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Relative magnetoresistance in polycrystalline In–Cu chalcogenides under high pressure up to 50 GPa

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Abstract. This paper is devoted to the investigation of relative magnetoresistance MR in semiconductor polycrystalline materials: $CuInAsS_3$, $CuInAsSe_3$, $CuInS_2$ and $CuInSe_2$ under high pressures up to 50 GPa and at a constant transverse magnetic field. The pressure ranges of significant changes in the behavior of electrical resistance and magnetoresistance were identified for these materials. The features in the properties of $CuInSe_2$, $CuInS_2$ and $CuInAsSe_3$ at these pressures are consistent with the data on the baric structural phase transitions in these materials. In the case of $CuInAsS_3$ and $CuInAsSe_3$ a shift of pressure intervals in which phase transitions can occur is observed that can be explained by an effect of chemical compression due to the changing the atom radii of the chemical elements forming the compounds.

1. Introduction

Polycrystalline indium and copper chalcogenides from the Cu–In–As–S (Se) and Cu–In–S (Se) systems have a profound scientific and practical interest because these materials can be used in various optical devices such as solar cells, LEDs, etc [1–7]. For the reliable operation of the devices based on them, it is necessary to investigate the physical properties of these materials in a wide range of external influences such as temperature, pressure, constant and alternating magnetic and electrical fields, etc.

The aim of this work is to study the behaviour of relative magnetoresistance MR of semiconductor polycrystalline materials: $CuInAsS_3$, $CuInAsSe_3$, $CuInS_2$ and $CuInSe_2$ under high pressures up to 50 GPa in a constant transverse magnetic field.

2. Materials and methods of study

The bulk polycrystalline materials $CuInAsS_3$, $CuInAsSe_3$, $CuInS_2$, $CuInSe_2$ were synthesized by melting the initial components in a quartz containers. First of all, when all components of synthesized material were placed in ampoule, a constriction that divides ampoule into two parts was made. Then the titanium sponge was placed in the second part of ampoule and the second constriction was made. Ampoule have been evacuated to a residual pressure of 10^{-4} Pa and filled with super pure argon to 0.5×10^5 Pa. The second constriction was sealed. After that, deoxygenation via annealing with titanium sponge was carried out. And finally, the volume of ampoule with the charge was sealed and placed in a muffle furnace for melting. A more detailed description of the synthesis process is given in [6].

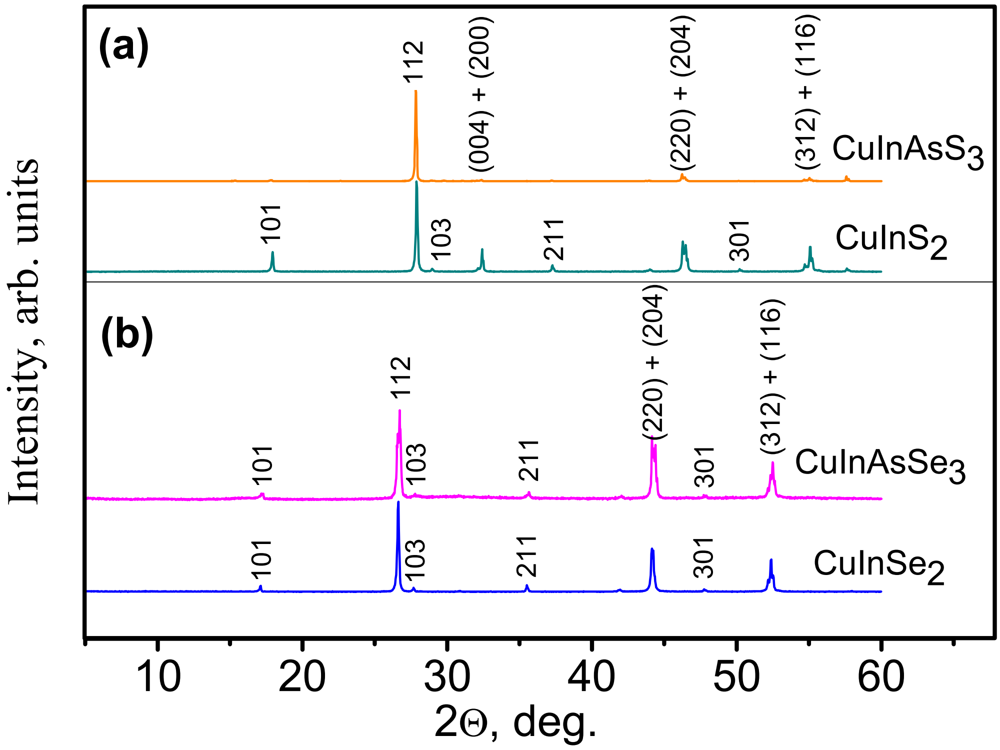

Figure 1. Powder x-ray diffractions of (*a*) $CuInAsS_3$, $CuInS_2$, (*b*) $CuInAsSe_3$ and $CuInSe_2$. A series of the reflections corresponding to the tetragonal chalcopyrite structure is visible on the diffraction patterns.

The compounds crystallized in the tetragonal chalcopyrite structure. The series of lines of chalcopyrite structure (figure 1) is presented on the diffraction patterns obtained by the x-ray diffractometer Shimadzu XRD 7000 (CuK_α radiation). For $CuInAsS_3$ the dominant orientation is in the $\langle 112 \rangle$ direction, the orientation degree is about 65%.

The lattice parameters are $a = 5.5227$ Å, $c = 11.1329$ Å and $a = 5.7820$ Å, $c = 11.6217$ Å for $CuInS_2$ and $CuInSe_2$ (refined formula, $Cu_{0.933}InSe_2$) respectively. The lattice parameters of $CuInAsS_3$ ($a = 5.5184$ Å, $c = 11.0845$ Å) and $CuInAsSe_3$ ($a = 5.7967$ Å, $c = 11.5471$ Å) are close to the lattice parameters of the compounds without arsenic. Arsenic atoms in these compounds can occupy the same tetrahedral sites that are occupied by copper and indium atoms in the structure of $CuInSe_2$ and $CuInS_2$, or As atoms can be placed in the tetrahedral voids in the chalcopyrite structure. The similar values of ionic radii and charges of the corresponding ions are also support this view [8].

The high pressures up to 50 GPa were produced in the high-pressure cell (HPC) with the anvils from the carbonado-type artificial diamonds with good conductivity that make it possible to examine the electrical properties of samples placed into HPC [9]. The studied samples with a diameter of ≈ 0.2 mm and thickness from 10 to 30 μm, were obtained by compression in HPC of the initial powdered materials.

The constant transverse magnetic field was produced by a testaceous electromagnet, the value of magnetic induction B varied from 0 to 1 T. Relative magnetoresistance (MR) was calculated

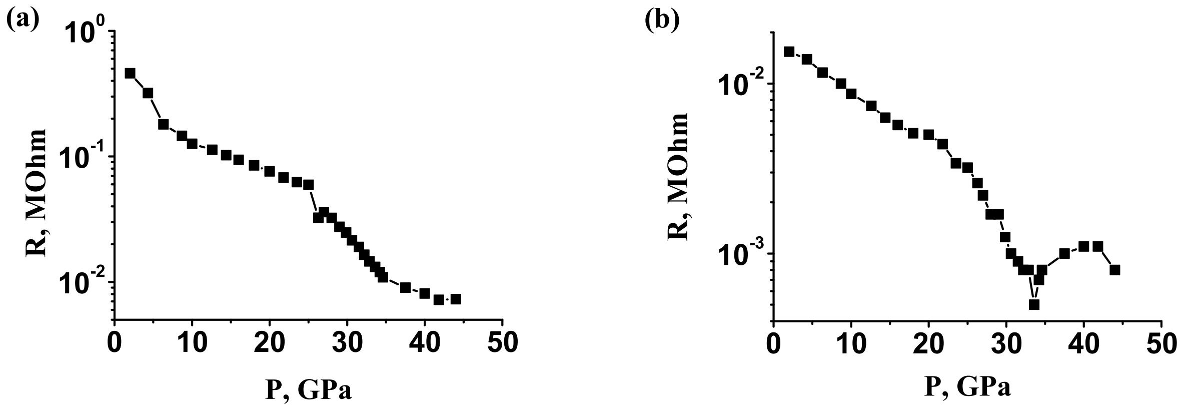

Figure 2. Dependences of resistance on pressure at $T = 300$ K for (a) $CuInS_2$ and (b) $CuInSe_2$.

using the following formula:

$$\mathrm{MR} = \frac{R(B) - R_0}{R_0}, \tag{1}$$

where $R(B)$ is the electrical resistance at fixed magnetic field and fixed pressure, and R_0 is the electrical resistance at the absence of magnetic field at the same pressure.

3. Results and discussion

The electrical resistance of $CuInSe_2$ and $CuInS_2$ shown in figure 2. The resistance of these materials decreases by 1.5–2 orders of magnitude when the pressure is raised from the atmospheric to 50 GPa.

As shown in figure 2(a), there are three inflections on the $CuInS_2$ baric dependence of resistance. They are near 9; 24 and 35 GPa. Features on the baric dependence of the resistance of $CuInSe_2$ are observed near 17 and 30 GPa respectively, see figure 2(b).

The structural changes at pressures up to 29 GPa and at further decrease to atmospheric pressure were studied via x-ray diffraction using a chamber with diamond anvils and synchrotron radiation. The authors of [10, 11] showed that the effect of high pressures on $CuInS_2$ and $CuInSe_2$ results in the transition of the chalcopyrite structure to the cubic NaCl type structure at the pressures of 9.5 GPa and 7.6 GPa, respectively. At 39.2 GPa the authors [11] observed a subsequent structural phase transition in $CuInSe_2$. The new phase was identified as an orthorhombic distortion of the NaCl structure, and it remained stable to the maximum pressure of 53.2 GPa reached in [11]. The structural changes in the opinion of authors [10] are irreversible, and phases formed after removing the pressure differ from the initial ones. The phase restored for $CuInSe_2$ after removing the high pressure was sphalerite-type cubic and it was amorphous for $CuInS_2$.

The features near 9 GPa and 27–35 GPa on the pressure dependence of the resistance of $CuInS_2$ can be associated with the structural transitions from a hexagonal chalcopyrite structure to a cubic NaCl type structure and with the beginning of amorphization respectively. In the case of $CuInSe_2$ the first transition occurs at 7.6 GPa [10], which is confirmed by the previous studies of thermo-EMF [12]. The features on the pressure dependence in the resistance of $CuInSe_2$ into the interval 30–40 GPa can be associated with the second structural phase transition at $\approx$ 39 GPa.

Our previous studies [12] have shown that in follow pressure intervals: 17–24 GPa, 27–35 GPa for $CuInS_2$; and 17–24 GPa, 30–35 GPa for $CuInSe_2$ features in the behaviour of the dielectric

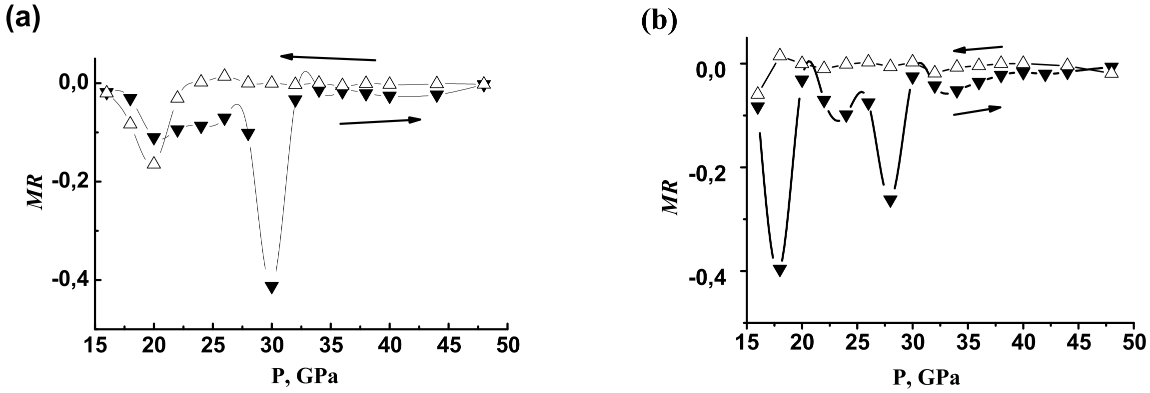

Figure 3. Pressure dependences of magnetoresistances MR with increasing (solid triangles) and decreasing (open triangles) of pressure at $T = 300$ K: (a) $CuInS_2$; (b) $CuInSe_2$; $B = 1$ T. The arrows indicate the direction of pressure variation.

loss tangent, imaginary and real parts of the impedance, thermo-EMF and MR are observed. Analysis of the magnetoresistance dependences in the pressure range from 15 to 50 GPa for $CuInS_2$ and $CuInSe_2$ revealed the presence of extrema on the MR(P) (figure 3). It is assumed that the magnetoresistance is more sensitive to structural phase transitions and features in the behaviour of MR(P) are beginning to show at lower pressures (for example, for $CuInSe_2$) that the phase transition pressure.

As mentioned before, at addition of As in the compounds from the systems of Cu–In–S and Cu–In–Se the arsenic atoms can occupy the same tetrahedral sites that are occupied by copper and indium atoms in the structure of $CuInSe_2$ and $CuInS_2$, or As atoms can be placed in the tetrahedral voids in the chalcopyrite structure [8]. Taking this into account, in the compounds of $CuInAsS_3$ and $CuInAsSe_3$, can be expected the similar magnetoresistance behaviour and the corresponding structural transitions as in $CuInS_2$ and $CuInSe_2$.

Figure 4 shows the pressure dependence of electric resistance of $CuInAsS_3$ and $CuInAsSe_3$ at 300 and 78 K. As can be seen from the figure 4 the electric resistance decreases with temperature increase that is typical for the semiconductors, and the electric resistance decreases with pressure increasing, and $\lg R(P)$ is almost linear dependence for $CuInAsS_3$.

During the measurements of electrical properties under pressure, the relaxation of resistance was observed. Such behaviour of the electrical resistance under pressure can be associated with relaxation processes connected with the change in crystal lattice, characteristics of the charge carriers, etc. In some cases, variation of relaxation time at pressure change can indicate the presence of phase transitions. Usually, in the region of possible baric phase transition the relaxation time increases. For the characterization of electro-resistance relaxation under pressure, the relative resistance was estimated as

$$\frac{\Delta R}{R} = \frac{R(t_{\rm rel}) - R(t_0)}{R(t_0)}, \qquad (2)$$

where $R(t_0)$—the electrical resistance of the sample immediately after the pressure fixing, and applying of the constant voltage to the cell, $R(t_{\rm rel})$—electrical resistance in the relaxed condition after some time interval $t_{\rm rel}$ at fixed pressure. For studied materials time interval $t_{\rm rel}$ varies from 150 to 200 seconds at room temperature and from 20 to 50 seconds at 78 K. The relative change in the electrical resistance at $T = 300$ K demonstrates the features in the behaviour at pressure increase in the follow intervals: 38–44 GPa for $CuInAsS_3$ and 32–42 GPa for $CuInAsSe_3$ (figure 5). When temperature is down to 78 K (at ambient pressure this temperature corresponds

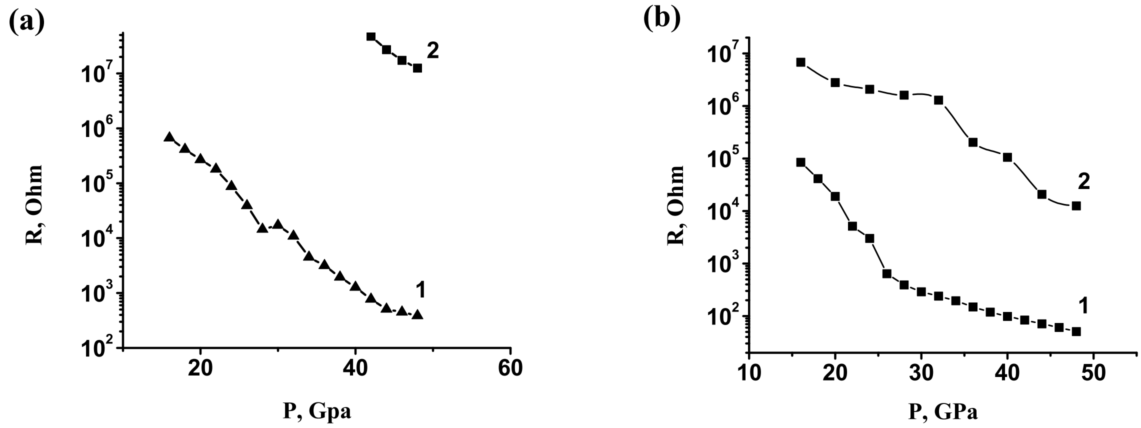

Figure 4. Pressure dependences of resistance at (*1*) $T = 300$ and (*2*) 78 K for (*a*) $CuInAsS_3$ and (*b*) $CuInAsSe_3$.

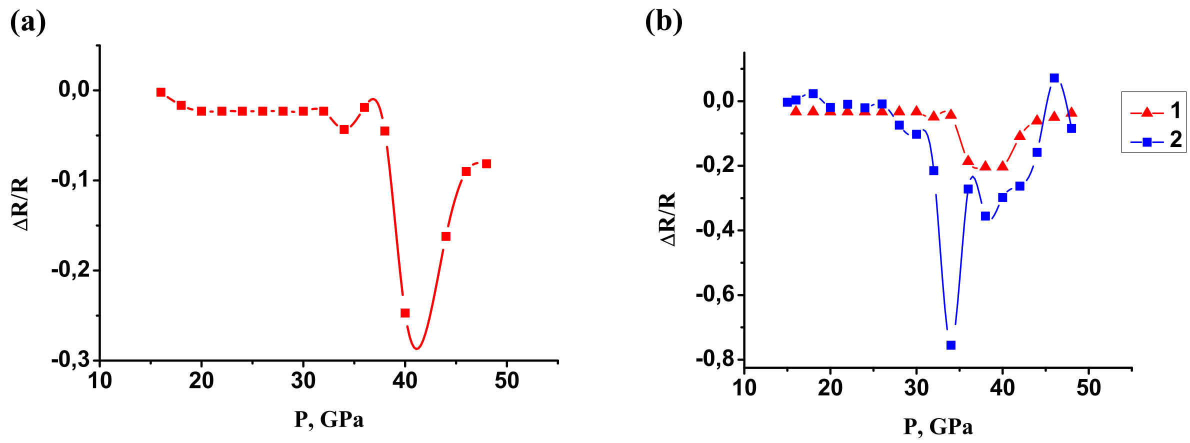

Figure 5. Pressure dependences of the relative resistivity for (*a*) $CuInAsS_3$ ($T = 300$ K) and (*b*) $CuInAsSe_3$ (*1*—$T = 300$ K; *2*—$T = 78$ K).

to the interval with impurity conductivity in $CuInAsSe_3$ [6]) the beginning of the pressure interval corresponding to the features in the behavior of the relative electrical resistance of the $CuInAsSe_3$, shifts toward lower pressures. This can indicate that precisely the impurity centers (the number of which are rising in the process of structural change with pressure increase) play a major role in the formation of the behavior of the investigated electrical parameters.

The features observed in the behaviour of the electrical characteristics of the $CuInAsS_3$ and $CuInAsSe_3$, in particular, the negative magnetoresistance (figure 6) can be manifestations of the supposed structural transitions like in $CuInSe_2$ and $CuInS_2$ (these materials have the chalcopyrite structure and the lattice parameters close to the materials under consideration at atmospheric pressure [8]). These transitions are accompanied by decrease in the width of the energy gap, changes in the impurity band structure in the magnetic field, defect states, and changes in the concentration and mobility of carriers with gradual pressure growth. The confirmations of this assumption are preliminary results of the crystal structure studies for $CuInAsSe_3$ at high pressure using synchrotron radiation [13]. The results of the study indicate the existence of two

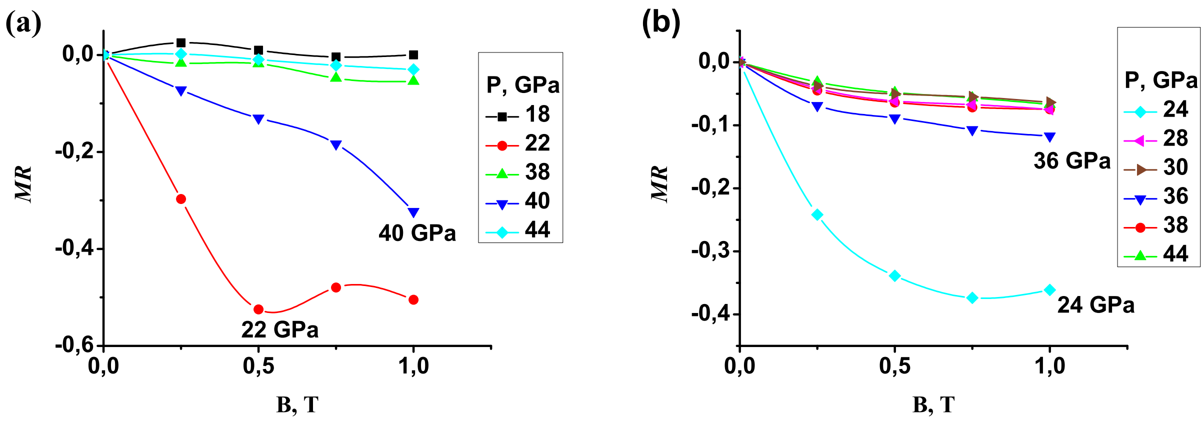

Figure 6. MR as a function of magnetic field at fixed pressures for (*a*) $CuInAsS_3$ and (*b*) $CuInAsSe_3$ ($T = 300$ K).

phase transitions: from the tetragonal to cubic structure ($\approx$ 8–10 GPa) and from the cubic to orthorhombic structure ($\approx$ 36–38 GPa).

Figure 6 shows the typical MR dependences upon magnetic field for $CuInAsS_3$ and $CuInAsSe_3$. In addition, the features (extrema) in the behavior of MR(P) are observed in the follow pressure intervals: 17–24 and $\approx$ 40 GPa for $CuInAsS_3$; 17–24 and $\approx$ 36 GPa for $CuInAsSe_3$ respectively.

Thus, considering this research and previous studies [8, 10–16] the features on the baric dependences of the electrical characteristics of materials under study, can be connected with the structural phase transitions at pressures $\approx$ 9 and 27–35 GPa for $CuInS_2$; 30–35 GPa for $CuInSe_2$; and with supposed structural phase transitions at 38–40 GPa for $CuInAsS_3$ and 36–38 GPa for $CuInAsSe_3$. These pressure ranges correlate with the previous estimated baric intervals, in which significant changes in the behaviour of electrical properties, measured under alternative current (such as impedance etc), are observed [14–16]. The shifts of intervals of possible structural transitions to the higher pressure (36–40 GPa) for $CuInAsS_3$ and $CuInAsSe_3$ compared with the materials without As, can be explained by an effect of chemical compression due to the changing the atom radii of the chemical elements forming the compounds.

4. Conclusion

Analysis of the pressure dependences of the electrical properties for the polycrystalline $CuInAsS_3$, $CuInAsSe_3$, $CuInS_2$, $CuInSe_2$ at high pressures up to 50 GPa allowed to establish the pressure ranges of the significant changes in the behaviour of electrical resistance and relative magnetoresistance. Observed features of the studied properties relate to the pressure-induced structural transitions.

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