Automated portable high-pressure setup for study of phase transitions in solids

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Abstract

The automated portable high-pressure setup developed for combined measurements of several properties of solids at ultrahigh pressure is discussed. The setup produces a high quasi-hydrostatic pressure $P$ (0–30 GPa) and permits to perform electrical, thermal and dilatometric measurements simultaneously. The setup registers changes both in electron and crystal structures of sample under nearly continuous variation of pressure. The results obtained demonstrate the advantages of the setup in studying both phase transformations and multiphase states in solids. The novel features of phase transitions in Si and ZnTe have been found. For silicon and zinc telluride, both the signs and values of thermoelectric power $S$ (Seebeck coefficient) of the several high-pressure phases have been established in the pressure range of 0–20 GPa. In ZnTe, a novel transient high-pressure phase has been observed of electron type of conductivity between the high-pressure trigonal (cinnabar) and orthorhombic ($Cmcm$) ones. Multiphase states of the semiconductors in vicinity of the structural transitions were analysed in the terms of the multiphase model of “orientated inclusions” permitting to vary configuration and concentration of phase inclusions.

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1. Introduction

In order to carry out comprehensive investigations of pressure-induced phase transitions in substances, the outstanding researcher in high-pressure physics—P.W. Bridgman—has proposed to control several parameters of sample simultaneously [1]. But as in the early Bridgman’s measurements of both the electrical resistance and volume contraction of sample [2,3] and even nowadays [4,5], high-pressure behaviour of various properties of substance as a rule is studied separately in different series of experiments. One can notice that structural, electrical, optical and other properties of substances have different sensitivities to appearance of inclusions of high-pressure phases and, hence, they exhibit anomalies at different values of pressure [6,7]. For example, X-ray measurements make it possible to estimate precisely a contraction of volume at phase transformation point, but usually they register a formation of new high-pressure phase already close to completion of transformation [4,5]; whereas, electrical resistance measurements allow to observe the beginning of transformation [7]. Bridgman has established that volumetric measurements give more precise values of phase transformation pressures $P_t$ in comparison with electrical resistance ones [1]. In case of semiconductors, the above-mentioned discrepancies between various techniques manifest very brightly [6,7]. Indeed, in the vicinity of phase transition point, a substance presents a mixture both of initial and novel phases [6,7], and that results in mixing of all properties but in a different manner [6]. “Effective"
properties of such a mixture crucially depend on concentration and geometrical configurations of phase inclusions [6]. So, the more various properties are registered simultaneously by a high-pressure setup, the more correct results may be obtained [1–3,6].

An additional obstacle in determination of phase transformations is a large step (≥1 GPa) in pressure variation, especially in optical and X-ray measurements [4,5]. So, a region of new phase existence may be overstepped. For instance, because of the above-mentioned problem, the high-pressure transient phases with a cinnabar structure in some zinc and cadmium chalcogenides have been found only recently after thorough experiments [4,5].

In the present paper, the automated portable high-pressure setup developed for investigation of phase transitions in the pressure range of 0–30 GPa is discussed. The novel results obtained at both elemental (Si) and binary (ZnTe) semiconductor systems in the phase transitions region illustrate the merits of the setup.

2. Experimental technique

The setup consists of a mechanical apparatus made mainly from titanium alloys (Fig. 1a) and registering block (not shown). There is a lever mechanism, 2 in Fig. 1a (three connected levers), and a pressure chamber, 3 in Fig. 1a, on the Table 1 of the apparatus (Fig. 1a). The reduction gear 5 with the electromotor (and handle) drive creates mechanical load transferring to high-pressure plungers. A high-pressure cell with a sample is located inside the portable cassette 6 which is introduced in the pressure chamber 3 (Fig. 1). The high-pressure setup contains both mechanical (4, 9) and digital sensors to register several properties of a sample simultaneously. So, the parameters which we are able to register by this setup (Fig. 1a) at nearly continuous variation of pressure up to 30 GPa are the following: applied force, sample’s contraction, anvils’ temperature, thermal difference \( \Delta T \) along a sample and electrical signal from a sample [8,9]. The experimental data are transferred to a computer. The autonomous versions of the setup contain a control unit with a microprocessor in order to operate experiments as well as an energy-independent RAM memory for data storing.

The high-pressure anvils were made from steel, hard alloys and superhard materials for pressure generation up to ~5, ~10 and ~30 GPa, respectively. Usage of anvils of different types with various shapes and volumes of high-pressure area has enabled us to improve the accuracy in phase transition determination [10,11]. Various kinds of synthetic superhard materials were applied in production of high-pressure anvils. Synthetic diamonds as well as boron-nitride (BN)-based superhard materials have a high compression stress and exhibit a resistance to cleavage propagation. So, they seemed rather convenient for construction of plungers for high-pressure apparatuses up to 50–60 GPa [10–13]. Sintered diamonds preserve both a high compression stress and high thermal conductivity and they also possess a high electrical conductivity due to metal inclusions [10–13].

For investigations of substances properties under variation of temperature or magnetic field, a miniaturised high-pressure apparatus has been developed, and it contains a system of titanium lever mechanisms for transmission of mechanical load to anvils placed inside a Dewar vessel or electromagnet. For such an apparatus, the non-magnetic
tungsten-free hard alloys based on titanium-carbide-nitride have been used for producing high pressure up to ~8 GPa. For higher pressures up to ~30 GPa, the insulating synthetic metal-free diamond anvils were used [10,11–14]. The above-mentioned miniaturised version of the setup allows to study the galvano- and thermomagnetic effects at ultrahigh pressure [14].

A quasihydrostatic pressure $P$ was produced in the anvil-type chambers [8,9–15]. To produce such a pressure, the gaskets (pressure-transmitting medium) are usually made from the soft solids such as lithographic stone, catlinite (materials based on CaCO$_3$), or pyrophyllite [16]. In our experiments, we used the gaskets from lithographic stone. The samples of sizes $\sim 200 \times 200 \times 20–50 \mu m$ were placed into a hole of 250–300 $\mu m$ in diameter drilled in the centre of the lithographic stone gasket. Values of pressure were estimated with 10% uncertainty from a “stress–pressure” calibration curve obtained with assistance of the known phase transitions in Bi, ZnS, GaP, etc. [15].

The thermoelectric measurements were carried out both in stationary conditions at fixed thermal gradient and in non-stationary thermal regime. A thermal difference was produced by heating the anvils (Fig. 1b). The diamond anvils served as a heater and a cooler in the thermoelectric measurements [15]. Sometimes synthetic diamonds served also as electrical outputs to a sample [8,9–15]. A temperature distribution in the anvils for different sample sizes and thermal conductivities [17] was used for estimation of error in determination of $\Delta T$ along a sample. To account an error introduced by the anvils themselves, a sample was replaced by a piece of lead whose room-temperature thermopower is close to zero, $S = -1.27 \mu V/K$ [18]. For the more precise measurements, the silver–platinum pressed tapes of 5 $\mu m$ in thickness were used. A majority of the thermopower data obtained by the above high-pressure technique (with a lithographic stone as a pressure-transmitting medium) was in a good agreement with data gathered in a truly hydrostatic pressure condition up to 2–9 GPa for a number of materials such as HgX, SmX (X=Te, Se, S), Bi$_2$Te$_3$, etc. [7–10,11–15]. Similar, but much more complicated techniques of thermoelectric measurements at high pressure have been developed recently based on natural diamonds [19–21].

Pressure-induced contraction of a sample placed inside a lithographic stone container (Fig. 1b) was measured with an assistance of electronic dilatometer 4 connected to the mechanical one (Fig. 1). An overall output signal from the dilatometer included an elastic contraction of the plungers and pressure chamber as well as a deformation of lithographic stone container. So, in order to pick out contribution from a sample, one has to exclude the linear effects arising both from the chamber and container which were obviously the same for all samples. A residual small effect appearing especially in vicinity of phase transitions both at pressurisation and pressure-releasing cycles is believed to exhibit volumetric anomalies of a sample.

The high-pressure setup developed was applied for investigation of microsamples cut from both single crystal of ZnTe and Si wafer grown by the Czochralski technique in nitrogen-rich medium (Si:N). The concentrations of interstitial residual oxygen, electrons and nitrogen in Si:N were, respectively, $9 \times 10^{17}$, $5.4 \times 10^{15}$ and $< 5 \times 10^{14}$ cm$^{-3}$. Initial crystal structure of the samples was controlled by the X-ray measurements.

3. Results and discussion

3.1. Si single crystals

In the $S(P)$ measurements, we observed the phase transformations in the Si:N sample from the diamond-like phase into the body-centred tetragonal $\beta$-Sn one, then into the body-centred orthorhombic lattice $Imma$, and finally into the simple hexagonal $sh$ phase at pressures above ~9, 12 and 16 GPa, respectively [4,5] (Fig. 2a). The transitions were seen also by change of both sample’s contraction and thermal gradient under pressurisation (Fig. 2b). By the abrupt changes of $dS/dP$ coefficient due to $P$ release, we obviously observed the structural transformations into Si-XII and Si-III lattices below ~9 and ~3 GPa, respectively [4,5] (Fig. 2a).

At nearly stationary conditions, the value of thermal difference along a sample is $\Delta T = qh/\lambda$, where $h$ is the thickness of a sample along a thermal flow, $q$ the density of thermal flow and $\lambda$ the thermal conductivity [15]. So, the change of $\Delta T$ under pressure at the phase transition point (Fig. 2b, inset) reflected a change in sample’s thickness (volume). An additional contribution into the $\Delta T(P)$ dependence might occur also due to variation in $\lambda$ value itself. Indeed, one can notice a correlation in phase transitions regions near ~10 and ~16 GPa between $\Delta x(P)$ on the one hand and $\Delta T(P)$ data on the other hand (Fig. 2b), as well as with $S(P)$ data (Fig. 2a). The transition near 13 GPa from the body-centred tetragonal into the body-centred orthorhombic structure was known to be accompanied by a negligible volume change (~0.2%) in comparison with the next transition into the simple hexagonal lattice above 16 GPa (~0.5%) [4]. We have observed some anomaly in contraction data near 13 GPa also (Fig. 2b), but it was comparable with experimental error. The similar results have been obtained for pure N-free Si single crystals grown by the Czochralski technique. As far as we know, the phase transitions in the metal phases of Si were earlier established only in structural and optical studies [4,5,22]. So, the setup developed has allowed to reveal the transitions happening both under pressurisation and $P$ decreasing by the speedy thermoelectric power measurements.

3.2. ZnTe single crystal

The results of the high-pressure study of the ZnTe single crystals are presented in Fig. 3. The phase transitions were
transition from the zinc blende into the trigonal phase of D (Fig. 2) was established between the same cycle of pressurisation within Refs. [4,5]. (b) The contraction curve is given after exclusion of the downward ones the transitions under pressurisation (Si-I → β-Sn → Imma → oh), while the upward arrows point the phase transition into the orthorhombic Cmcm (III) phase [23–29]. The high-pressure “metal” phases of other zinc chalcogenides (ZnSe, ZnS) possessing NaCl structure had a negative sign of S [32]. In a transition region from the semiconductor into the metal phase, the drop was noticed at S(P) dependencies (Fig. 3b). The sign inversion of thermopower at P releasing permitted to suppose an appearance of electrons (Fig. 3b). R(P) curve did not exhibit any anomaly in this region (Fig. 3a) as resistivity is insensitive to change of sign of dominant charge carriers.

This negative contribution into thermopower might reflect the formation of a new transient high-pressure phase. Earlier in the Raman scattering measurements, some unknown weak phonons were observed near the direct semiconductor–metal transition but these peaks were not associated with a new transient phase [34]. In mercury and cadmium chalcogenides HgTe, HgSe, CdTe (and also in ZnSe at decrease of P), the NaCl lattice Fm3m is an intermediate between the cinnabar and the orthorhombic Cmcm ones [4,5]. In ZnTe, the rock salt structure was observed earlier only under the high-temperature conditions [35]. So, one might propose that the new phase observed possessed a NaCl lattice. By the way, the NaCl phases of other Zn (and also Cd) chalcogenides have an electron type of thermopower [32,36]. The sample’s thickness (Fig. 3c) and a thermal difference along a sample (Fig. 3d) also had the obvious anomalies near 3 GPa that corresponded to the return transition from transient phase (with negative sign of thermopower) to the initial one (Fig. 3b). Thus, the measurements performed in the setup have revealed a new transient phase in ZnTe which was not detected earlier by other techniques (insensitive to sign of charge carriers).

The increase of R above ~9 GPa reflected the structural transition from the zinc blende into the trigonal phase of cinnabar (II) [23]; the subsequent drop of R by ~6 orders of magnitude near 12–13 GPa was related to the next transition into the orthorhombic Cmcm (III) phase [23–29]. In the subsequent cycles of compression of the sample, the drop of electrical resistance corresponding to II → III transformation shifted to the smaller values of pressure (Fig. 3a), whereas, the increase of R observed at the first I → II transition came to naught (Fig. 3a). The sharp drop of sample’s thickness near 13 GPa (Fig. 3c, curve 1) was due to passing of the phase transition (Fig. 3a,4) into the high-pressure phase with less lattice volume [4,5].

At the S(P) dependencies, the transition from the trigonal into the orthorhombic phase was seen by the abrupt drop of thermopower value by ~40–50 times (Fig. 3b). At the orthorhombic lattice, the thermopower had typical low values for metals, S ≈ +10 μV/K. That agreed both with ~1 eV overlapping of the valence and conductor bands found in the calculations [30,31], and also with the high value of charge carrier concentration 1.5 × 10^{22} cm^{-3} estimated from the optical reflectance measurements [22]. Values of S of the high-pressure metal phase of ZnTe were approximately the same as for the high-pressure metal phases of CdTe, HgTe, HgSe [14,32] possessing the orthorhombic crystal structure Cmcm too [4,5,22,33].

0 5 10 15 20
20 15 10 5 0

(a)

(b)

Fig. 2. Dependencies of thermoelectric power S (a) and relative contraction Δα of Si:N single crystal (b) under pressure P at T = 293 K. (a) The big open points correspond to pressurisation, while the small closed ones to releasing cycle. The upward arrows point the phase transitions under pressurisation (Si-I → β-Sn → Imma → oh), while the downward ones the transitions under P releasing (sh → Si-XII → Si-III) [4,5]; the shaded rectangles show the data from the other works (references within Refs. [4,5]). (b) The contraction curve is given after exclusion of the main linear slope (see the text). In the inset, the dependence is given of thermal difference along a sample ΔT (after exclusion of a linear slope) for the same cycle of pressurisation.

studied in the measurements of electrical resistance R (Fig. 3a), thermoelectric power S (Fig. 3b), sample’s contraction Δα (Fig. 3c) and of thermal difference along a sample ΔT (Fig. 3d). A correlation similar to the one for Si (Fig. 2) was established between R(P), S(P), Δα(P) and ΔT(P) curves in the phase transitions region (Figs. 3 and 4).

The increase of R above ~9 GPa reflected the structural transition from the zinc blende into the trigonal phase of 

\[ \Delta T \text{ (K)} \]

\[ \Delta \alpha \text{ (um)} \]

\[ P \text{ (GPa)} \]

0 5 10 15 20 20 15 10 5 0

(a)

(b)

In the inset, the dependence is given of thermal difference along a sample ΔT (after exclusion of a linear slope) for the same cycle of pressurisation.
3.3. Model of “orientated inclusions” for investigation of multiphase states in vicinity of phase transitions: application to ZnTe

The dependence of electrical resistance of ZnTe sample on time $t$ during the phase transition (near 13.3 GPa at Fig. 3a) is shown in Fig. 4. Passing of phase transformations depends on nucleation and growth mechanism and may be described by the Avrami equation [37]:

$$c_2(t) = 1 - \exp(-Kt^n),$$

(1)

where $t$ is the time, $K$ the rate of reaction and $n$ ($1 \leq n \leq 4$) is a constant depending on nucleation conditions [37].
When constant $A$ equals to 0, 3 or 1, Eqs. (2) and (3) coincide with ones for the above-mentioned cases of parallel and consequent electrical connections as well as for spherical shape of phases’ inclusions, respectively [39–41]. Intermediate values of $A$ ($0<A<3$) correspond to interpolated configuration of inclusions in a certain direction like elongated or contracted ellipsoids [6,42,43].

For $m$-phase system, the Eq. (2) for effective value of resistivity transforms into a polynomial algebraic equation of power $m$. In our case of $m=3$ (corresponding to a mixture of trigonal, new transient and orthorhombic phases in ZnTe near 13–14 GPa (Fig. 3)), the equation appears as follows:

$$A^2\rho^3 + \rho^2A\left[\rho_1(3c_3 + 3c_2 - A) + \rho_2(3c_3 + 3c_1 - A) +\rho_3(3c_1 - A) + \rho_4(3c_2 - A)\right] - (3-A)^2\rho_1\rho_2\rho_3 = 0.$$  

(5)

In order to establish the dependence of the extent of completion of the transformation on time, the fittings for three-phases mixture have been performed. Still, due to equality of the electrical resistance of the orthorhombic and the new transient phases (Fig. 3a), Eq. (5) reduced to a two-phase case ($m=2$) [6]. In the inset of Fig. 4, the dependencies (points) of extent of transformation completion are given, calculated with assistance of Eqs. (2)–(4) for $m=2$ for various configurations of inclusions ($0<A<3$).

One can notice that a value of $c_2$ and, hence, parameters $K$ and $n$ (estimated with assistance of Eq. (1)) depend on the configuration of inclusions. The least-squares method gave a variation of $n$ from 1.2 to 1.5 for the range of $1<A<3$ (Fig. 4, inset). By the way, usually, extent of transformation completion (concentration of new phase $c_2$) is extracted from resistivity data with assistance of simplified form of polynomial equation (Eq. (2)) only for case $m=2$ and spherical-shape of inclusions ($A=1$) [37].

The calculations performed in terms of the model (Fig. 4) have revealed the dependencies of both volume fraction of new phase $c_2(t)$, and corresponding parameters of transformation ($n, K$) on geometrical configuration of inclusions [37]. In order to choose the correct real parameters from the calculated ones, one has to perform independent treatment of volume fraction or shape of inclusions in a body of crystal.

4. Conclusions

The automated high-pressure setup developed made it possible to measure several properties of sample and environment simultaneously and that resulted in improvement of both the accuracy and reliability of phase transformation detection in a wide range of pressures (0–30 GPa). The examples shown for the Si:N and ZnTe samples demonstrated the advantages of the above approach in observation of novel features of known phase transitions as well as the novel high-pressure phases in the...
known substances. A correlation has been established between electrical, thermoelectric, thermal and volumetric properties in a vicinity of the phase transitions, although different properties exhibited various sensitivities to the phase transformations (leading to different transition pressures). The multiphase model for systems with variable configuration has allowed both to explain the visible discrepancies in detection of phase transformations by different techniques (firstly observed by Bridgman), and also to obtain the parameters of phase transformation (volume fraction of new phase, inclusions configuration, etc.). Alternative experimental high-pressure techniques are being developed at present permitting to register simultaneously, for example, only X-ray pattern and electrical resistivity [44,45].

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