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Phase transitions in PbSe under actions of fast neutron bombardment and pressure

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Abstract
In this paper, the influences of fast neutron bombardment, high pressure and chemical substitution on the electronic properties of PbSe single crystals are studied. For the first time in p-PbSe an electronic transition has been established of 'metal–semiconductor' type accompanied by an increase of resistivity of several orders of magnitude under the action of fast neutron bombardment. A similar increase in electrical resistance R was observed also under application of high pressure P above ∼3–4 GPa. The last increase was associated with the phase transformation from the NaCl-lattice to the GeS-lattice, which was seen also in sharp jumps of thermopower S. From the $R(P)$ and $S(P)$ dependences a linear decrease has been found of pressure of the above phase transition with increase of ⟨Sn⟩ content for n-$Pb_{1-x}Sn_xSe$ ($x = 0.06, 0.08, 0.125$) compounds.

1. Introduction

For investigations of electron structure parameters as well as for the modification of properties of semiconductors the following actions are usually applied: (i) irradiation with high-energy particles, (ii) application of external pressure, and also (iii) chemical substitution [1]. The above influences possess some general features in their action on crystal lattices and parameters of electron structure. For example, all of them are able to induce an electronic transition of 'metal–semiconductor' type [1].

Lead selenide (PbSe) is a representative of narrow-gap semiconductors ($E_g = 0.26$ at $T = 300$ K) [2] which is applied in infrared radiation detectors, thermoelectric devices, photoresistances, etc. According to the recent research [3], devices with lead-chalcogenides-based elements are able to compete successfully with the best analogues on the basis of 'classical' semiconductors: Si and Ge. But in comparison with these latter ones lead chalcogenides are more irradiation stable, due to the high density of states stabilizing the Fermi level [3].

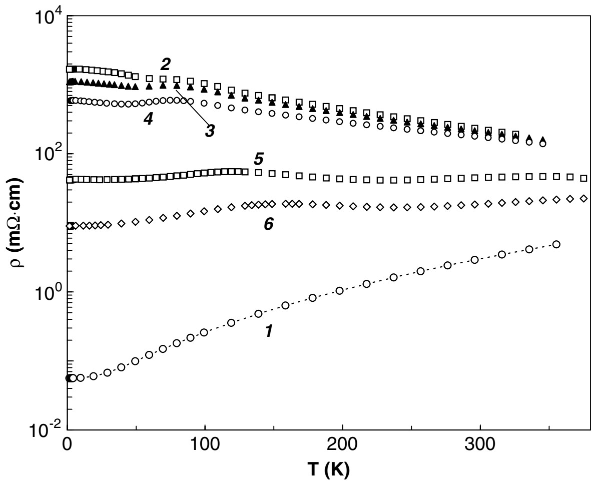

Figure 1. The dependences of electrical resistivity on temperature for p-PbSe single crystals at ambient pressure: (**1**) before irradiation; (**2**) after irradiation with fast neutrons to $\Phi = 1 \times 10^{19}$ cm^{-2}; (**3–6**) after subsequent 20 min annealing at $T = 350$ (**3**), 360 (**4**), 370 (**5**), and 380 K (**6**).

In the present work we applied the above-mentioned influences (bombardment with fast neutrons, high quasihydrostatic pressure, chemical substitution) for the study of the electron structure modification of PbSe-based single crystals: p-PbSe, n-$Pb_{1-x}Sn_xSe$ ($x = 0.06, 0.08, 0.125$).

2. Experiment

Single crystals of p-PbSe ($n_p = 2 \times 10^{18}$ cm^{-3}) were irradiated with a fluency ($\Phi = 1 \times 10^{19}$ cm^{-2}) of fast neutrons possessing energies above 1 MeV at a temperature of $T = 320 \pm 5$ K and ambient pressure. After the irradiation electrical contacts were ultrasonically applied to the samples with an indium-based solder. The measurements of resistivity and Hall constant were performed by the conventional Montgomery technique (modification of the Van der Pauw method) in the broad ranges of temperatures $T = 1.7$–390 K and stationary magnetic fields $B = 0$–13.6 T in an Oxford Instruments set up [4]. The irradiated samples were subjected to a sequential annealing at temperatures up to $T \approx 390$ K.

The high-pressure electrical and thermoelectric measurements were carried out in anvil-type chambers made from tungsten carbide and synthetic diamonds [5, 6]. The automated set-up used [5, 6] allowed us to register simultaneously several parameters (pressure, signal from a sample, thermal gradient, sample's contraction) under 'continuous' variation of pressure. A high effectiveness of the above high-pressure techniques was confirmed in the recent observation of a new intermediate phase in ZnTe [7, 8], phase transitions in Si [9, 10] and Ce [11]; detailed descriptions of the techniques are given in [5–11].

3. Results and discussion

Under irradiation with fast neutrons the electrical resistivity of p-PbSe single crystal increased by several orders and changed the sign of its temperature coefficient (figure 1); that corresponded to an electronic transition of 'metal–semiconductor' type. Irradiation of PbSe

Table 1. The pressures P_t of the NaCl–GeS phase transition in the $Pb_{1-x}Sn_xSe$ solid solutions estimated from the $R(P)$ dependences.

$Pb_{1-x}Sn_xSe$, at x =:	P_t (GPa) established in the anvil-type chamber from	
	Tungsten carbide	Synthetic diamonds
0	4.05	4.65
0.06	3.35	3.9
0.08	3.25	3.25
0.125	2.75	3.0
0.36	0.8 GPa (from [15])	

by high-energy particles is known to result in the formation of donor-type defects in the Se sublattice [13], but the concentration of donors created in such a way is believed to be limited ($\leqslant\sim 10^{17}$ cm^{-3}) [14]. This circumstance explained a conservation of p-type conductivity for our sample, as its hole concentration ($n_p = 10^{18}$ cm^{-3}) exceeded this maximal limit. At the subsequent anneals a tendency to property restoration manifested itself, and the return electronic transition occurred (figure 1). From the Hall coefficient and resistivity measurements the mobility of the charge carriers was estimated. It was found that the hole mobility had decreased after the neutron irradiation, but still its value remained sufficiently high (not shown); that attested to the high irradiation stability of this thermoelectric material.

Under the action of applied high pressure, PbSe underwent a phase transition from the NaCl-type to the GeS-type of lattice at $P_t \approx 4$ GPa (figure 2(a)). The transition was accomplished by an increase of R of several orders of magnitude as well as by a jump of the thermopower S (figure 2(b)). So, the structural NaCl → GeS transformation also corresponded to 'metal–semiconductor' type [4, 5]. Earlier in the thermomagnetic measurements it was found that the semiconductor energy gap in PbSe closed at the NaCl phase at $P \approx 3$ GPa [5, 6]. The present data of $S(P)$ (figure 2(b)) also attested to that. A cation substitution of Pb atoms by Sn ones resulted in both the narrowing of the semiconductor gap at the initial NaCl phase [15, 16] and a shift of the phase transition pressure (figure 2). The shift was found to be linear-like (table 1). The Raman measurements did not exhibit any significant effect of Sn doping [12].

After the high-pressure treatment up to 7 GPa the p-PbSe sample irreversibly changed the type of dominant charge carriers to electrons (not shown at the figures), whereas all n-PbSnSe samples maintained their initial electron type of conductivity (figure 2). A similar situation was also noted for a number of PbTe-based thermoelectric materials [17]. One may note the significant variations and high absolute value of thermopower at the high-pressure phase (especially at P releasing). So, the application of high pressure to PbSe is able to change both its thermoelectric figure of merit (æ $= S^2/\rho$) and thermoelectric effectiveness ($Z = S^2/\rho\lambda$) significantly. In [18] Zhu *et al* achieved an improvement in the above thermoelectric parameters in high-pressure (up to 5 GPa) synthesized PbTe crystals.

4. Conclusions

For the first time an electronic transition of 'metal–semiconductor' type has been established in p-PbSe single crystals under fast neutron bombardment. A similar behaviour of resistivity was observed during the NaCl → GeS phase transition under pressure. In the resistivity and thermopower measurements a linear decrease has been found of the NaCl → GeS transition pressure with Sn content in $Pb_{1-x}Sn_xSe$ solid solutions; that suggested a substitution-induced transition at $x \gtrsim 0.4$. The results obtained demonstrated the possibility of variations

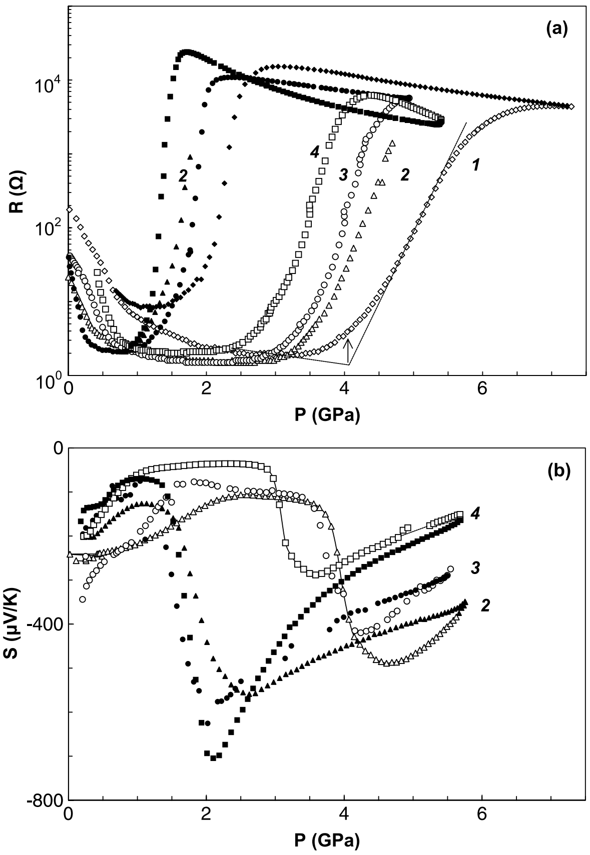

Figure 2. The dependences of electrical resistance R (a) and thermoelectric power S (b) on pressure for: p-PbSe (**1**), and n-$Pb_{1-x}Sn_xSe$ (**2**: $x = 0.06$, **3**: $x = 0.08$, **4**: $x = 0.125$) at $T = 298$ K. The open symbols correspond to pressurization, and the closed ones to pressure releasing. A method for estimation of the NaCl → GeS phase transition pressure is shown for sample (**1**).

of electronic properties of PbSe-based materials under actions of neutron irradiation, high pressure, and chemical substitution to achieve various goals.

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