An approach is suggested for the investigation of pressure-induced semiconductor–metal phase transitions in a wide group of materials based on both the model of p-bonds and Peierls distortion of lattice and the experimental results of thermoelectrical and magnetoresistance measurements at high pressures \( P \) up to 30 GPa. Cubic sphalerite (HgSe and HgTeS), sphalerite with 1/3 vacancy in cation sites (In\(_2\)Te\(_3\) and Ga\(_2\)Te\(_3\)), trigonal chain semiconductors (Te and Se), I\(_2\), and chalcogenides (Zn, Cd, Sm, Eu) are analyzed in the frame of this approach.

**Introduction**

The development of magnetoresistance (MR) and thermoelectric power \( (S) \) measurements at pressures in the range 0–30 GPa by using sintered diamond apparatuses [1–3] made it possible to investigate electronic structure parameters such as energy gap, type of charge carriers and its concentrations and mobilities. It allows to study the trends occurring in the electronic structures of materials undergoing pressure-induced phase transitions [4–6]. Up to now the main methods of investigation of semiconductor–metal transitions have been resistivity measurements [4]. But there is a discrepancy between the electrical and optical data of high-pressure “metal” phases of certain substances [4, 6]. The aim of this work was to propose an approach for the systematic investigation of pressure-induced semiconductor–metal transitions in a wide group of materials, which includes the overall model consideration and gives the base of applying \( S(P) \) and MR\( (P) \) measurements [1–3].

At present, adequate calculations of the electronic structure of high-pressure phases with non-cubic lattices are only performed for a few part of materials, so this gives the base for the applying simplified approaches. A model, taking p-bonds and the Peierls distortion of lattices into account, was used to explain the crystal and electronic structure of group V, VI and VII elements [7, 8] and some selected chalcogenides of groups II, IV and V [8]. The base of p-model is that p-electrons relating to a partially filled band play a dominant role in cohesion, while s-electrons lying lower in energy form a nearly full band and do not contribute appreciably to cohesion [7]. In the tight-binding approximation ppo interactions stabilize the simple cubic structure in order to achieve 6 p lobes along three orthogonal directions. The problem of cubic lattice is decoupled into three independent linear chains, which are partially filled with p-electrons and is consequently metallic. A one-dimensional metal lowers its electronic energy distorting the lattice by a Peierls distortion, causing a gap opening at the Fermi level [7, 8].

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of Te, Se and iodine six equivalent bonds are replaced by two short and four long ones, and one short and five long (van der Waals) ones, respectively. The simple cubic structures are then deformed into spiral chains of divalent Te and Se atoms, orientated along the [111] direction, and molecular I$_2$ crystal. The corresponding three- and sixfold enlargement of lattice parameter tends to a splitting of the p-band having four electrons for Te, Se and five electrons for I$_2$ and the forbidden band opens at the Fermi level [7, 8]. As the Peierls structures have a lower density than undistorted lattices, so the calculations for group V, VI and VII elements reveal that at a certain pressure $P$ the repulsion of ions made the distortion energetically disadvantageous [7], what agrees with the experimental data for metallization of these substances at high pressure [4, 6, 7].

**Results and Discussion** In this paper, the results of magnetoresistance measurements at high pressure for Te by the technique used previously for mercury chalcogenides [1] and Se [3] are presented. The semiconductor–metal transitions are discussed for the materials listed above in the frame of the approach proposed.

The semiconductor gap of cinnabar structure of HgTe and HgSe high-pressure phases, which have nearly twofold elongated (along the spiral axis) Te and Se lattices may be explained by the analogous sixfold splitting of p-band filled by 1/3 [8]. Note, that electrical properties of the rest members of group VI, S and O$_2$, at high pressure [9–12] also seem to be similar to those of HgS and HgO [1]. For the ternary mercury chalcogenides HgCdSe, HgTeS, and HgSeS the only change consists in the increase of the energy gap with a variation in the composition [1]. The application of p-model to layered Bi$_2$Te$_3$ structure, which is viewed as distorted NaCl one by change of the upper and lower bond lengths with a resulting fivefold enlarging of lattice parameter, predicts a fivefold splitting of the p-band [8]. The p-bands of In$_2$Te$_3$ and Ga$_2$Te$_3$ in the high-pressure Bi$_2$Te$_3$ structure are filled by 7/15, so they show metal type conductivity unlike semiconductor type one for Bi$_2$Te$_3$, where the p-band is filled by 3/5 and fivefold splitting opens the gap at the Fermi level [13]. The other high-pressure phases with NaCl structure, EuX, SmX, ZnX, and CdX also demonstrate metallic-like electrical properties [14–16], though it was pointed out in [17], that band calculations predict insulating properties of rocksalt phases of II–VI compounds.

Thus, the model used explains the type of crystal structure, the origin of semiconductor gap and the closing of it under pressure for the substances with different kinds of lattices, cubic, layered, chain structure, molecular crystals in agreement with resistivity data. But the model can say only little about the type of energy gap and the details of electronic structure.

Thermoelectric measurements revealed the differences between the high-pressure "metal" phases of various materials, which had similar electrical properties [1–4, 13–16, 18–20]. For the semiconductor phases $S(P)$ characterizes the behaviour of $E_g(P)$, the sign and concentration of charge carriers [21]. Indeed, the variation of $S(P)$ is similar to the known dependences of optical gap on $P$ [4, 6]. For the typical metal phases of Ge, Si, I$_2$, CdTe, HgTe, HgSe, GaP the values of $S$ are positive and less than +20 $\mu$V/K [1–3, 13–16]. For the "poor" metal phases of ZnX, CdX, which conserve sufficient optical gap in the electron spectrum [4, 6] the values of $S$ are negative and large $|S| \approx 100$ $\mu$V/K [14].

The next step is the separation of high-pressure phases by the magnetoresistance effect. It turns out, that even for high-pressure "metal" phases with similar values of $S$ the behaviour of MR is rather different [1, 3, 13, 14, 18, 20].
The magnetoresistance MR is connected with the turning of electron path by Lorentz force, and usually is an increasing function of magnetic (induction) field $B$,

$$\frac{\Delta \rho}{\rho} = T_M \left( e \frac{\langle \tau_m \rangle B}{m} \right)^2, \quad T_M = \frac{\langle \tau_m^3 \rangle \langle \tau_m \rangle - \langle \tau_m^2 \rangle^2}{\langle \tau_m \rangle^4} \quad (\mu B < 1),$$

where $k$ is the Boltzmann constant, $\mu = e \langle \tau \rangle / m$ is the mobility of charge carriers, $\tau$ is the relaxation time, the angular brackets correspond to averaging [5]. For the degenerated electron gas (Fermi energy $\xi \gg kT$) the value of MR is reduced by the factor $(\zeta/kT)^{-2} \ll 1$ [5]. The effective mass of electrons $m$ in the free electron approximation for a one-dimensional lattice is $m = m_0/(1 + 4E_0/E_g)$. Here $a$ is the lattice parameter, $m_0$ the free electron effective mass, $E_a = (\pi/a)^2 \hbar^2/2m_0$. At $E_g \to 0$, the effective mass is proportional to the energy gap $m \propto E_g$. For the direct-gap semiconductors InSb, HgTe (at the $\Gamma$-point) and Te (at the $H$-point of the Brillouin zone) there are theoretical [5] as well as experimental evidences for the $m \propto E_g$ relation established from electrical and optical measurements at high pressure [22]. The effective mass depends also on the band width $\Delta E$, $m^{-1} = a^2/6\hbar^2 \Delta E$ [5]. In narrow-band materials (d-band, impurity bands, ionic crystals) $m$ is large, and so the mobility is low [5]. Thus, positive MR characterizes the mobility $\mu(P)$ of light carriers, and hence the peculiarity of electron bands.

In particular cases negative MR is observed. Some reasons which may tend to negative MR effect are: (i) the interference quantum additions to $\sigma$ [23], (ii) magnetic impurities [23], (iii) “warm” electrons in heating electric field $E$, where the electron mobility is $\mu = \mu_0(1 + \gamma E_z^2 + K \ldots) \quad (\gamma < 0)$ [5]. So, the behaviour of MR under pressure shows a change in the scattering mechanism of light carriers during electron structure transformations.

Fig. 1. Dependence of transverse magnetoresistance $\Delta \rho/\rho$ on magnetic field $B$ of tellurium at $T = 77$ K: (1) 0.3, (2) 2.2, (3) 3.2, (4) 4.4, (5) 6, (6) 7.7, (7) 8, (8) 10, (9) 14.2 GPa, and at $T = 300$ K: (1) 0.3, (2) 0.6, (3) 1.3, (4) 2.2, (5) 3.2, (6) 6, (7) 7.7, (8) 10, (9) 12, (10) 13.7, (11) 14.2 GPa.
For the direct-gap semiconductor Te an exponential rising of MR effect under pressure was observed (Fig. 1) related to a decrease of $E_g$ and effective mass of holes [22]. There is a quadratic dependence of MR on magnetic field according to Eq. (1). An analogous exponential rising of mobility near the forbidden gap closing was observed in Se, which becomes a direct-gap semiconductor under pressures $P < 5 \text{ GPa}$ [3]. At low pressure near the point of valence band reconstruction [22] at low temperature in Te there is a negative MR effect, connected supposedly with the scattering of “warm” electrons (Fig. 1) [5]. Near the disappearance of saddle point at $\sim 2 \text{ GPa}$ there are closely lying valence band tops [22], and the heating of charge carriers by electron field ought to transfer “warm” holes to the lower one. The cooling of “warm” holes by magnetic field and the corresponding increase of mobility may cause the negative MR effect observed [5]. The inversion of MR from negative to positive occurs in Se at $P < 6 \text{ GPa}$ (Fig. 2) [3]. Above this pressure Se transforms from amorphous to trigonal phase, where MR $> 0$ [3, 24]. The absence of positive MR below 6 GPa shows that the hole mobilities in amorphous Se are small.

Metallic high-pressure phases of Te conserve structural [25] and electron band similarities [26], which is revealed by the magnetoresistance effect (Figs. 1 and 2). The chains of trigonal Te transform to layers which become more regular under pressure [25]. So, in some directions the semiconductor gap remains even in metal phases [26], and the MR effect (Figs. 1, 2) is appreciable in comparison with that for normal metals [5]. The drop and the following increase of MR near 12 GPa (Fig. 1) may be connected with the structural transformation of Te into $\beta$-Po structure [25, 26]. The inversion of MR sign was previously observed in mercury chalcogenides HgTe, HgSe during phase transition from sphalerite to cinnabar and then to the high-pressure metal phase (Fig. 2) [1]. The values of MR which are proportional to the hole mobilities for Te and Se became as high as in the gap-less semiconductors HgTe and HgSe, and vice versa, the MR of mercury chalcogenides in the high-pressure phases became negative and small as in molecular iodine and amorphous selenium. From the MR data one may conclude that presumably the high-pressure cinnabar phases of HgX ($X = \text{Te, Se, S}$) are indirect-gap semiconductors.

![Fig. 2. Dependences of transverse magnetoresistance $\Delta \rho / \rho$ on pressure $P$ at fixed magnetic field $B \approx 1 \text{T}$ for Te, Se and HgX crystals at $T = 77$ and 293 K. The inversion of the sign of magnetoresistance corresponds to changes in the band structure and mechanisms of charge carrier scattering. The different points for Te correspond to the measurements at tungsten carbide and sintered diamond high-pressure anvils](image-url)
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References
