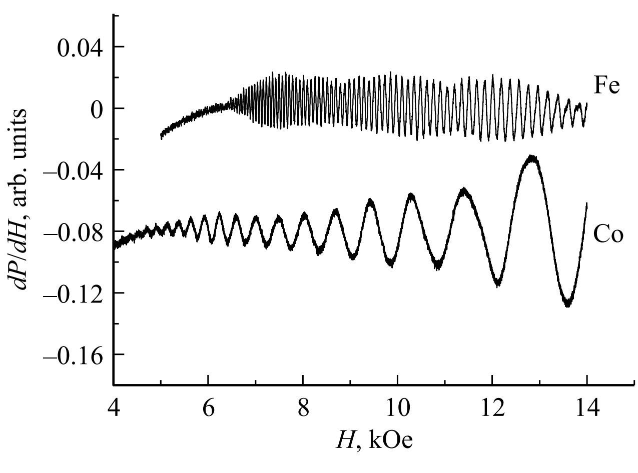

Figure 1. Typical type of SdH oscillations in monocrystals of HgSe:Fe(Co) at close impurity concentrations ($N_{Fe} = 7 \cdot 10^{18}\,cm^{-3}$, $N_{Co} = 7 \cdot 10^{18}\,cm^{-3}$) and the same crystallographic orientations $[1\bar{1}0]$ ($T = 3$ K).

As seen in the figure, at higher concentration of Co impurities ($7 \cdot 10^{18}\,\text{cm}^{-3}$) the oscillations have larger amplitude and are more suitable for analysis. Let's examine angular dependencies of the effect at low temperature, when they are defined by SdH effect.

Figure 3 shows the dependencies of amplitude and shape of oscillations for this sample ($7 \cdot 10^{18}\,\text{cm}^{-3}$) on magnetic field direction relating to crystallographic axes at $T = 3\,\text{K}$. The monofrequency oscillations are observed only in direction $[1\bar{1}0]$, while in other directions the beatings are observed that are related to low distortions of Fermi surface in HgSe. Such beatings are also observed in HgSe:Fe [23]. Thus, the angular dependencies in HgSe:Co are related with peculiarities of the matrix electronic structure, not with impurity properties, i.e. the highest distortion of Fermi surface is observed in direction [111], while in direction [110] it is slightly distorted.

At monofrequency SdH oscillations spectrum it is easy to define the quantum limit of oscillations, using the technique, described in study [3]. It is convenient when using the EPR technique, when magnetic field is rather homogeneous and can be defined with high accuracy. The technique is based on dependence of the quantization effect of electrons density states in magnetic field at their movement in a plane, perpendicular to magnetic field direction, that is defined with relation

$$\varepsilon = (n + 1/2)\hbar\omega_c, \tag{1}$$

where $n = 0, 1, 2,$ $\omega_c = eH/m^*c$ — cyclotron frequency, m^* — electron effective mass.

Curve analysis at 90° (Fig. 3) showed that quantum limit field is 111.5 kOe, that is much less than at HgSe doping with Fe ions ($\sim 850\,\text{kOe}$) [4].

Oscillations temperature dependences were unexpected. In the area of low temperatures ($T \leq 10\,\text{K}$) they correspond to all peculiarities of SdH effect. However, at higher temperatures their properties sharply change. These dependencies at various temperatures are shown in Fig. 4.

As seen in Fig. 4, opposed to InSb [3] and HgSe:Fe [4], SdH oscillations do not disappear in the temperature range of (10−20) K, and only oscillation frequency changes. These relatively high-temperature oscillations, slowly decreasing in terms of amplitude, were observed up to temperatures of (100−150) K.

Field dependencies of oscillations at low temperatures can be related to SdH effect. In this case for their analysis the relations, proposed by Schoenberg [1], can be used. He showed that with lack of beatings at fields, much less than quantum limit, between derivative of oscillation amplitude, magnetic field and temperature, there is a relation

$$dP/dH = 294p(m/m_0)(T/H)\exp\left[-147p(m/m_0)(T/H)\right], \tag{2}$$

where H is the magnetic field expressed in kOe, $p = 1$ or 2 depending on spin component impact; the remaining

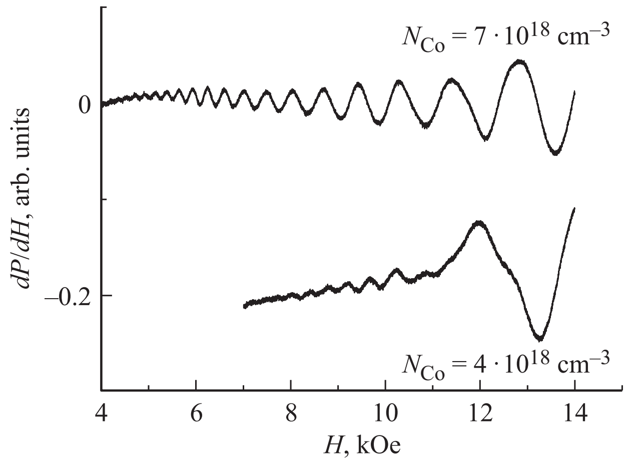

Figure 2. SdH oscillations in monocrystal of HgSe:Co at various concentrations of Co impurity (magnetic field $H \parallel [1\bar{1}0]$, $T = 3\,\text{K}$).

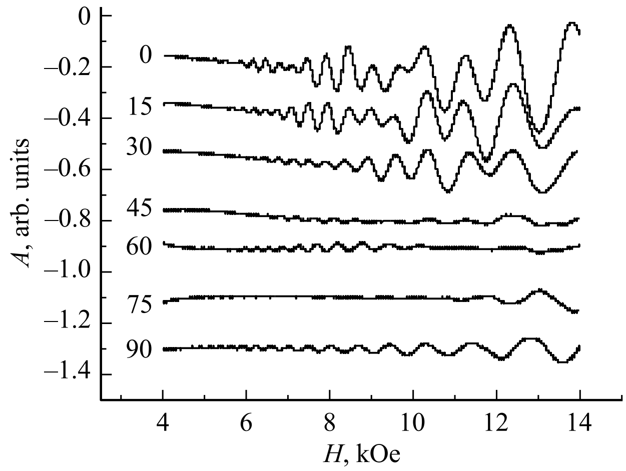

Figure 3. Angular dependencies of SdH oscillations in monocrystal of HgSe:Co ($N_{Co} = 7 \cdot 10^{18}\,\text{cm}^{-3}$). Rotation was performed from direction [010] to direction $[1\bar{1}0]$ in a plane (011). Temperature $T = 3\,\text{K}$.

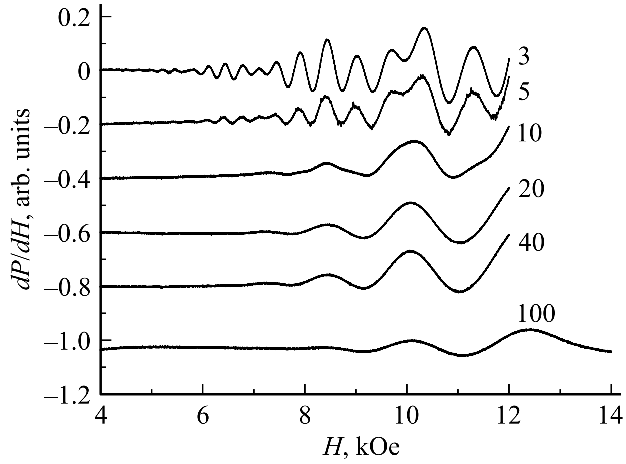

Figure 4. Temperature dependencies of magnetic oscillations in monocrystal of HgSe:Co with impurity concentration $N_{Co} = 7 \cdot 10^{18}\,\text{cm}^{-3}$ (magnetic field $H \parallel [100]$).

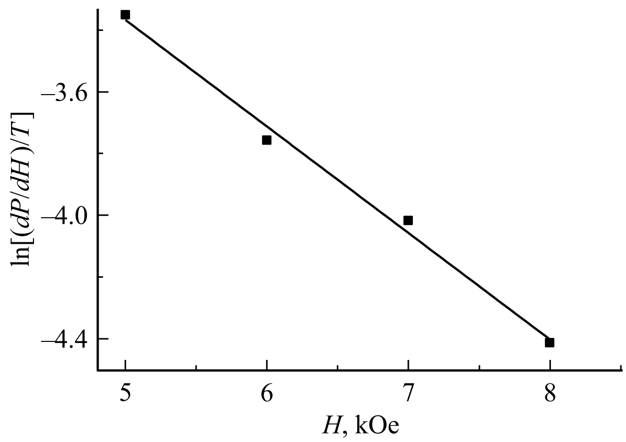

Figure 5. Dependence of $\ln[(dP/dH)/T]$ on temperature.

designations are common. We assumed that $p = 1$, since spin splitting of oscillations were not observed during the experiment.

As per formula (2), with temperature increase, the dependence of signal amplitude on temperature is described with the relation

$$\ln[(dP/dH)/T] = \ln\left[294p(m/m_0)(1/H)\right] - 147p(m/m_0)(T/H), \quad (3)$$

while the value of the effective mass is defined with the relation

$$m/m_0 = \Big(d\big(\ln[(dP/dH)/T]/dT\big)H/(147p). \quad (4)$$

Figure 5 shows the dependence of $\ln[(dP/dH)/T]$ on temperature T. It is seen that they are proportional, i.e. the effective mass remains constant within the measured temperature range, and $m/m_0 = 0.019$, that corresponds with the value, observed in study [24].

From the observed patterns it was not possible to define the value of Dingle temperature, as it was made in study [4]. It was observed that SdH oscillation amplitudes are distorted due to mixing of two oscillation types and do not comply with the relation (2). While at direction of magnetic field $[1\bar{1}0]$ these distortions are unnoticed, the dependence $dP/dH = f(H)$ does not comply with the relation (2).

Analyzing the Fig. 4, it should be noted that maximums of SdH oscillations are almost the same as maximum values of high-temperature oscillations. It can be assumed that not only weak distortions of Fermi surface, but also the simultaneous appearance of two types of oscillations of various origin in the sample can act as the beatings source.

3.2. Magnetophonon oscillations

Peculiarities of oscillation spectra at temperatures $T \geq 10\,\text{K}$ allow to assume that they are caused by a magnetophonon effect, that is described in detail in monographs [21,22]. In degenerated semiconductors this effect is described in study [25]. Oscillations are related with electron scattering on longitudinal optical phonons with energy $\hbar\omega_0$. Scattering act is happened, when the optical phonon energy becomes divisible by Landau

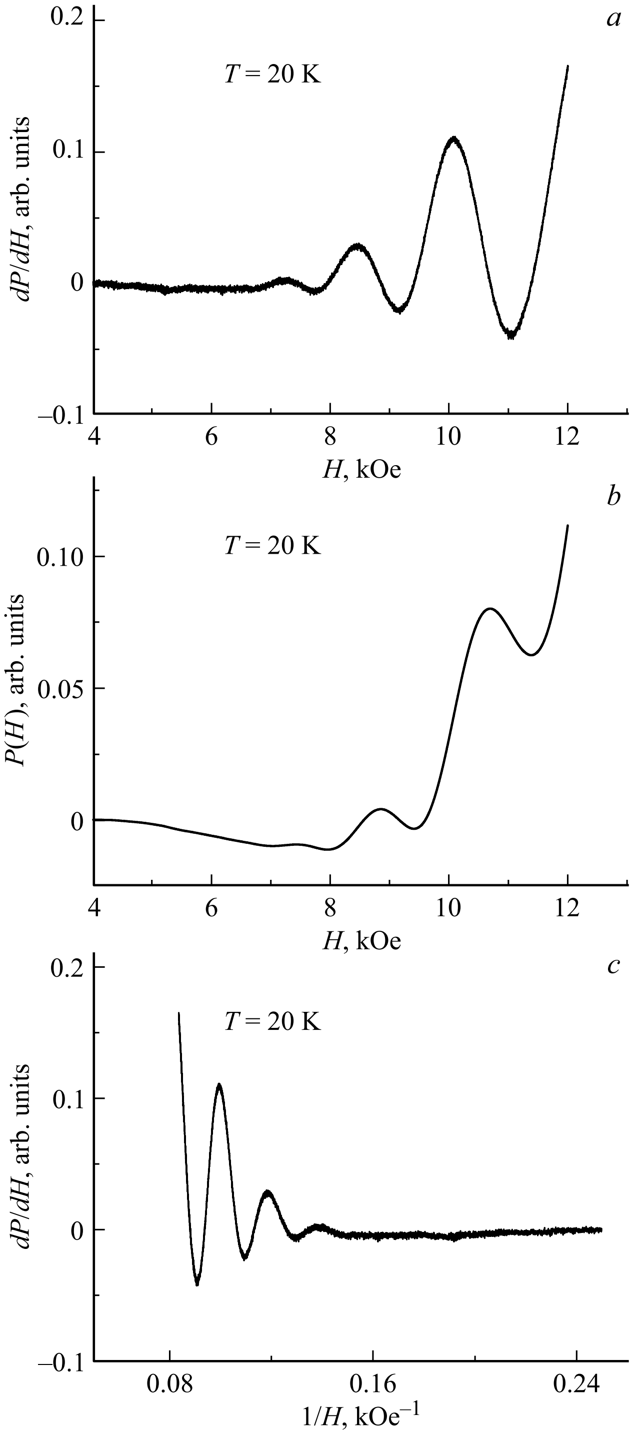

Figure 6. Visualization of magnetophonon oscillations with various parameters: a is the microwave absorption derivative; b is the microwave absorption; c is the microwave absorption derivative in reverse fields ($T = 20\,\text{K}$).

level energy $\hbar\omega_c$:

$$\hbar\omega_0 = n\hbar\omega_c, \quad n = 1, 2, 3, \ldots \tag{5}$$

Electron, emitting phonon, transfers from the area with high states density to the area with low density. The strongest effect appears when electron from Fermi level transfers to the bottom of conductivity band. As a result, the sample resistance increases, and oscillations, related to the sample resistance increase, are experimentally observed.

Figure 6 shows such oscillations with various visualization at temperature $T = 20\,\mathrm{K}$, when SdH oscillations do not appear. As per Fig. 6, the sample resistance usually increases, since at scattering on optical phonons the electrons transfer from the area with energy of about kT near Fermi surface, where they participate in conductivity, to area, far from Fermi surface, and thus they are excluded from this process. This is a characteristic peculiarity of magnetophonon oscillations.

For HgSe crystal the values of phonon frequencies are defined in articles [26,27]. They are also presented in the handbook [28]. Frequency of optical phonon $\omega_0 \approx 3 \cdot 10^{13}$ s. Its energy $\hbar\omega_0 \approx 20\,\mathrm{meV}$. Thus, the optical phonon energy is close to doubled energy of the resonance level of Co, when magnetophonon effect appears in the optimal way.

According to theory, the period of magnetophonon oscillations in reverse field is constant and defined only with the effective mass:

$$\Delta(1/H) = e/(m\omega_0). \tag{6}$$

But the Fig. 7 shows that oscillations period is constant only at sufficiently high temperatures. At $T \leq 20\,\mathrm{K}$ this period is not constant, while the distance between the first and second maximum increases, and between the second and third — decreases. Origin of this peculiarity remains uncertain. At higher temperatures the behavior of

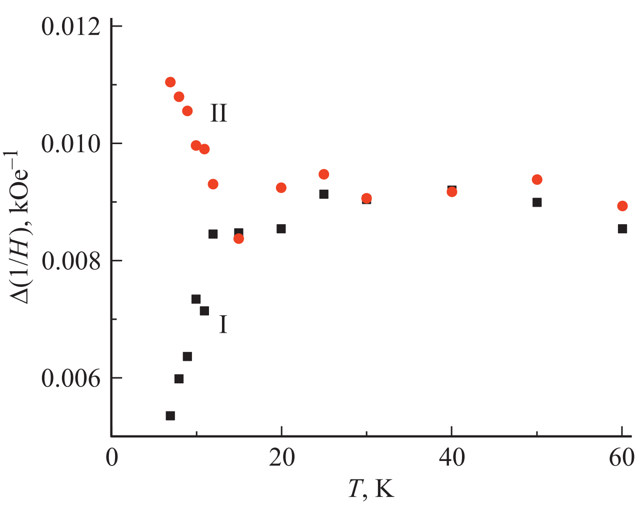

Figure 7. Dependence of distance between the first and second maximum (I) and the second and third maximum (II) on temperature.

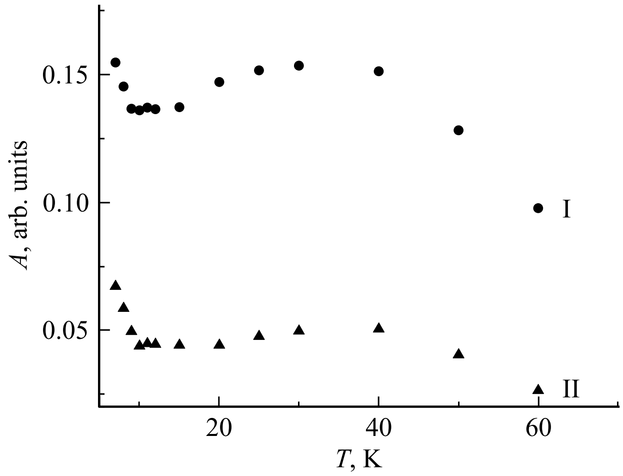

Figure 8. Temperature dependencies of amplitudes of the first (I) and second (II) oscillation maximums.

oscillations period corresponds to theory and indicates that the electrons effective mass remains almost constant within this temperature range.

Temperature dependencies of oscillation amplitudes present interesting information on nature of electrons interaction with optical phonons. They are shown in Fig. 8. It is seen that at low temperatures the peaks amplitudes reduce at some extent with temperature increase, while the first and the second peaks decrease similarly. At $T \geq 20\,\mathrm{K}$ the peaks amplitudes act rather predictable. The slowly increase according to increase of density of optical phonons, participating in scattering. This process continues up to temperatures $T \geq 40\,\mathrm{K}$, when scattering becomes maximum.

However, along with scattering on optical phonons, electrons are also scattered on other particles. In this temperature range the scattering on the charged impurities should not be significant, but elastic scattering on acoustic phonons can suppress contribution of inelastic scattering on optical phonons. As a result the contribution of inelastic scattering decreases with temperature rise.

Thus, the application of the sensitive electron paramagnetic resonance technique allows to study the weak magnetophonon oscillations, that present useful information on electron-phonon interactions in degenerated semiconductors.

4. Conclusion

According to experiments, the application of EPR technique allows to register not only SdH oscillations, but also the weaker magnetophonon oscillations. This technique allows to simplify the oscillations registration due to lack of contacts and to increase the signal/noise ratio.

As a result of analysis of the field dependencies of SdH oscillations amplitudes the quantum limit field for HgSe:Co monocrystal with low concentration of cobalt impurities was defined. It was observed equal to 111.5 kOe, that is much lower than similar parameter for HgSe : Fe (850 kOe). Temperature dependencies of oscillations amplitudes in the temperature range of $T \le 10$ K showed that the effective mass for this material is $m/m_0 = 0.019$, that corresponds to literature data [21].

Analysis of magnetophonon oscillations spectrum showed that as a result of oscillations the sample resistance increases, since electron at interaction with optical phonon transfers from Fermi surface, where it participates in conductivity, to the area, far from this level, thus excluding from the conductivity process.

It was shown, that the distance between the oscillation peaks $\Delta(1/H)$ does not depend on temperature in temperature range $T \ge 20$ K, and at lower temperature it changes significantly and in different directions. It seems that this is related to SdH effect.

Amplitude of oscillating peak changes with temperature in rather complicated way. In the area of the lowest temperatures the peaks amplitudes decrease. It seems that is also related with SdH effect. At higher temperature, $T \ge 10$ K, the amplitudes increase according to the optical phonons density growth. At $T \ge 40$ K the amplitudes decrease due to competition of other interaction mechanisms.

Thus, the analysis of spectra of microwave absorption effects in some cases allows to observe the important information on properties of the electronic system of degenerated semiconductors and nature of their interaction with lattice.

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Conflict of interest

The authors declare that they have no conflict of interest.

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