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Phase transitions investigation in ZnTe by thermoelectric power measurements at high pressure

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Abstract

The pressure-induced phase transitions were studied in ZnTe by the thermoelectric power (S) technique. For the high-pressure trigonal phase $P3_121$ cinnabar the large thermopower values $S \approx +400$ correspond to semiconductor hole conductivity. During a transition into the orthorhombic structure *Cmcm* the value of S dropped by 40–50 times indicating metallic hole conductivity, like in the high pressure phases of other chalcogenides of II Group (HgSe, HgTe, CdTe) with *Cmcm* structure. In a transient region between the trigonal and orthorhombic phase (especially under decreasing pressure) a novel phase has been observed with a negative value of S. By analogy with other Zn and Cd chalcogenides whose NaCl phases have an electron type of conductivity the phase observed may have a NaCl structure.
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1. Introduction

Investigation of electron and crystal structure of Group II–VI compounds attracts a stable attention cause of their scientific importance and high technological potential [1–9]. Polymorph transformations under action of pressure present the most interest as they lead to sharp changes both of crystal lattice and also of electron structure, including 'semiconductor–metal' transitions for the majority of II–VI materials [5,6,10–25].

Development of effective methods of crystal structure study under pressure including X-ray absorption spectroscopy [12,13], angle- and energy-dispersive diffraction of synchrotron radiation with the Image-plate area detectors [4,6] has allowed to exact the structure types for HgX, CdX, ZnX (X—Te, Se, S, O) at high pressure P [4,6]. As it has been found the d-states play an important role in determination of structural and electron properties of II–VI compounds, so in modern calculations of electron structure and total energy of lattice [1–3] as 3d-orbitals of Zn as well as 4d-orbitals of Te have to be taken into account [13]. The results obtained [1–3] have allowed to forecast the crystal structure of stable phase and to find phase transitions pressure in agreement with experiments [4,6].

Investigation of thermoelectric properties of different structural modifications of II–VI compounds under ultra-high P [18–21,25–26] in its turn made it possible to detail the charge carrier sign and character of conductivity and, thus, to complete the controversial data of optical absorption [5,24] and electrical resistance [11,24]. In particular, in thermopower measurements [18,26,27] the difference of high pressure phases has been found between the true metallic phases with high concentration of holes on the one

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hand and semiconductor-like phases with relatively low concentration of electrons on the other hand where temperature dependence of electrical resistivity is a metal-like, but significant optical energy gap $E_g > 1$ eV is still conserved (ZnS, ZnSe, CdSe, etc.) [5,24].

Direct-gap semiconductor ZnTe is the less studied among II Group chalcogenides as its thermoelectric properties at high pressure up to 20 GPa were not investigated. There are three structural modifications in pressure interval 0–20 GPa in ZnTe: up to 8.9–9.5 GPa—cubic phase I (zinc blende $F\bar{4}3m$), above 8,9–9.5 GPa—trigonal II (cinnabar $P3_121$), and above 11.5–13 GPa—orthorhombic III (*Cmcm*) phase [1–10,12–15]. However, cinnabar structure in ZnTe is quite different from one in mercury chalcogenides, where it consists from separate spiral chains [4,6,14]. In ZnTe the cinnabar structure keeps coordination number the same ($z=4$) as in initial cubic phase [14]. Consequence of crystal lattice transformations under pressure in ZnTe differs from transformations in other zinc chalcogenides ZnSe and ZnS, in which between cubic ($F\bar{4}3m$) and orthorhombic (*Cmcm*) phases the phase with NaCl structure (*Fm3m*) exists [4–6, 15]. Recently, in Raman scattering measurements the unknown transient phase has been revealed at ZnTe in pressure diapason 12.2–13.7 GPa [7]. By author's of Ref. [7] opinion the reasons this phase was not observed in structural experiments [4,6] are a narrow region of stability in compare with pressure variation steps (~0.5–1 GPa) and also a difference of materials treated: polycrystalline or powder samples in the diffraction experiments [4,6] in contrary to single crystals—in the optical ones [7]. Observation of the intermediate phase is encumbered by mixture of phases in transition region—the initial cubic and trigonal phases in diapason 9.5–11 GPa [14] and trigonal and orthorhombic phases at 11.5–15.7 GPa [8], 12–13.7 GPa [7].

Thus, a goal of the present research consisted in investigation of phase transitions in ZnTe by thermopower method, which is sensitive to changes of sign of dominant charge carriers usually occurring under phase transformations [18,19,25–32]. Investigation of charge carriers sign in ZnTe and also of value and pressure dependence of thermopower S being also a purpose of the work.

2. Experiment

The measurements of electrical resistance R and thermoelectric power S under high pressure P were performed in synthetic diamond anvils possessing high electrical conductivity [18,19,25–32]. Catlinit gasket was used as a pressure-transmitting medium. Non-doped transparent red single crystals of ZnTe with sizes ~$0.2\times0.2\times0.1$ mm^3 were putted into hole ~0.25 mm in catlinit gasket. Synthetic diamond anvils were used as electrical outputs to a sample; an error contribution into thermopower value was accounted by measurements of pure Pb samples with close to zero thermopower $S\approx -1.27$ μV/K [27–33]. Diamond anvils served as a heater and a cooler for creation of thermal gradient ΔT along a sample. Thermopower measurements were carried out by two methods: at fixed pressure from linear dependence of thermoelectric voltage on thermal difference, and at fixed thermal difference under gradual variation of pressure. The automated setup was used allowing to register simultaneously all parameters of experiment: pressure (stress), anvils' displacement (contraction of gasket with a sample), thermal difference, electrical signal from a sample [27–33]. Values of pressure P were estimated with an error ±10% from calibration curve [10,18,19]; the errors in ρ and S determination did not exceed 5 and 20%, respectively. For comparison the similar measurements were carried out on previously tested ZnS and ZnSe single crystals [18].

3. Results and discussion

A dependence of electrical resistance R of ZnTe on pressure P (Fig. 1) agreed with previously published data of other authors [10–11,16]. One can see $R(P)$ curve did not reflect the behaviour of minimal semiconductor gap (Fig. 1) found in optical experiments [17]. Thus, a drop of $R(P)$ above ~5 GPa (Fig. 1) observed also in Ref. [10] is related to creation of point defects [13]. An increasing of R above ~9 GPa is connected with structural transition into trigonal phase of cinnabar [10], and a drop by 6 orders of magnitude

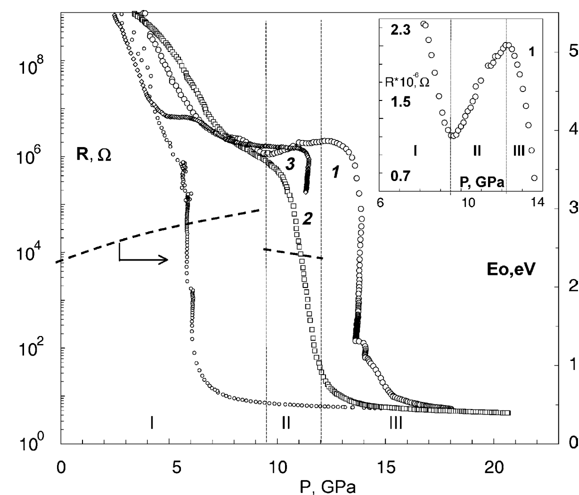

Fig. 1. The dependencies of electrical resistance R on pressure P for sample 1 (curves 1, 2) and sample 2 (curve 3) of ZnTe single crystals at $T=295$ K. 1 and 2 obtained at two consequent cycles of P increasing; small symbols correspond to P decreasing. By vertical dashed lines the boundaries are marked between I, II and *Cmcm* (III) phases according to the optical absorption data [17]. By slanting dashed lines the behaviour of minimal semiconductor gap E_o under pressure is shown taken from Ref. [17]. At the insert the part of $\rho(P)$ dependence 1 is shown in enlarged scale.

near 12–13 GPa is related to the next transition in orthorhombic *Cmcm* phase [4,6,8,10,12–14]. In subsequent cycles of sample compression the drop of resistivity corresponding to II → III transformation shifted to smaller pressures (Fig. 1), and increasing of R at the first I → II transitions was absent.

Measurements of S were carried out in a region of stability of trigonal and orthorhombic phases, where electrical resistance of the samples were less than $10^6\ \Omega$ (Fig. 1). At dependencies of $S(P)$ the transition from trigonal into orthorhombic phase was seen by sharp drop of thermopower value by ~40–50 times (Fig. 2). Thermopower of ZnTe indicates a hole type of conductivity both in trigonal phase and in orthorhombic one (Fig. 2). A large value of $S \approx 400\ \mu V/K$ attests about semiconductor character of conductivity at trigonal phase, that is consisted with optical absorption data (Fig. 1). At orthorhombic lattice the thermopower has typical for metals low values $S \approx +10\ \mu V/K$ in agreement with ~1 eV overlapping of valence and conductor bands found in calculations [2,3] and also with a high value of carrier concentration $1.5 \times 10^{22}\ cm^{-3}$ estimated from optical reflectance measurements [5]. Close positive values of S under pressure near 20 GPa have been obtained in Ref. [34], but there are no data below 20 GPa confirming the first and the second phase transformations at ZnTe in this paper. Thermopower of high-pressure metal phase of ZnTe has approximately the same value and sign as high-pressure metal phases of CdTe, HgTe, HgSe [18,20] possessing also orthorhombic structure *Cmcm* [4–6,15]; high-pressure 'metal' phases with NaCl structure of other zinc chalcogenides (ZnSe, ZnS) have a negative sign of S (Fig. 2, curves 9, 10) [18].

In transient region from semiconductor to metal phase the drop was observed at $S(P)$ dependencies (Figs. 2 and 3). At decreasing of P the drop manifested more brightly (even in cases when at P increasing no anomaly was observed (Fig. 2)). A sign inversion of thermopower at P decreasing allows to suppose an appearance of charge carriers of opposite sign—electrons (Fig. 3). The last explained the absence of any anomalies in R [10,11] insensitive to the sign changes of dominant charge carriers. The drop of S was observed only in cases the transition into metal phase was completed fully (Figs. 2 and 3).

This negative contribution into thermopower may be attributed to the new high-pressure phase observed earlier in Raman scattering measurements [7]. In mercury and cadmium chalcogenides HgTe, HgSe, CdTe and also in ZnSe (at decrease of P) a rock salt lattice *Fm3m* being intermediate between cinnabar and orthorhombic *Cmcm* phases [4,6,15]. In ZnTe the rock salt structure was observed earlier only under temperature conditions [9]. So, one may to suppose that the phase observed in our experiments possesses a rock salt lattice the more so that rock salt lattice of other zinc chalcogenides (and also cadmium chalcogenides) has an electron type of thermopower (Fig. 2) [18,27].

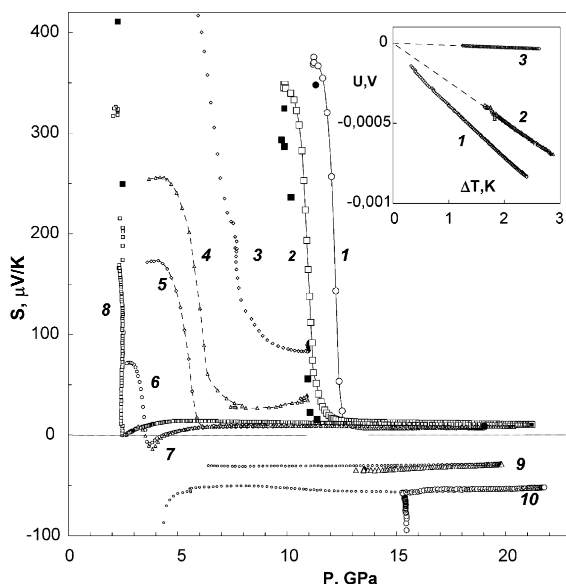

Fig. 2. The dependencies of thermopower S on pressure P for sample 1 (curve 1) and sample 2 (curve 2) of ZnTe single crystals at $T = 295$ K for several cycles of increasing (1 and 2) and decreasing (3–8) of pressure. The decreasing cycles were started from different values of pressure (11–21 GPa). Curves 9 and 10 correspond to the dependencies of thermopower on pressure for ZnS and ZnSe, respectively obtained at $T = 295$ K. Closed symbols correspond to thermopower values obtained for several cycles from dependence of thermoelectric voltage on thermal difference at fixed pressure. At the insert the above dependencies are given for sample 1 at P, GPa: 1—9.7, 2—2.5, 3—11.3.

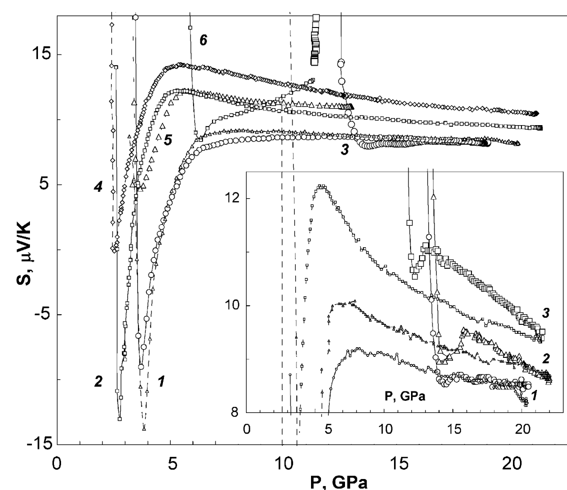

Fig. 3. The 'drops' of thermopower S for ZnTe at $T = 295$ K in enlarged scale obtained at decreasing of pressure P for samples 1 (1 and 2) and 2 (3–6). The decreasing cycles were started from different values of pressure (11–21 GPa), that resulted in variation of S drops. At the insert the similar S peculiarities are shown for sample 1 at consequent cycles (1–3) of P increasing (big) and decreasing (small symbols).

Based on thermopower behaviour (Fig. 3) the new transient phase is easy to observe at P decreasing.

4. Conclusion

The first investigation of phase transitions in ZnTe performed thermoelectric measurements under pressure has given original results inaccessible to other experimental techniques. A hole conductivity has been established both for the trigonal and orthorhombic high-pressure phases of ZnTe, and their semiconducting and metallic nature has been confirmed by the S values. The phase transitions ‘insulator–low resistivity phase’ in Zn chalcogenides (ZnTe, ZnSe, ZnS) occurred approximately at the same pressure region ($\sim$11–14 GPa) and exhibited very similar $R(P)$ dependence [11,18]. However, the thermoelectric data obtained in the present paper allowed us to reveal a basic difference between the high-pressure ‘metal’ phases of these compounds and, so, to remove a discrepancy between the optical [5,24] and resistance data [11,14]. In the transition region between trigonal and orthorhombic phases, the unknown phase was observed, with electron-like conductivity, supposedly with rock salt structure. The new phase observed may be the same one discovered recently by Raman scattering at 12.2–13.7 GPa [7].

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