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High Pressure Treatment of Semiconductor-Metal Heterophase Structures

S.V. Ovsyannikov[1], V.V. Shchennikov[2], A.Yu. Derevskov[2] and V.V. Osotov[2]

[1] Department of Physics, Ural State University, Lenin Avenue 51, RU-620083 Yekaterinburg, Russia

[2] Institute of Metal Physics, Ural Division of RAS, GSP-170, RU-620219 Yekaterinburg, Russia

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Abstract. Semiconductor-metal (SC-M) phase transition was investigated in lead chalcogenides PbX (X=Te,Se,S) at pressures up to 9 GPa. In vicinity of the SC-M phase transition the relation between thermoelectric power S and electrical resistance ρ was found to agree with results of calculations according to the heterophase model with variable configuration of phase inclusions.

Introduction.

Pressure treatment of semiconductors above the phase transition point is known to be a method of producing nanocrystals [1]. In the vicinity of SC-M phase transformations a sample may be viewed as a model of heterophase (and, in particular, layered) systems. Most of the properties depend on the concentration and configuration of inclusions [2-3]. The theoretical approach to the real heterophase structures was developed based on the ordered inclusions model [2-4]. The relationships between the values of resistivity ρ, Hall coefficient R, thermoelectric power S and magnetoresistence MR were calculated for variable configuration of phase inclusions [2-5]. The data of MR, R, S and the value and temperature dependence of ρ for ternary mercury chalcogenides were compared with crystal structure investigations. This comparison allowed to attribute the origin of unusual properties at high pressure to inclusions of semimetal and semiconductor phases [5-7]. These experimental data in the vicinity of pressure-induced SC-M phase transformations were found to be in good agreement with the above model calculations. In the present paper experimental and theoretical investigations of the two-phase state were performed for PBX crystals, which are known to undergo pressure-induced phase transitions like mercury chalcogenides [8-13]. Lead chalcogenides are now being used for preparing misfit crystals consisting of alternating atomic layers of PbX and DX_2 (D-transition metal), with perspective for applications in electronics [14].

Experimental technique and model of calculations.

The automated set up for simultaneous investigations of electrical, thermal and volumetric properties of thin microsamples at high pressures up to 30 GPa was used for phase transition investigations of PbX crystals [2-4]. A sample is placed between two opposite plungers of Bridgman anvils made of tungsten carbide and superhard materials (diamonds, boron nitride). The plunger displacement X, pressure P (stress F), temperature T, and electrical voltage U of sample are recorded. The values of P were estimated from the acting stress F and tabulated dependencies $P(F)$. The usual size of samples was ~0.4 mm in diameter and ~0.1 mm in thickness. The pressure transmitting medium was a lithographic stone [2-4].

The calculations of the properties of two-phase states near the phase transition point were performed using a graphic model of the multiphase system [2,4]. Unlike most previous models where the shape of the inclusions is fixed [15], the configuration parameter of phase inclusions in the present model is variable between the cases of needles and sheets (parallel and consequent electrical and thermal connection). The second novel feature is that several properties of the material are considered simultaneously. The effective ρ or conductivity $\sigma = 1/\rho$ (and thermal conductivity λ) in this approach are viewed as a normalized sum of phase contributions in two

equivalent considerations of "consequent" and "parallel" electrical (thermal) connection of phases [2-4].

$$\rho = \sum c_i \cdot \rho_i \cdot f_i \cdot (\sum c_i \cdot f_i)^{-1}, \quad \sigma = \sum c_i \cdot \sigma_i \cdot f_i(\sigma) \cdot (\sum c_i \cdot f_i(\sigma))^{-1} \qquad (1),$$

where sum of phase concentrations c_i is equal to 1 and the configuration parameters along electrical (thermal) current are: $f_i = 3\rho/[A\rho + (3-A)\rho_i]$, $f_i(\sigma) = 3\sigma_i/[A\sigma_i + (3-A)\sigma]$. Eqs.1 are the interpolation of known limiting cases of parallel (parameter A) and consequent (A=3) electrical connections, and the spherical shape of phase inclusions (A=1) for elongated (0<A<1) and contracted (1<A<3) ellipsoidal inclusions.

By using of the same approach, the corresponding equations, for S, R, MR were derived in [2-5]. From these equations a simple relationship between ρ, λ and S follows [2-5]:

$$(S - S_2)/(S_1 - S_2) = (\rho\lambda - \rho_2\lambda_2)/(\rho_1\lambda_1 - \rho_2\lambda_2) \qquad (2)$$

Near the threshold of forward and reverse SC-M phase transitions in PbX (X=Te,Se,S) the calculations of the relationship between ρ and S were performed by Eq.2. The results of calculations were compared with the present data of ρ and S- measurements under pressure.

Results

Reversible phase transitions in PbS, PbSe and PbTe samples are seen by jumps of resistance above 2.5, 4.5 and 6.5 GPa and – during the decreasing of P (Fig.1,2).

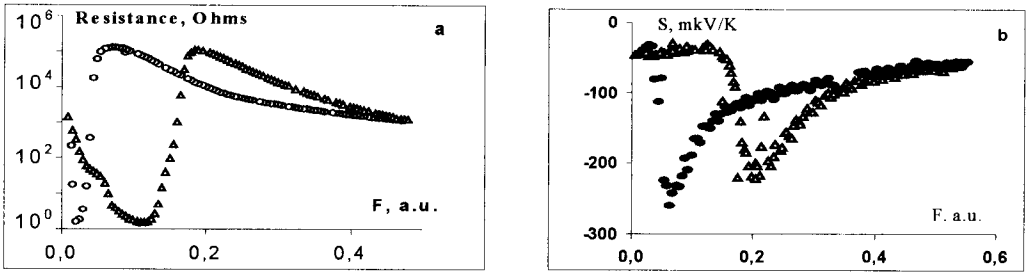

Fig. 1. The dependencies of the relative resistance ρ/ρ_2 (a) and thermoelectric power S (b) on the force acting (F) at T=293 K for PbS in pressure range 0 – 9 GPa. The triangles correspond to the pressure increasing cycle, and circles correspond to the pressure decreasing cycle. The beginning of phase transition is shown by arrows.

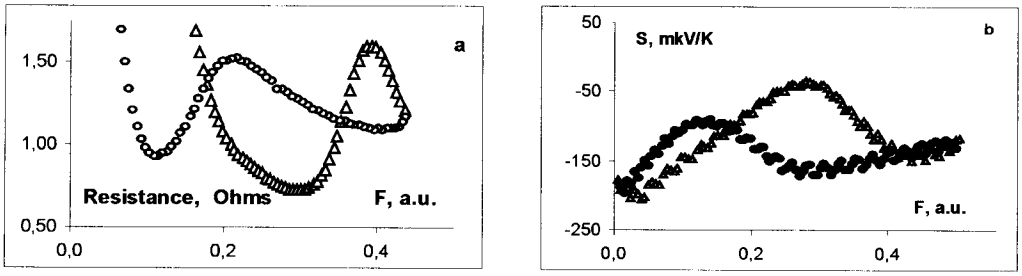

Fig. 2. The same dependencies as at Fig.1 for PbTe samples.

The results for PbSe the results are not shown. The wide width of the resistivity "jumps" observed is connected with the inhomogenity of samples under compression. The increase of the thermoelectric signal above phase transition point were later than changes of resistance (Fig1,2) The values of ρ and S for phases "1" and "2" in calculations were taken at the boundaries of the transition interval (Fig.3). Thermal conductivities of low and high pressure phases were taken to be equal ($\lambda_1 = \lambda_2$).

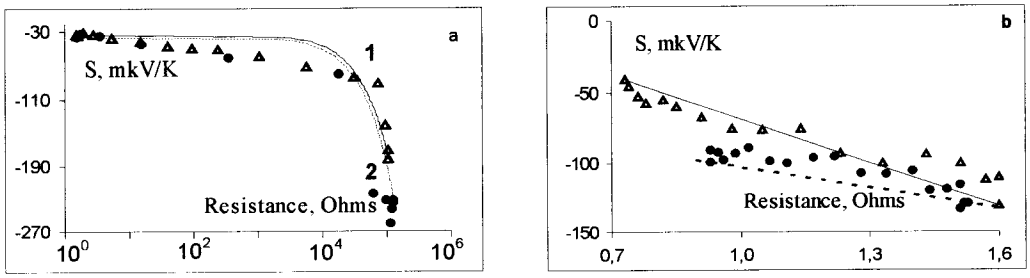

Fig. 3. Experimental data points and calculated using Eq.2 relations (lines) between thermoelectric power (S) and resistance (ρ) for PbS(a), PbTe(b) in phase transition regions. The open triangles correspond to the pressure increasing cycle, and filled symbols correspond to the pressure decreasing cycle. The solid and dashed lines correspond to the increase and decrease of P respectively.

Discussion

At initial state corresponding to the NaCl-phase all PbX compounds are narrow gap semiconductors with direct electron energy gap ε_G of about 0.3 eV, which decreases under the pressure applied ($d\varepsilon_G/dP \approx -60$ meV/GPa [9]). Taking into account values of ε_G and $d\varepsilon_G/dP$, one can see, that PBX ought to reach the near metal state (labeled phase "2" in calculations) before the structural transformation pressure. The jumps of absolute values of S in high pressure phase (labeled as phase "1") reflect the corresponding abrupt increase of energy gap ε_G. To discuss the pressure dependence observed we have used a model where *p*-bonds and the Peierls distortion of lattices are taken into account. It allowed to describe the type of crystal and electronic structure of V, VI and VII Group elements as well as some chalcogenides [6,7,16]. In particular, it explained the origin of semiconductor gap and the closing of it under pressure for substances with different kind of lattice: cubic, layered, chain structure, molecular crystals [6,7,16]. According to this model the metal state of PbX ought to be unstable in NaCl structure due to energy advantage of Peierls distortion. As p-band of PbX in NaCl phase is half filed with electrons, so the two-fold enlarging of cell parameter at high pressure orthorhombic phase [17] and corresponding two-fold splitting of p-electron band [6,7,16] is preferable. Thus opening of energy gap at Fermi level in high pressure phase of PbX and negative pressure coefficient of ε_G may be be explained in this model.

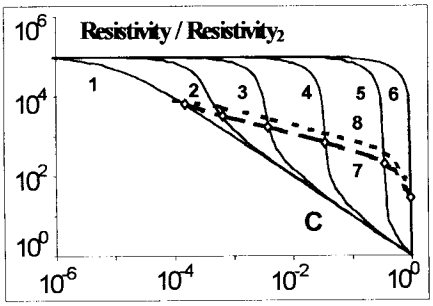

Fig. 4. Dependencies of normalized resistivity of two-phase material (solid curves 1-6) and boundaries of sign inversion of temperature coefficient of ρ (dash curves 7-8) at 300 K on M concentration C for various configuration parameters of inclusions A: **1** – $A=10^{-10}$ (parallel connection of phase, "needles"). **2** –$A=10^{-3}$; **3** – $A=10^{-2}$; **4** – $A=10^{-1}$; **5** – A=1 (spherical inclusions). **6** – A=3 (consequent connection of phases, "layers"). **7** – boundary of SC-M transition at 300 K. **8** – boundary of SC-M transition at 300 K for case, accounting the influence of interphase boundaries (see the text).

Relation between ρ and S for electron type materials PbS and PbTe in the vicinity of phase transition (Fig.3) is well described by Eq.2, while for PbSe (not shown) there is a divergence due to strong holes contribution in S. The approach allow to separate the physical and "geometrical" reasons of disproportional variation of S and ρ at phase transformation region. For PbS and PbTe the inclusions of metal phase "2" play main part in pressure dependencies of S and ρ near phase transition point (Fig1,2).

To describe the variation of ρ in two phase model we have performed the calculations of ρ by Eqs.1 and put the ratio of ρ for "1" and "2" phase ρ_1/ρ_2 to be equal 10^5 at T=300 K, as was observed for PbS (Fig. 4). Temperature dependencies of ρ for M ("2") and SC("1") phase were taken $\rho_2 = \rho_{20}+3*10^{-3}*T$, and $\rho_1=\rho_{10}*\exp(\varepsilon_G/kT)$, ε_G=0,3 eV. The threshold of SC–M and corresponding drop of ρ is shifted to lower values of concentrations of M phase when parameter A is decreasing (Fig. 4).The influence of phase boundaries was taken into account by increasing of parameter ρ_{20} by 5 times (Fig. 4) [5].There is certain upward change of boundary of SC–M transition. For mixtures above SC-M transition temperature coefficient of resistance ought to be equal to one of metal phase [5], So, the model used explained the weakening of temperature dependencies of resistance in agreement with our experiments.

Conclusions

In present paper the influence of phase boundaries and other defects on resistivity and temperature- and magnetic field- coefficients of resistivity was investigated in the vicinity of pressure–induced phase–transition for PbX- crystals. The model of ordered phase inclusions gave adequate description of entities measured.

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