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v. v. Shchennikov [a], A. N. Titov [b], s. v. Popova [a] & S. V. Ovsyannikov [b]

[a] Institute of Metals Physics Ural Division of RAS, Ekaterinburg, GSP-I 70, Russia

[b] Ural State University, Department of Physics, Lenin Av, 51, Ekaterinburg, 620083, Russia

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ELECTRICAL PROPERTIES OF $(PbS)_{0.59}TiS_2$ CRYSTALS AT HIGH PRESSURES UP TO 20 GPa

V. V. SHCHENNIKOV[a,*], A. N. TITOV[b], S. V. POPOVA[a] and S. V. OVSYANNIKOV[b]

[a]*Institute of Metals Physics Ural Division of RAS, Ekaterinburg, GSP-170, Russia;* [b]*Ural State University, Department of Physics, Lenin Av, 51, Ekaterinburg, 620083, Russia*

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The measurements of thermoelectric power S and resistance ρ at high pressure synthetic diamond anvils cell were performed for $(PbS)_{0.59}TiS_2$ and TiS_2 crystals. The phase transition was found at $P \approx 2$ GPa accompanied by descend of ρ and $|S|$ for $(PbS)_{0.59}TiS_2$. This transition is connected with structural change of PbS fragment from pseudocubic cell to orthorombic one and as consequence, with change of the electron concentration in TiS_2-layers. From the electronic structure calculations for TiS_2, the semiconductor-metal transition occurs at pressure $P \geq 4$ GPa. Experimentally at this pressure range the decrease of $\rho(P)$ was observed for $(PbS)_{0.59}TiS_2$ crystals.

Keywords: Electrical resistance; ThermoEMF; Misfit crystals; High pressure; Phase transition

The layered dichalcogenides of transition metals and their intercalates are the perspective materials for electronics and have interesting electrical, structural and mechanical properties [1–3]. The misfit chalcogenide crystals $(PbS)_{0.59}TiS_2$ corresponding to this group of materials consist of the weakly linked atomic layers of PbS and (TiS_2-TiS_2) (Fig. 1) [1] and may be considered as intercalation compounds where PbS-layers are inserted in TiS_2-matrix. In the

*Address for correspondence: Institute of Metals Physics Ural Division of RAS, S. Kovalevskaya st., 18, Ekaterinburg, GSP-170, 620219, Russia. Tel.: +7(3432)744494, Fax: +7(3432)745244, e-mail: phisica@ifm.e-burg.su

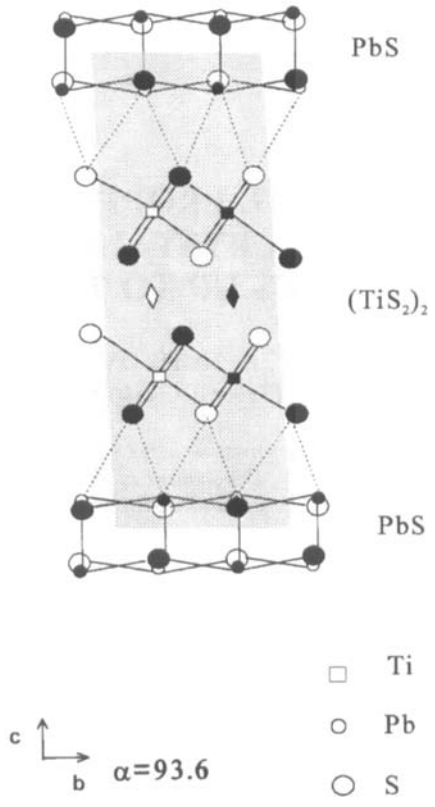

FIGURE 1 Projection of the structure of $(PbS)_{0.59}TiS_2$ along [100] [1, 19]. Dark area shows unit cell. Rhombuses are octahedral non-occupied sites at Van-der-Vaals gap between TiS_2-layers.

(*a*, *b*)-plane the PbS sublattice is deformed in comparison with bulk material with the rock salt structure ($a = 5.936$ Å) while TiS_2 layers remain almost unchanged. In *b*-direction unit cell parameters of PbS and TiS_2 parts are equal ($b = 5.783$ Å), but in *a*-direction the sublattices are incommensurate with parameters $a(PbS) = 5.761$ Å and $a(TiS_2) = 3.390$ Å [1]. Each TiS_2-layer has a form of sandwich, where Ti-atoms are placed between S-ones (Fig. 1), the layers having weak Van-der-Vaals links in *c*-direction, as for TiS_2 crystals [1–2].

Such a layered structure of considered materials leads to high anisotropy of their electric and mechanic properties in (*a*, *b*)-plane and in perpendicular *c*-direction [1], and also in commensurate *b*- and incommensurate *a*-directions [3]. A compressing of layers

$(PbS)_{0.59}TiS_2$ crystals by the isotropic pressure must cause different change of electric properties in different crystallographic directions.

The aim of this work is an investigation of pressure influence on conductivity ρ and thermoelectric power (S) for $(PbS)_{0.59}TiS_2$ crystals. For a comparison the same measurements are performed for TiS_2 crystals with the same temperature dependence of ρ and S in (a, b)-plane at ambient pressure as for $(PbS)_{0.59}TiS_2$ [1].

EXPERIMENTAL

For the high pressure measurements we have used the anvil cell with tungsten carbide (up to 8 GPa) [4] and synthetic diamond anvils (up to 30 GPa) [5–7]. The P values in the pressure media (pyrophyllite, catlinite) were estimated on base of phase transitions in standard materials (Bi, GaP and others) [5–7]. The measurements were done at few increase–decrease pressure cycles.

The $(PbS)_{0.59}TiS_2$ and TiS_2 crystals with size $\sim 15 \times 1.0 \times 0.01$ mm were prepared by method of gas transport reaction with small sulphur excess [3]. The unit cell parameters of $(PbS)_{0.59}TiS_2$ coincide with data from Ref. [1]. The electron concentration determined from the Hall effect measurement in temperature range $T = 77-350$ K was equal to $n = 3 \cdot 10^{21}$ cm^{-3}.

The crystals in form of plates $\sim 0.5 \times 0.2 \times 0.01$ mm were placed into 0.3 mm hole in a container with an angle to anvils plane. We used the Pt-Ag ribbons for electrical contact. The S-measurements were made along (a, b)-plane; because of small thickness of sample, temperature gradient in this case along c-axe was significally smaller than at the (a, b)-plane. The method of S-measurements was tested earlier for certain semiconducting materials SmX (X = Te, Se, S), EuX, Bi_2Te_3, and the results had a good agreement with hydrostatic pressure data below 9 GPa [4, 6, 7]. The relative deviations of the results (without account of change of geometric form of the sample upon compress) was estimated as $\sim 5\%$ for ρ and $\sim 20\%$ for S [3, 4].

RESULTS

The pressure dependences of ρ and S obtained in diamond and tungsten carbide anvil cells had a good agreement (Figs. 2 and 3). For

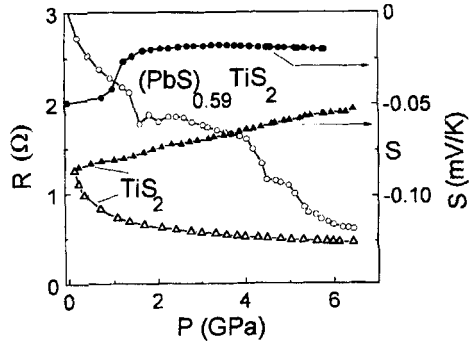

FIGURE 2 Dependences of resistance (left axis) and thermoEMF (right axis) on pressure of $(PbS)_{0.59}TiS_2$ and TiS_2 crystals along layers plane at $T = 293\,K$ measured at anvil cell with tungsten carbide.

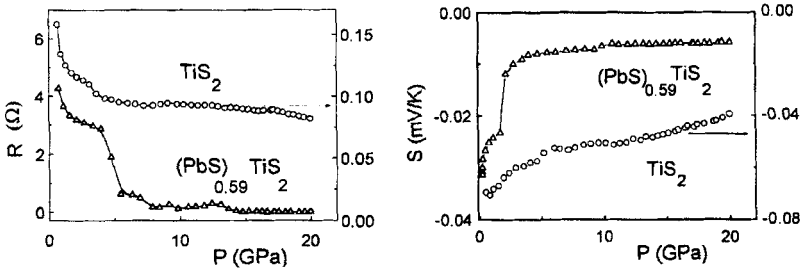

FIGURE 3 Dependences of resistance (left plot) and thermoEMF (right plot) on pressure of $(PbS)_{0.59}TiS_2$ and TiS_2 crystals along layers plane at $T = 293\,K$ measured at diamond anvil cell.

the $(PbS)_{0.59}TiS_2$ sample at $P \approx 2$GPa the descend of ρ and $|S|$ was observed. One more bend of ρ at $P \geq 4$ GPa was detected. In contrary, $S(P)$ and $\rho(P)$ curves for TiS_2 demonstrate only gradual decrease (see Figs. 2, 3). The similar results were obtained in Ref. [8] for TiS_2 crystals with high electron concentration $n = 1.4 \cdot 10^{20}\,cm^{-3}$, the data for $S(P)$ at $P > 5$ GPa being in a good accordance with the present ones.

The drop of ρ and S for $(PbS)_{0.59}TiS_2$ crystal may be caused by phase transition in PbS and TiS_2 layers, as their behaviour under pressure may be similar with the behaviour of bulk PbS and TiS_2 [1]. For TiS_2 at P up to 9 GPa no structural transformation was found

[8–10], but PbS at pressure ~2.5 GPa has a transformation from NaCl to orthorombic phase with parameters $a = 11.28$, $b = 3.98$, $c = 4.21$ Å [11–13], and at $P = 21.5$ GPa it has the transformation into CsCl structure [14]. On base of these data the change of ρ and S for $(PbS)_{0.59}TiS_2$ at ~2 GPa may be connected with phase transition in PbS-layers.

The possible mechanism of decrease of ρ and S for $(PbS)_{0.59}TiS_2$ crystals due to structural transformation in PbS-part is difficult to discuss without structural investigations at high pressure. One of the explanations may be the increasing of Ti-atoms concentration into the Van-der-Vaals gap between TiS_2-layers and, as consequence, increase of electrons in the conducting band [1, 8], because at high sulphur pressure TiS_2 has a tendency to transform into TiS_3 [15]. Another possible explanation may be based on a partial connection between cell parameters of layers which has to lead to cell parameters changes for TiS_2 layer and to a corresponding change of the electronic structure as a result of structural transformation in PbS part [14].

One may note that in Ref. [4], where the mechanical properties of the same samples of $(PbS)_{0.59}TiS_2$ crystals were tested, the similar structural transition seems to occur [16, 17], that probably led to a strong residual deformation along incommensurate direction.

The weak anomaly of ρ and S for TiS_2 at $P > 4$ GPa perhaps is caused by decrease of the forbidden band and semiconductor–semimetal transition, predicted by electronic structure calculations [9] and observed experimentally [8]. According to X-ray diffraction data [9], the pressure leads to compressing of distances between TiS_2-layers and increasing of their thickness (see Fig. 1), and these factors have a result increase of density of electrical charge between layers and enhancement of bonds between S-atoms [9]. The lowest conducting band of TiS_2 from M-point of the Brillouin zone shifts under the pressure in L-point, and at $P = 6–8$GPa the overlap with valence band in Γ-point appears [9]. The descend of ρ at $P > 4$ GPa observed for $(PbS)_{0.59}TiS_2$ (see Figs. 2, 3) in framework of model of weakly interacted layers we explain as result of electronic transition semiconductor–semimetal in TiS_2-layers [9]. The model of weakly interacted layers has a good agreement with electronic structure calculation results for misfit compounds [18, 19].

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