A composite high-pressure cell with sintered diamond insets for study of thermoelectric and thermomagnetic properties in a range up to 30 GPa: Application to Pr and PbTe

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1. Introduction

Application of high pressure to solids can induce a transformation in their electron, magnetic and phonon subsystems. For some of the materials, the pressure-induced changes are significant and sometimes irreversible, while others “resist” and exhibit only negligible altering in properties. Owing to a limitation of maximal sizes of a sample in a high-pressure cell, basically “contact-less” techniques are employed for probing of properties. They include X-ray diffraction, Raman, Infrared, and Mössbauer spectroscopy, magnetization and others [1].

The transport properties carry the information about charge carriers and pressure-driven modification of an electron structure, and thereby form an own independent point of view of pressure-induced changes in conducting materials. However, at present the electrical resistivity is the only distributed and common-use technique in high-pressure experiments [1–4]. Measurement of other effects, such as thermal conductivity [5], thermopower (Seebeck effect) [6,7], Hall effect [8], magnetoresistance [9], longitudinal and transverse Nernst–Ettingshausen (N–E) effects (magnetothermopower) under high P is explained.

With an example of lead telluride (PbTe), it is demonstrated that magnetic field can significantly improve the thermoelectric efficiency under pressure. The merits of the cell developed are discussed concerning basic research and technologies.

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search for states with improved thermoelectric properties in the known and new promising thermoelectric materials and (ii) to investigate phase transitions in solids. For gathering of pressure dependencies of the thermopower under continuous variation in $P$ at ambient temperature, a cell was proposed to be used in automated multi-cycle experiments. The last circumstance suggests using materials with improved strength characteristics for manufacture of this cell.

So, we report both a composite high-pressure cell and the new approaches for investigation of transport properties of conducting materials. In the present work we: (i) describe the principal design of the high-pressure cell (Section 2), (ii) give the results of calculations of a temperature distribution inside a cell (Section 3), (iii) display the new results on the thermopower of praseodymium (Pr) and speculate about its pressure-driven phase transitions (Section 4) and (iv) describe a technique of measurement of the longitudinal and the transverse N–E effects under high pressure and possibilities of this technique as well (Section 5).

2. A composite high-pressure cell with sintered diamond insets

The principal design of a composite high-pressure cell is shown in Fig. 1. It presents a modification of the Bridgman–Drickamer–Bundy apparatus but without a chamber generating an external supporting pressure for anvils [20]. In our construction, the two-layer plungers of the cell consist of the inset tips and the matrixes sintered at high pressures and high temperatures (HP–HT) (Fig. 1a). Basic materials for manufacture of the insets are synthetic polycrystalline diamond and boron nitride. Natural jewellery diamonds can also serve as the insets, but owing to their fragility it seems difficult to employ such a cell in automated multi-cycle experiments. Tungsten carbide and tungsten-free hard alloys (Ti–C–N and “Russian” alloy Ni–Cr–Al [21,22]) are suitable materials for the matrixes. In our experiments, basically we employ the insets made of sintered diamonds, which are characterized both by a high compression stress and by a resistance to cleavage propagation. According to the literature [20], sintered diamonds permit generating pressures as high as $P$–30–50 GPa.

A range of pressures up to $P$–20 GPa may be calibrated by the known and distinctly observed phase transitions in the number of solids [23], as follows: Bi [24], PbS and PbSe [25], ZnSe, ZnS and CdTe [26], ZnTe [27], GaP [28] and others (Fig. 2). An uncertainty in $P$ determination by the above calibration curve (Fig. 2) was estimated to be less than $\sim$10%. Pressures higher than $P$–20 GPa—the transition in GaP [28] are determined with assistance of an approximation fitting (Fig. 2). This approximation works well in a $P$ range from $\sim$20 up to $\sim$30 GPa, for which the data on phase transitions in solids are available for comparison from structural and optical studies. Generation of pressures as high as $P$–40–50 GPa is also possible in our cell [29,30]. Pressure inside the cell may be determined in-situ by an equation of state of a substance, for example, with the assistance of radial X-ray diffraction.

Conventional DACs for structural, optical and other studies use metal gaskets, where a sample is put in a hole usually filled with liquids (mixture of alcohols) or gases (He, Ar, Ne, etc.) [29]. Such assembly serves both to confine a sample between the anvil tips and to create hydrostatic conditions around a sample. In order to achieve these goals in our cell, we employ (i) a peculiar shape of a solid-state gasket and the corresponding concavities in the high-pressure plungers (Fig. 1b) and (ii) a special kind of material for the gasket–lithographic stone (soft CaCO$_3$–based material [1]). After the beginning of a pressurization cycle, the lithographic stone becomes high-plastic and itself can serve as a pressure-transmitting medium for a sample (Fig. 1b); simultaneously, a supporting pressure (up to $P_s$–10 GPa) is being created in the ring-like bulges of the gasket around the tips of the anvils. This supporting pressure confines a sample in a central region between the tips of the anvils, where an ultra-high pressure is being generated (Fig. 1b). The ratio of the gasket’s thickness in its central part to the working diameter of the anvils in our case is lower than an experimentally theoretical threshold (0.055–0.057) separating (quasi-)hydrostatic and axial contractions [31]. It verifies the quasi-hydrostatic character of compression in our cell. The lithographic stone was experimentally chosen as the most suitable from the known solid materials with low shear yield strength for pressure-transmitting media, such as pipestone (catlinite) and pyrophyllite [1,31].

We found a good agreement between the data gathered by a similar cell with those available from hydrostatic studies up to $P$–10 GPa for the number of materials, for example HgX (X–Te, Se, S) [6,7], SmX [32], PbX [25] and ZnX [26,27]. Abruptness of drops/jumps in the electrical resistance or the thermopower during a phase transformation (for example, in ZnSe—in the inset in Fig. 2) can evidence a good uniformity of pressure in the central
part of the gasket (Fig. 1b). Meanwhile, a difference with true hydrostatics can manifest in materials, for which several high-pressure phases with close energies of lattices compete with each other. Stresses and small non-hydrostaticity around a sample can lead to variation in a transition path relatively true hydrostatics (non-observation of the known phases or observation of unknown ones [33]).

The thermal conductivity of diamonds is several times higher than that of copper. So, in case of sintered diamond anvils with metal inclusions that are characterized by a high value of electrical conductivity, the anvils themselves may serve both as electrical probes to a sample and as a heater–cooler pair [34,35]. In other cases the pressed platinum–silver ribbons of \( \rho_{\text{metal}} \) thickness are applied for the electrical outputs to a sample.

3. Calculation of temperature distribution in the high-pressure cell

A temperature distribution inside the high-pressure cell is a key point for techniques of measurement of all thermoeffects. The results of this calculation permit estimating possible uncertainties both in a temperature difference along a sample \( \Delta T \) and in related effects.

3.1. A model of calculation

To calculate the temperature distribution we employed a simplified model of the cell (Fig. 3a, inset), for which the diamond plungers are considered as cylinders [36]. In all elements of the cell, an equation of the thermal conductivity was solved, as follows [37]:

\[
C_{\rho} \frac{\partial T}{\partial \tau} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial T}{\partial r} \right] + \frac{\partial}{\partial z} \left[ \frac{\partial T}{\partial z} \right].
\] (3.1)
where r and z are the radial and the axial coordinates, \( \lambda \) and c are, respectively, the thermal conductivity and the heat capacity of a material, \( t \) is the time, and \( \rho \) is the density of a material. As the model was characterized by a cylindrical symmetry, a two-dimensional \( T \) field was considered.

Near the boundary \( x \) (\( x = r, z \)) separating different elements, the thermal resistance was adopted to be zero:

\[
\frac{\partial T}{\partial x} \bigg|_{x=0} = \frac{\partial T}{\partial x} \bigg|_{x=0}.
\]

A heat exchange of the side surfaces with air is described by Newton's law, as follows [37]:

\[
\frac{\partial T}{\partial x} = \alpha (T_m - T_b),
\]

where \( T_m \) and \( T_b \) are the temperatures of the environment and the plunger's surfaces, respectively, \( x \) is the coefficient of the heat exchange by convection. The temperatures of the lower \( T_l \) and the upper \( T_u \) surfaces of the cell were assumed to be constants. The task was solved by the finite element method using a differential scheme.

Substituting the partial derivatives in Eqs. (3.1) and (3.2) by the differential expressions, we derived the following:

\[
\frac{\partial T}{\partial r} + \frac{z}{r} \frac{\partial T}{\partial z} = \frac{\lambda_j}{a_j} \left( T_{i,j+1,k} - 2T_{i,j,k} + T_{i,j-1,k} \right),
\]

(3.4)

where \( T_m \) and \( T_b \) are the temperatures of the environment and the plunger's surfaces, respectively, \( x \) is the coefficient of the heat exchange by convection. The temperatures of the lower \( T_l \) and the upper \( T_u \) surfaces of the cell were assumed to be constants. The task was solved by the finite element method using a differential scheme.

We assumed the approximation below in order to reach a stable scheme of solution:

\[
T_{i,j,k} = \frac{T_{i,j,k+1} + T_{i,j,k-1}}{2},
\]

(3.7)

After a series of simple manipulations, the finite-difference analogue of Eq. (3.2) was derived as follows:

\[
T_{i,j,k+1} = \left\{ T_{i,j,k} - 0.5 - a_j \Delta t \left( \frac{1}{a_j^2} + \frac{1}{a_l^2} \right) + \frac{a_l \Delta t}{a_l^2} \left( T_{i,j+1,k} + T_{i,j-1,k} \right) \right\}
\]

\[
+ \frac{a_j \Delta t}{a_j^2} \left( \frac{1}{a_j^2} \frac{\Delta T}{T_{j+1,k}} + \frac{1}{a_j^2} \frac{\Delta T}{T_{j-1,k}} \right)
\]

\[
\cdot \left\{ 0.5 + a_j \Delta t \left( \frac{1}{a_j^2} + \frac{1}{a_l^2} \right) \right\}^{-1}. \quad (3.8)
\]

Here \( a_j = \lambda_j \rho_j c_j \) is the coefficient of the thermal diffusivity in \((i,j)\) bundle, \( \Delta t \) is the time step obeying the following limiting condition: \( \Delta t \leq \min(\Delta r, \Delta z) / \max(a) \) (\( \Delta r \) and \( \Delta z \) are the fixed steps in coordinates) [36].

To account for the boundary conditions, a fictitious external half-layer with temperature \( T_f \) was added, a temperature of the surface \( T_s \) was determined as follows:

\[
T_s = \frac{1}{2}(T_f + T_b), \quad (3.9)
\]

where \( T_b \) is the temperature inside a layer, bordering the body's surface. So, an account for the boundary conditions led to \( T_f \) determination, and the normal derivative in Eqs. (3.2) and (3.4) was substituted by the following expression:

\[
\frac{\partial T}{\partial r} = \frac{T_b - T_f}{\delta}, \quad (3.10)
\]

where \( \delta \) value equals \( \Delta r \) or \( \Delta z \), respectively. Under the boundary conditions as in Eq. (3.9), a temperature of the fictitious external half-layer \( T_f \) was determined by a method of sequent approximations as follows:

\[
T_f = \frac{1 - \Delta r^2 / 2\delta T_b + (\Delta r^2 / \delta) T_m}{1 - \Delta r^2 / 2\delta}. \quad (3.11)
\]

We calculated temperatures inside each element and fictitious half-layers as well. A condition of stationarity of the temperature field was checked. The parameters of the materials used for the calculations are summarized in Table 1. They correspond to conditions of real experiments in the composite high-pressure cell (Fig. 1). The number of semiconductors (Si, Te, Se) and metals (Pt, Cu, Au) was considered as samples [38,39], and the lithographic stone as a gasket [40]. A temperature difference \( T_2 - T_1 \) was varied in a range from \( T = 0 \) to 10 K at fixed \( T_1 = 293 \) K. The coefficient of the heat exchange was assumed to be \( a = 7 \) W/(m²K) [37]. As the thermal conductivity \( \lambda \) for the synthetic diamonds at ambient conditions is equal to \( \sim (0.5/2) \lambda_{Cu} \) (for natural \( \sim 2\lambda_{Cu} \), Cu—copper) [41], in the calculations \( \lambda \) of the plungers was taken to be equal to \( \lambda_{Cu} \).

<table>
<thead>
<tr>
<th>Table 1: Heat properties (from Refs. [37,39,41])</th>
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<tbody>
<tr>
<td>Element</td>
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<tr>
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<tr>
<td>Air [37]</td>
</tr>
<tr>
<td>Plunger [39,41]</td>
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<tr>
<td>Gasket from lithographic stone [37]</td>
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<tr>
<td>Sample [39]</td>
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2.6. Results of the Calculation

Fig. 3 shows that a variation in parameters alters the temperature distribution in the cell. A dependence of a temperature difference \( \Delta T \) along a sample on its thickness \( h \) and thermal conductivity \( \lambda \) is as follows [37]:

\[
\Delta T = \frac{q}{h} \cdot \frac{1}{\lambda}, \quad (3.12)
\]

where \( q \) is the density of thermal flow, which is also a function of \( \lambda \). Due to increase in \( q \) with \( \lambda \), a significant temperature difference \( \Delta T \) appears even for samples characterized by a high thermal conductivity (Fig. 3). Real diamond anvils have conical facets (Fig. 1) increasing a density of \( q \) through a sample (and therefore \( \Delta T \)), compared with the calculated values (Fig. 3). A cylindrical shape of the plungers as well as \( \lambda = \lambda_{Cu} \) were used as a limit case, which is very unfavourable to measure thermoeffects. Owing to a very high thermal conductivity of the anvils, inside them \( \Delta T \to 0 \), and hence creation of a temperature difference \( \Delta T \) in a sample in a direction transverse to the cell axis (i.e. along with the working surfaces of the diamonds [36]) seems hardly possible.
allows the measuring of electrical resistance by a two-probe with a liquid media [42,43], DACs with a cross-temperature measurement, including the large-volume compressible capsules only a few types of high-pressure cells for thermopower.

At present there are difference [44–47], and some others [48]. The cell developed allows the measuring of electrical resistance by a two-probe method [25–27]. Below, we describe the technique of thermopower measurements and its application to Pr.

4. Experimental details

To investigate the pressure dependence of thermopower (Seebeck effect) at room temperature, the cell is placed in a centering cassette, which is introduced into an automated high-pressure set-up [49]. The set-up was designed according to Bridgman’s conception of the simultaneous control of several parameters of a sample under pressure [50]. Pressurization and decompression cycles in this set-up are accomplished with the assistance of an electromotor, and hence the set-up supplies data on alteration of properties of a sample under almost continuous variation in pressure [49]. Besides the thermopower, the set-up permits investigating a pressure dependence both of a contraction of a sample (related to compressibility) and of a temperature difference ΔT along the sample; the latter reflects a change both in the compressibility and in the thermal conductivity (Eq. (3.12)) [49].

Thermoelectric measurements are being carried out in the following three regimes: (i) at fixed P under variation in ΔT; (ii) at fixed ΔT (or fixed density of a thermal flow q) under variation in P; and (iii) in a non-stationary regime under monotonic changing both in ΔT and in P. All three methods give the same results. ΔT is produced by heating the upper anvil (Fig. 1b), so the diamond anvils serve as a heater–cooler pair. In some cases, the synthetic diamonds also serve as the electrical probes to a sample, while, for more precise measurements, the ~5-μm-thick silver–platinum pressed tapes are more preferable for electrical outputs. In order to check a possible contribution of the anvils themselves to thermopower, a sample of Pb (S ≈ −1.27 μV/K) [51] is measured under the same conditions. An uncertainty in ΔT results in a similar experimentally verified uncertainty (less than ~20%) in an absolute value of thermopower. However, as the uncertainty in ΔT is not a function of applied pressure, a pressure dependence of S has the same accuracy as that of the thermoelectric voltage (a relative error is less than ~1%).

4.2. Praseodymium: two scenarios of the pressure-driven phase transitions up to P~22 GPa?

Through the row of rare-earth metals, an evident structural systematic is seen as a function of the atomic number [52,53]. Pr is the second element in this row, after the contradictory cerium, so an understanding of its high-pressure behaviour is important for the whole group. At ambient pressure Pr adopts the double hexagonal close packed (dhcp) structure with 4f²5d¹6s¹ electron configuration. A recognized sequence of the room temperature pressure-driven phase transformations in Pr is as follows [52,54]: dhcp → fcc (face-centred cubic) → distorted fcc (d-fcc) → bcc (body-centred) mononclonic (C2/m) → z-uranium (z-U), around P~4–5, 7–8, 12, and ~19–25 GPa, respectively. The second high-pressure phase, d-fcc, was attributed to the rhombohedral phase R3m (space group 166) [54], while in other works it was attributed to the hexagonal (space group 166), hR24, structure [55]. The monoclinic phase (C2/m) was established in a number of studies [54,56,57], and the widest region of its stability was found to be from P~10 up to ~25 GPa [54]. Meanwhile, in other works [55], the monoclinic phase was not detected. One more controversial point is the onset of the transformation to the z-U phase, concurrent with a volume collapse of ΔV~−9% [55–16%] [57]. Thus, according to Ref. [54], the transition begins around P~25 GPa, while in other studies it was already found near P~19 GPa [55–57].
The pressure dependence of the thermopower of Pr has already been measured in the range up to \( P = 17.5 \) GPa at room temperature [58]. In Ref. [58] a similarity was noticed between the \( S(P) \) curves for Pr and La [48], characterized by an empty 4f band, while both were significantly different from the one for Ce [59] characterized by one electron at the 4f band. In the present work we undertake a new study of the thermopower of polycrystals of Pr (99.99%) in the pressure range up to \( P = 22 \) GPa, aiming to clarify the path of the structural transformations under pressure, and in particular, to search for features around \( P \approx 12 \) and \( 19 \) GPa, which might be attributed to the above-mentioned dispute transitions.

At ambient \( P \) the thermopower of Pr was found to be negative in the range of temperatures from 5 to 1000 K [60,61], but applied pressure shifts it to a positive region (Fig. 5a and [58]). One can notice that the features in the \( S(P) \) curve for Pr (Fig. 5a) correspond well to the above phase transformations, as well as to the data of previous work [58]. In fact, around \( P = 12 \) GPa some transition (to the monoclinic lattice) is seen in the \( S(P) \) curve for the first cycle of pressurization (Fig. 5a, 1st cycle). However, there are no further distinct peculiarities until \( P = 19 \) GPa, which might be attributed to the phase transition to the \( \alpha \)-U structure concurrent with the volume collapse (Fig. 5a, 1st cycle). The \( S(P) \) curve for decompression exhibits a typical structural transformation hysteresis loop, which begins below \( P = 12-13 \) GPa (Fig. 5a, 1st cycle). Moreover, the behaviour of the \( S(P) \) curve on the first decompression cycle is different from the one on pressurization, but is more resembling to the one for the second pressurization cycle (Fig. 5a). It seems the return phase transitions in Pr occur by a different scenario for which some of the intermediate phases may be absent. On further pressurization cycles, a differing transition path is realized too (Fig. 5a). This effect was clearly observed for two samples cut from the same ingot of Pr. Unlike situation is in Ce for which all pressurization cycles exhibited the same features in \( S(P) \), hinting at the same sequence of phase transitions (Fig. 5a, inset) [59]. Note that the \( S(P) \) curves for Pr obtained, both in stationary and in non-stationary thermal regimes, are in good agreement (Fig. 5).

Following the supposition of similarity of the phase transitions in these two lanthanides, the transformations in Pr also should be reversible [54]. Then, a possible reason of alteration in the behaviour of the \( S(P) \) curves after the first cycle of pressurization might consist in a change in elastic strains inside a sample (owing to the accumulation of pressure-induced defects in the crystal lattice), shifting the boundaries of thermodynamic stability of the phases [54]. Ref. [55] reported on the onsets of the transformations to the \( fcc \), \( d-fcc \) and \( \alpha-U \) phases around \( P = 4-7 \) and \( 19 \) GPa, respectively. In our case, the distinct bends are seen in the \( S(P) \) curves near \( P = 4-5 \) GPa (Fig. 5a, 2nd, 4th and 5th cycles) and in the \( \Delta T(P) \) dependencies around \( P = 8 \) GPa (Fig. 5b). The last transition to the \( \alpha-U \) lattice might be responsible for a growth in \( S \) around \( P > 18 \) GPa and a corresponding hysteresis persisting down to \( P = 8 \) GPa, which are obviously seen, for example, in the \( S(P) \) curves gathered for the 4th cycle (Fig. 5a).

So, probably, on the second pressurization cycles we observe a transformation sequence excluding the monoclinic phase [55]. Then, one can infer that the scenario of the phase transitions in Pr suggesting the stable monoclinic lattice [52,54,56,57], is principal. However, defects and distortions in the crystal lattice can crucially change conditions of thermodynamic stability of this phase and even suppress it [55]. The non-observation of abrupt jumps in the \( S(P) \) curves around \( P = 18 \) GPa hints that the transition to the \( \alpha-U \) phase happens through a heterophase mixture smoothing the volume collapse [55,57]. In the pressure dependencies of a temperature difference along a sample \( \Delta T(P) \), some peculiarities are also noticed near the phase transition pressures (Fig. 5b). As a \( \Delta T(P) \) curve reflects a change in the sample's compressibility

**Fig. 5.** The pressure \( P \) dependencies of the thermopower \( S(a) \) and the temperature difference \( \Delta T \) along a sample (b) for polycrystalline praseodymium (Pr) at \( T = 295 \) K for pressurization and decompression cycles (shown by the arrows). (a) The dashed lines and the bulk arrows mark the structural phase transformations near \( P = 5, \approx 8, \approx 12 \) and \( 19 \) GPa [52,54]. Phases: I—double hexagonal close packed (dhcp); II—face-centred cubic (fcc); III—distorted fcc (rhombohedral phase \( \bar{R}3m \) [54] or hexagonal (space group \( \text{h} \)66), hR24 structure [55]); IV—body-centred monoclinic (\( \text{C}2/m \)) (see the text); V—\( \alpha-U \). The \( S(P) \) curve for the 5th cycle was measured in a non-stationary thermal regime (see plot b). In the inset the \( S(P) \) curves for the neighbouring rare earth–cerium (Ce) (from Ref. [59]) are given for comparison of two pressurization cycles. The bulk arrows point to the structural transformations in Ce as follows: fcc \( \leftrightarrow \) distorted, fcc \( \leftrightarrow \) bcc (monoclinic, \( \sigma \)-phase (\( \text{C}2/m \)) or \( \sigma \)-uranium phase (distorted variants of fcc lattice)) \( \leftrightarrow \) bcc tetragonal \( \zeta \)-phase (\( \text{I}4/\text{mmm} \)), around \( P = 0.8-1, \approx 5-7 \) and \( 12-17 \) GPa, respectively [52,54]. (b) The \( \Delta T(P) \) curves for Pr for all cycles exhibited a distinct bend near \( P = 8 \) GPa obviously related to the II–III transition. In some of the \( \Delta T(P) \) curves a bend near \( P = 4-5 \) GPa attributed to the I–II transition was also observed.
(Eq. (3.13)), the bends in the $\Delta T(P)$ curves corroborate the above interplay between thermopower alteration (Fig. 5b) and structural transformations in Pr.

5. Application of the cell for measurement of the thermomagnetic Nernst–Ettingshausen effects (magnetothermopower) under high pressure

As the composite high-pressure cell consists of non-magnetic materials, it may be also employed in investigations in magnetic fields. Using similar cells for the first time, the transverse magnetoresistance [9] and the longitudinal and the transverse N–E effects [10,11] were investigated at pressures as high as $P \approx 30$ GPa. Below we give a short introduction on the N–E effects, describe our technique and display its application for improvement of the thermoelectric efficiency of PbTe.

5.1. Longitudinal and transverse Nernst–Ettingshausen effects

The thermomagnetic effects (in contrary to their galvanomagnetic analogues) crucially depend both on a scattering mechanism of charge carriers and on a type of energy gap (direct or indirect), and therefore carry a unique information concerning pressure-driven modification in the electron structure [62–65]. The longitudinal N–E effect consists in a variation in the thermopower $S$ along a temperature difference $\Delta T$ in a transverse magnetic field $B$. While, the transverse N–E one consists in the appearance of a thermoelectric voltage $U$ in the direction perpendicular both to $\Delta T$ and to $B$ ("Hall" direction). Measurements of the above effects using a "classical" scheme [62] (Fig. 6a) are available only for a low-pressure range up to $P \approx 2–3$ GPa [66–68].

For intrinsic semiconductors with one-band conductivity, the mathematical equations for the transverse magnetoresistance ($MR$) (for a sample of shape of the Carbino disc [65]), the longitudinal ($\Delta S_l$) and the transverse ($\Delta S_t$) N–E effects in weak magnetic fields ($\mu B < 1$) are as follows [62,65]:

$$ MR \equiv \frac{\Delta T(B)}{\rho} = A_1(\mu B)^2, \quad (5.1) $$

$$ \Delta S_l(B) = A_2 \left( \frac{k}{e} \right) (\mu B)^2, \quad (5.2) $$

$$ Q = A_3 \left( \frac{k}{e} \right) \mu, \quad (5.3) $$

where $\rho$ is the electrical resistivity, $Q$ is the coefficient of the transverse N–E effect [62,65], $e$ is the electron charge, $k$ is the Boltzmann constant, $\mu = e\tau/m$ is the mobility of charge carriers ($m$ is the effective mass), $\tau$ is the impulsion relaxation time of charge carriers and $r$ is the scattering parameter describing a dependence of $r$ on the electron energy $e$, $r(e) \approx e / kT$ [62,65]). The constants $A_1$, $A_2$ and $A_3$ are the functions of $r$ and are determined by Fermi integrals [62,65]. $\Delta S_t$ depends on $r$ in a hidden manner (Eq. (5.2)); thus, for example, for two opposite cases of scattering by acoustic phonons ($r = -\frac{1}{2}$) and by charged centres ($r = \frac{1}{2}$), the constant $A_2$, respectively equals $A_2 \approx 9\pi / 16(1 - n/8)$ and $A_2 \approx 30$, and hence the $S$ value either increases ($r = -\frac{1}{2}$) or decreases ($r = \frac{1}{2}$) with $B$ [64,65].

5.2. Experimental details

For measurement of properties under variation either in magnetic field $B$ or in temperature, a miniaturized high-pressure apparatus is employed, for which a transmission of a mechanical load to the plungers is accomplished via a system of titanium lever mechanisms [49]. To investigate in magnetic fields, a high-pressure cell of the same design (Fig. 1) is assembled from the plungers made of the non-magnetic tungsten-free hard alloys on the basis of “titanium–carbide–nitride”, and the insulating synthetic metal-free diamond anvil inserts. This cell also permits
generating pressures as high as 30 GPa. The pressed platinum-silver ribbons of \( \sim 5 \mu m \) thickness are being used for electrical outputs to a sample. Other details correspond to the technique of measurement of thermopower (see Section 4.1).

The principal scheme of measurement of both N–E effects may be assumed to be similar to the one shown in Fig. 6b, when the anvils are as in Fig. 1b. Because of an asymmetric location of the electrical probes on the surfaces of a micro-sample (Fig. 6b), turning of the cell around its axis in a non-zero magnetic field has to lead to a variation in \( S \). One can surmise there are two positions of the cell, corresponding to the maximal variation in \( S \) because of contributions of both the longitudinal and the maximal (for certain setting of the probes) transverse N–E effects (Figs. 7 and 8) in a non-zero magnetic field. As the transverse N–E effect is extracted from a projection of the \( \Delta x \) distance on the “plain” normal to the \( B \) direction (i.e. from the “Hall distance”—perpendicular both to \( B \) and to the thermal flux \( W \)), it achieves a maximum when this projection is maximal (i.e. equals \( \Delta x \)) (Fig. 6b). When the projection of the \( \Delta x \) distance to the “plain” normal to the \( B \) direction is negligible (Fig. 6b), only the longitudinal N–E effect is extracted. Fig. 7 displays the experimental \( \Delta S(B) \) data for \( p \)-PbSe at \( P = 3.7 \) GPa obtained for several turns of the cell around its axis and corroborates the above speculations. From Fig. 7 one can learn that the correct values of the longitudinal N–E effect are obtained when the transverse one is minimal. Fig. 8 accumulates several series of experimental data for the transverse N–E effect as a function of an angle of a turn and demonstrates their good fitting by the cos function.

In experiments one can directly measure a longitudinal thermoelectric voltage \( \Delta U_1(B) \) and extract a transverse one (linear on \( B \))–\( \Delta U_2(B) \), which are related to the longitudinal (Eq. (5.2)) and the coefficient \( Q \) of the transverse (Eq. (5.3)) N–E effects as follows:

\[
\frac{\Delta U_1(B)}{\Delta y} = \Delta S_1(B) \frac{\Delta T}{\Delta y}, \quad \frac{\Delta U_2(B)}{\Delta x} = Q \Delta T \frac{\Delta x}{\Delta y}.
\]  

where \( \Delta y \) is the thickness of a sample and \( \Delta x \) is the above-mentioned distance between the electrical probes in the “Hall” direction. From Eq. (5.4) it follows that the longitudinal effect (\( \Delta U_1(B) \)) is independent on the sizes (\( \Delta x, \Delta y \)), while the transverse one (\( \Delta U_2(B) \)) strongly depends on the \( \Delta x/\Delta y \) ratio. Thus, in experiments one cannot determine \( Q \) but an absolute value of the transverse N–E effect \( \Delta S_1 \) itself, i.e. \( \Delta S_1 = Q \Delta x/\Delta y \). In the present work we use a spontaneous asymmetry (always exists) of the electrical probes on the surfaces of a micro-sample, while, for more precise experiments and for technologies as well, a designed asymmetry is required; an asymmetry of the electrical probes may be realized with the assistance of modern nanotechnologies for DACs [12–14,69].

This new approach for measurement of the N–E effects under high pressure was realized both on the elemental semiconductors (Te, Se) in a range of \( P \) up to 30 GPa [10,11] and on the compound ones (PbS, PbSe, PbTe) in a range of \( P \) up to 20 GPa [70]; for the latter case the equations for the thermomagnetic N–E effects for two-band conductivity were applied [70]. A proof that an output voltage from the “Hall distance” \( \Delta x \) is indeed the thermomagnetic effect but not the galvanomagnetic one (Hall effect) is seen in persisting of the effect after shutting off of the heating electrical current. A comparative measurement of the MR effect in two positions corresponding to zero and the maximal transverse N–E

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**Fig. 7.** The relative variations in the thermopower \( \Delta S \) for \( p \)-PbSe in magnetic field \( B \) at \( P = 3.7 \) GPa and \( T = 295 \) K. The initial position 1 corresponds to the maximal transverse Nernst–Ettingshausen effect (linear on magnetic field, Eq. (5.3)) with a small quadratic contribution from the longitudinal one (Eq. (5.2)). Turning the high-pressure cell around its axis (Fig. 6b) one can alter a contribution of the transverse N–E effect, so its absolute value reduces in a magnitude from position 1 to 5, and then inverts its sign—positions 6–8. Disappearance of the transverse N–E effect should correspond to a turn through 90°, while the position 8 is achieved (Fig. 8). The polynomial fits of the curves (given in the plot) show that the correct value of the longitudinal N–E effect is obtained when the transverse one is minimal (the position 5).

**Fig. 8.** Relative amplitude modulation of the transverse Nernst–Ettingshausen effect in dependence on an angle of a turn of the high-pressure cell around its axis in a non-zero magnetic field (Figs. 1b and 6b): 1—data of the present work for PbSe at \( P = 3.7 \) GPa (Fig. 7), 2—data for PbS at \( P = 2.4 \) GPa from Ref. [70], 3—data for PbTe at \( P = 2.6 \) GPa (unpublished), 4—data for PbTe at \( P = 4.5 \) GPa (unpublished), 5—data for Se at \( P = 13.6 \) GPa from Ref. [79], 6—data for Te at \( P = 2.5 \) GPa from Ref. [79]. The solid line is a fitting by the cos(angle) function. The positions corresponding to the maximal magnitude of the transverse N–E effect (0° and 180°) are being searched experimentally by a slow turning of the cell in the maximal magnetic field (8–1.85 T). The circle diagrams put in the plot sketch out the upper view of a “thin” sample with the electrical contacts (Fig. 6b). They illustrate that one can reach the maximal transverse N–E effect of both signs, when the “Hall” projection of the \( \Delta x \) distance between the contacts \( A \) (lies on the upper plane of a sample) and \( C \) (at the lower one) is maximal. When the “Hall” projection of the \( \Delta x \) distance →0 (a turn through ~90°) no transverse N–E effect is observed but only the longitudinal one from the \( \Delta y \) distance (Fig. 6b).
5.3. Improvement of the thermoelectric efficiency of PbTe owing to the Nernst–Ettingshausen effects under high pressure

A change in the thermopower in magnetic field $B$ may be used for improvement of the thermoelectric efficiency $\alpha = S^2/\rho$ ($\rho$ is the electrical resistivity) and the figure of merit $ZT = (S^2/\rho)T$ of materials. So, in a non-zero magnetic field, $S \to (S_0 + \Delta S_+ + \Delta S_-)$ and $\rho \to \rho(1+MR)$, where $S_0$ is the thermopower at $B = 0$, $\Delta S_+$ and $\Delta S_-$ are, respectively, the contributions of the longitudinal and transverse N–E effects, and MR is the magnetoresistance. In a number of works [71–73], a positive influence of $B$ on $\alpha$ and $ZT$ was experimentally established. An alternative method for improving $\alpha$ and $ZT$ in PbTe is an HP–HT synthesis [74].

Recently, the colossal values of the thermoelectric efficiency were found in PbTe [75] near a pressure-induced gapless state [70]. In the present work we investigate a possibility of additional $B$-driven enhancement of $\alpha$ on a single crystal of n-type PbTe ($n = 1.5 \times 10^{18}$ cm$^{-3}$) in a potentially interesting range of pressure ($P = 1.5–5$ GPa [75]), preceding a structural transformation to the Pnma lattice [76,77]. So, in the inset in Fig. 9, the shown absolute changes in $S$ arise from both the longitudinal and the transverse N–E effects (Eqs. (5.2) and (5.3)).

![Fig. 9. The dependencies of a relative change in the thermoelectric efficiency $\alpha$ on magnetic field $B$, $\alpha(B)/\alpha(B = 0)$ for a single crystal of n-PbTe at fixed pressures $P$. $1–P = 2.0$ GPa, the thermopower value determined from a linear dependence of $\Delta U$ on $J$. $S_0 = 8(B = 0) = 190 \mu V/K$. $2–P = 2.6$ GPa, $S_0 = 138 \mu V/K$. $3–P = 3.2$ GPa, $S_0 = -127 \mu V/K$. $4–P = 4.0$ GPa, $S_0 = -120 \mu V/K$. $5–P = 4.5$ GPa, $S_0 = -79 \mu V/K$. In the inset, the corresponding (1–5) dependencies of the thermoelectric variation $\Delta S$ on magnetic field $B$ are shown; the $\Delta S(P)$ curves correspond to a sum of the longitudinal and the transverse Nernst–Ettingshausen effects.](image)

The principal design of the composite high-pressure cell with the insets made of the sintered diamonds has been reported as an effective tool for the investigation of thermoelectric and thermomagnetic effects. A calculation of a temperature distribution inside the cell during “thermo-” experiments has been performed. Using such a cell, the thermopower, the magnetoresistance [9], and both the longitudinal and the transverse thermomagnetic N–E effects have been measured in a range of pressures beyond $P = 10$ GPa for the first time. The pressure dependence of the thermopower of praseodymium as well as the thermomagnetic N–E effects, both in PbSe and in PbTe, have been deployed as the new examples illustrating the cell possibilities. In the thermopower study we have established that a high-pressure treatment leads to a variation in a scenario of the pressure-driven transitions in Pr (in contrary to Ce). Thus, for the first cycle of pressurization, the transition path in Pr looked similar to the one proposed in Refs. [52,54], while the second and further cycles suggested a non-manifestation of the monoclinic C2/m phase [55]. The thermomagnetic effects in PbTe at $P = 2–4$ GPa have demonstrated a possibility of additional improvement of the giant value of the thermoelectric efficiency in PbTe [75] by a weak magnetic field.

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References
