SEMICONDUCTORS
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Electrical Properties of (PbS)$_{0.59}$TiS$_2$ Crystals at High Pressure up to 20 GPa

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Abstract—The electrical resistance ρ and thermopower S of the (PbS)$_{0.59}$TiS$_2$ single-crystal compound with mismatched layers and the TiS$_2$ crystals have been investigated at room temperature in high-pressure chambers with synthetic diamond dies. The decrease in ρ and $|S|$ observed in (PbS)$_{0.59}$TiS$_2$ under the pressure $P \approx 2$ GPa is associated with the structural transformation of PbS from the cubic phase into the orthorhombic phase. The jumps of ρ and $|S|$ are presumably caused by the increase in the electron concentration in the TiS$_2$ layers. For $P \geq 4$ GPa, at which the gap is absent in the electronic spectrum of TiS$_2$, a decrease in $\rho(P)$ is observed for the (PbS)$_{0.59}$TiS$_2$ samples. © 2000 MAIK "Nauka/Interperiodica".

Layered transition-metal dichalcogenides and their intercalates are promising materials for electronics. This explains considerable interest in studies of their properties [1–4]. The (PbS)$_{0.59}$TiS$_2$ crystals, which belong to these materials, consist of PbS and (TiS$_2$–TiS$_2$) alternating layers (Fig. 1) and can be considered as an intercalation of PbS into TiS$_2$ [1, 2]. The PbS lattice is distorted in the plane of layers as compared to the bulk crystal, which has the structure of a rock salt ($a = 5.936$ Å), and TiS$_2$ practically retains the structure of the bulk material (Fig. 1) [2]. The parameters of PbS and TiS$_2$ lattices coincide along the b axis ($b = 5.783$ Å), whereas in the perpendicular direction a, they are incommensurate: $a = 5.761$ Å for PbS and $a = 3.390$ Å for TiS$_2$ [1, 2]. Each layer of TiS$_2$ has a "sandwich" structure, in which Ti atoms are located between two interlayers of sulfur atoms (Fig. 1); as in the TiS$_2$ crystal, the layers are linked together by a weak van der Waals interaction [1–3].

A strong anisotropy of the electrical and mechanical properties is observed in the (PbS)$_{0.59}$TiS$_2$ crystals in the (ab) plane and in the perpendicular direction c [1, 2], as well as in the commensurate (b) and incommensurate (a) directions [4]. Since these crystals consist of mismatched layers, one can expect unusual behavior of the properties under the hydrostatic compression. The aim of this work was to study the influence of pressure P on the electrical resistance ρ and thermopower S of the (PbS)$_{0.59}$TiS$_2$ crystals. For comparison, similar studies were carried out on TiS$_2$ crystals, which exhibit similar temperature dependences of ρ and S along the plane (ab) of the layers at atmospheric pressure [1, 2].

The measurements were performed in high-pressure chambers with dies made of a BK6 hard alloy (up to 8 GPa) [5] and synthetic diamond (up to 30 GPa), in several cycles of the increase and decrease in P [6–8]. The values of P in a pressure-transferring medium (pyrophyllite, catlinite) were estimated from the calibrated dependences, which were drawn according to the phase transitions in the reference species (Bi, GaP, etc.) [6–8]. The (PbS)$_{0.59}$TiS$_2$ single crystals (~15 × 1.0 × 0.01 mm in size) were grown by the method of gas-transport reaction with a slight excess of sulfur as a carrier [4]. The lattice parameters of samples coincided with those given in [2]. The initial batch contained Pb (99.9%), S (99.99%), and TiS$_2$ powder in the ratio 0.59 : 0.59 : 1 [4]. The electron concentration determined from the Hall effect in the temperature range $T = 77$–350 K was $n = 3 \times 10^{21}$ cm^{-3}.

The samples in the form of plates ~0.5 × 0.2 × 0.01 mm in size were placed in an orifice with a diameter of 0.3 mm in a container made of catlinite (diamond chamber) or pyrophyllite (hard-alloy chamber [5]) at an angle to the plane of dies, which served as heaters and coolers in the thermopower measurements [6, 7]. The clamping electrical probes were the Pt–Ag ribbons 5 μm thick. The geometry of the experiments actually corresponded to the measurements of ρ and S along the (ab) plane. The relative errors in measurements of ρ and S (without regard for the change in the sample shape under compression) were ~5 and ~20%, respectively [4, 5].
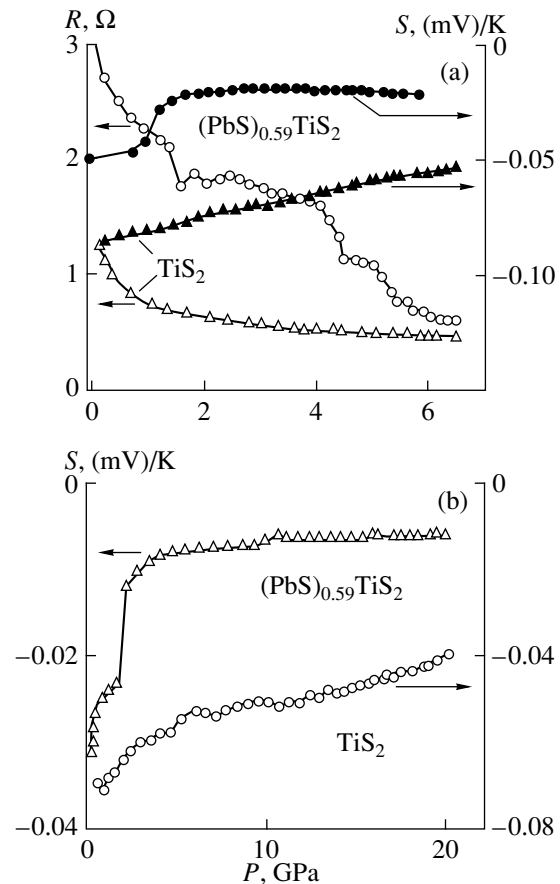
The pressure dependences of ρ and S for each of the studied materials, which were measured in diamond and hard-alloy chambers, qualitatively coincide (Figs. 2a, 2b; the data on $\rho(P)$ are presented only for the hard-alloy chamber). The drop of ρ and $|S|$ is observed in the (PbS)$_{0.59}$TiS$_2$ sample at $P \approx 2$ GPa, and one more decay, at $P \geq 4$ GPa. The dependences $\rho(P)$ and $S(P)$ for TiS$_2$ samples have no anomalies (Fig. 2). In [9], TiS$_2$
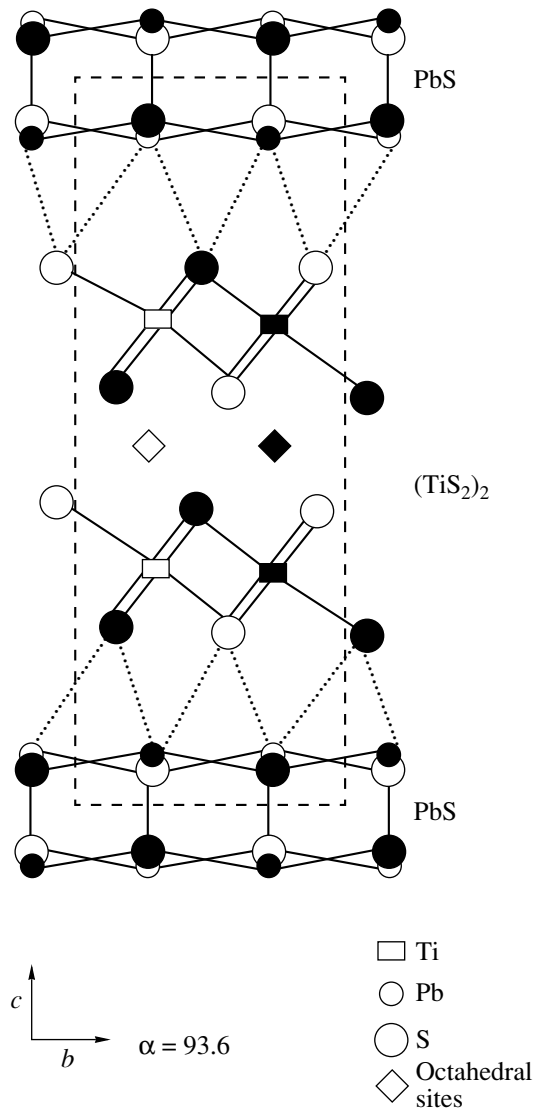
Fig. 1. Projection of the $(PbS)_{0.59}TiS_2$ crystal structure along the [100] axis [2]. The unit cell is shown by the dashed line. Solid lines represent the bonds in PbS and TiS_2 layers, and dotted lines are the bonds between these layers. Rhombs designate the positions of octahedral holes. Dark symbols correspond to the positions of atoms in the figure plane, and open symbols, to the positions of atoms in the lower-lying plane.

Fig. 2. Dependences of (a) the resistance and (a, b) the thermopower on pressure for $(PbS)_{0.59}TiS_2$ and TiS_2 crystals along the plane of layers at $T = 293$ K. Measurements are made in (a) a hard-alloy chamber and (b) a diamond chamber.

samples with the low electron concentration $n < 10^{21}$ cm^{-3} near $P = 4$–5 GPa showed the same decay of ρ as for the $(PbS)_{0.59}TiS_2$ crystal.

The sharp changes in ρ and S for $(PbS)_{0.59}TiS_2$ crystals can be induced by the phase transformations in PbS and TiS_2 layers. In bulk TiS_2 at P up to 9 GPa, the structural transformations were not established [9–11]; PbS under a pressure of 2.5 GPa transforms from the phase with a NaCl structure into the orthorhombic phase with the parameters $a = 11.28$ Å, $b = 3.98$ Å, and $c = 4.21$ Å [12–14], and at 21.5 GPa, PbS transforms into the phase with a bcc CsCl structure [15]. Thus, the jumps

of ρ and S in $(PbS)_{0.59}TiS_2$ at ~2 GPa can be connected with the phase transition in the PbS layers. Simultaneous decays of ρ and S in the $(PbS)_{0.59}TiS_2$ crystals upon structural transformations in the PbS layers show that the conduction electron concentration increases. This can be due to an increase in the content of Ti atoms (which supply electrons in the conduction band [1, 2, 9]) in the van der Waals gap between TiS_2 layers. Indeed, at a high sulfur pressure, there is a tendency toward the transition $TiS_2 \longrightarrow TiS_3$ [16]. The electron concentration can also change by "readjusting" the TiS_2 lattice to PbS due to matching of the layers [1, 2, 15]. Note that the identation of similar $(PbS)_{0.59}TiS_2$ samples led to a strong residual deformation along the incommensurable direction [4], which could be a consequence of structural transitions in the PbS layers upon penetration of a diamond indenter [17, 18].

The drop of ρ in $(PbS)_{0.59}TiS_2$ at $P > 4$ GPa (Fig. 2) can be related to the semiconductor–semimetal transition in TiS_2 layers, which was predicted by the calculations of electronic structure [10] and experimentally observed in dependences of $\rho(P)$ and $S(P)$ [9]. Accord-

ing to the x-ray data [10], the pressure results in the compression of interlayers between TiS_2 layers and in the thickening of the layers themselves (Fig. 1). This corresponds to an increase in the charge density between the layers and the strengthening of the bonds between sulfur atoms [10]. According to the calculations made in [10] for $P = 6–8$ GPa, the conduction band of TiS_2 overlaps with the valence band. The electronic structures of TiS_2 and $(PbS)_{0.59}TiS_2$ in the model of weakly interacting layers likely are similar [19, 20].

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