Thermoelectric power and phase transitions in lanthanides under pressure up to 20 GPa

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Received 29 August 2005; received in revised form 10 April 2006; accepted 11 April 2006

Abstract

Pressure dependencies of thermopower $S$ of rare-earth metals (Ce and Pr) in a pressure $P$ range of 0–20 GPa and at room temperature are reported. A non-monotonic behaviour of $S(P)$ has been established both at pressure-induced phase transitions: fcc $\rightarrow$ modified fcc $\rightarrow$ monoclinic $\rightarrow$ tetragonal lattice for Ce, and double hexagonal close packed (dhcp) $\rightarrow$ fcc $\rightarrow$ modified fcc $\rightarrow$ monoclinic for Pr. $S$ kept a positive sign for the all high-pressure phases mentioned. Simultaneous measurements of sample contraction have revealed anomalies in the vicinity of the transitions in qualitative agreement with diffraction volumetric data published before. The $S(P)$ dependencies were analysed on the basis of the known results of electronic structure calculation for the Ce and Pr phases. An advantage was demonstrated of the thermopower method in the study of phase transitions and electronic structure of high-pressure phases.

Keywords: Lanthanides (Ce and Pr); High pressure; Phase transitions; Thermoelectric power (Seebeck coefficient); Resistivity; Mechanical properties (compressibility)

1. Introduction

In rare-earth metals an evident systematics is observed regarding crystal structures either as a function of atomic number in the lanthanide row or as a function of pressure [1–5]. Cerium is the first metal in lanthanide row exhibiting a significant occupancy of f-orbitals. Variations of electron structure of Ce during phase transitions under pressure and, in particular, behaviour of the f-band is information important for understanding of general rules of formation of both crystal lattice and electron structure of lanthanides. Up to now Ce is still actively investigated by theoretical and experimental methods [1–14]. Indeed, a consequence of lattice variations during phase transitions at the nearest neighbour of Ce–Pr seems to be rather similar [4].

In the initial fcc structure, Ce exhibits $4f^15d^16s^2$ electron configuration. Pr at ambient pressure has a double hexagonal close packed (dhcp) structure and $4f^25d^16s^2$ electron configuration. A sequence of the phase transformations in Ce under pressurisation looks as following: near 0.8 GPa from fcc into fcc$'$ lattice, then near 5–7 GPa into bcc monoclinic $\alpha''$-phase ($C2/m$) or $\alpha$-uranium phase (distorted variants of fcc lattice), and then near 12–17 GPa into bcc tetragonal $e$-phase ($I4/mmm$) [3–5]. For Pr, the following sequence of structural transformations was registered [3,4]: dhcp $\rightarrow$ fcc $\rightarrow$ fcc$'$ (fcc distorted-rhombohedral phase $R\bar{3}m$) $\rightarrow$ monoclinic ($C2/m$) $\rightarrow$ $\alpha$-U near about 5, 8, 12, and 25 GPa, respectively.

Applying for phase transition investigation, the different methods register changes in various subsystems (electron, phonon, and magnetic ones) [1–4,11,13]. For example, at the first phase transition in Ce near 0.8 GPa from fcc into fcc$'$ lattice the appreciable variations were observed in all subsystems listed [1–4,11,13]. In the present work, the phase transitions in Ce and Pr were investigated by the technique of high-pressure thermopower measurements reflecting behaviour of electron and crystal structure under pressure [15–18]. The above method was found to be effective for registration of changes in electron subsystem of metal phases, where several types of charge carriers (electrons and holes, for instance) contribute into conductivity [16–18]. In Ce and Pr, f-, d- and s-electrons can

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actually participate in electrical conduction. Thermopower behaviour in a wide pressure range where several structural modifications happen allows us to estimate values and pressure coefficients of $S$ in the all phases obtaining so a qualitative information on electron structure changes.

2. Experiment details

The chemically pure Ce and Pr polycrystals were used for the study. The initial structure of Ce was tested by the neutron diffraction method and was found to be the fcc with a lattice parameter $a = 1.1534 \pm 0.0004$ Å.

Originally, two alternative techniques of thermopower measurements at ultrahigh quasi-hydrostatic pressure up to 25–30 GPa have been developed distinguishing by mutual orientation of thermal gradient and diamond anvils axis: perpendicular [19,20] or parallel [15,21–23]. In the modern version of the first technique (perpendicular orientation), the thermal gradient is created by laser heating, but presently accessible pressure range is restricted by 10–12 GPa because of difficulties related to attachment of thermocouples to a sample ends [24]. But in such pressure range the thermopower measurements may be performed in a more suitable apparatuses with a large-volume compressible capsule with liquid media [6–8]. In the present study, we used the second technique mentioned (parallel orientation) [15,21,22].

The measurements were carried out in an automated set-up permitting simultaneous registration of pressure values, thermal difference along a sample, electrical voltage from a sample, and contraction of sample thickness [16–18,25–27] (Fig. 1a). The dependencies of the thermopower $S(P)$ and electrical resistance $R(P)$ of microsamples ($0.2 \text{ mm} \times 0.2 \text{ mm} \times 0.05 \text{ mm}$) were measured in the two-stage apparatus with the sintered diamond anvils supported by external pressure [15,21,22] (Fig. 1b). A quasi-hydrostatic pressure $P$ in a compressible gasket from the lithographic stone (soft CaCO$_3$-based material) was determined with assistance of a calibration curve based on the well-known phase transitions in ZnSe, CdTe, etc. with uncertainty of $\sim10\%$ [15–18].

For producing the thermal gradient one anvil was heated, and temperature difference was measured in the fixed points of the anvils by means of the thermocouples [15–18]. An equation of thermal diffusion was solved by the finite difference method for a host of points of every element of the high-pressure apparatus used [25–27] (Fig. 1a). A temperature distribution in the anvils was calculated under variation of both the sample sizes and thermal conductivity [25–27]. The errors in measurements of electrical resistance $R$ and $S$ were estimated to be less than $\sim5$ and $20\%$, respectively. The thermopower values were measured both in stationary conditions at fixed thermal gradient and in non-stationary thermal regime [28]. We performed five circles of compression–decompression at several samples of each material (Ce, Pr) cut from the same ingots.

Its hardly possible to reconcile wide pressure interval with high accuracy and high efficiency of $S(P)$ measurements. In order to solve this problem one can use a combine method (parallel studies at ultrahigh quasi-hydrostatic and moderate hydrostatic pressures) as it was suggested in Refs. [25–27]. For Ce and Pr, the $S(P)$ curves have been already studied under hydrostatic pressures up to 9 GPa [6–8].

A displacement of a lower diamond anvil during the pressurisation was used for estimation of contraction of sample thickness. A large linear contribution arising from
elastic deformations of both the high-pressure set-up itself and a lithographo-stone gasket was subtracted to reveal anomalies of sample compressibility in the phase transition regions.

3. Results and discussion

$S(P)$ dependencies for Ce and Pr samples reflected the variations in both crystal lattice and electron structure (Fig. 2). In the initial fcc ($\gamma$) phase of Ce, $S$ increased with $P$ by a factor of $\sim$1.3–2 (Fig. 2a). The results obtained agreed with the data of hydrostatic pressure study of the thermopower of Ce in the pressure range of 0–9 GPa [8,29–33]. Near $P \sim$ 0 GPa, $S$ values of Ce and Pr (Fig. 2) slightly differed (less than $\pm$2 $\mu$V/K) from the ones gathered at ambient conditions [29–31], probably because of non-hydrostatic stresses in a sample. The $S(P)$ dependence observed in Ce correlated with $R(P)$ behaviour established in Refs. [1,2,4–8]. In a vicinity of structural transformations near $\sim$1–2 and 5–6 GPa [3–5] the thermopower value abruptly decreased (at the first transformation) and increased (at the second one) (Fig. 2a and [8]). The “jumps” of $S$ during the second transition into the monoclinic bcc $\alpha''$-phase [3,4,32,33] were more abrupt (Fig. 2a, no. 3) than ones in the previous studies [8,29–33]. According to Ref. [4], the elastic stresses influence on the phase stability, and at elevated temperatures it is more energetically profitable to transform into the $\alpha$-uranium phase, whereas in case of “cold” pressurisation (corresponding to the present work) Ce crystallises into the monoclinic bcc phase. Above 12 GPa the sign of $dS/dP$ changed—the thermopower value began to decrease with pressure. The change of sign of pressure coefficient of $S$ near 12 GPa might be related to the beginning of transition into the tetragonal phase. According to the synchrotron and X-ray studies [3,5,34], this transition is completed to 15 GPa. Notice that in our experiments $R(P)$ curve had a bend near about 15 GPa (not shown). The curve of contraction of sample thickness exhibited the anomalies (change of a slope) near the all phase transition points (Fig. 2a, inset).

As for Pr, the results of the present work as well as the data obtained earlier [1,2,6] exhibited the rather moderate changes both of electronic and volume properties. Near about 5, 8, and 12 GPa, the peculiarities were noted at the $S(P)$ curve (Fig. 2b) which might be related to the structural transitions into the fcc, fcc$'$ and monoclinic structures [4]. In Ref. [6], the only tiny change of $S(P)$ was established near the fcc $\rightarrow$ distorted fcc transition. We registered no abrupt changes at the curve of sample thickness contraction under pressure (Fig. 2b, inset); that agreed with the data obtained both by Bridgman [1,2] and in the latest diffraction structural study [4]. The changes of the electrical resistance during the transitions in both Ce and Pr were found to be much weaker in comparison with $S(P)$ [1,2,7,8].

The general expressions for electrical conductivity $\sigma$ and thermopower $S$ are as following [35–37]:

$$\sigma = - \int \sigma(E) \frac{df}{dE} dE, \quad S = - \frac{k_0}{|e|} \int \frac{E - E_F}{k_B T} \frac{\sigma(E) \frac{df}{dE}}{\sigma} dE$$

(1)

Fig. 2. Dependencies of thermolectric power $S$ on pressurization $P$ at $T = 293$ K for Ce (sample no. 3) (a) and Pr (b). The arrows indicate the phase transitions, while the dashed rectangles—the regions of phase co-existing (heterophase state) both for Ce [4] and Pr [3,4]. (a) The part of $S(P)$ curve in a vicinity of the phase transition near about 5 GPa is shown also for Ce sample no. 1: I—fcc; II—modified fcc; III—bcc monoclinic $\alpha''$-phase (C2/m); IV—bcc tetragonal $\varepsilon$-phase ($I4/mmm$) (see the text) and (b) the closed symbols correspond to the values obtained from the linear slopes: thermolectric voltage vs. thermal difference: I—dhcp; II—fcc; III—modified fcc (rhombohedral phase $R3m$); IV—monoclinic (C2/m) phase (see the text). The insets show the corresponding curves of sample contraction $\Delta x$ obtained simultaneously with the $S(P)$ curves. The curves confirm the appreciable changes of sample volume for Ce and negligible ones for Pr. The large linear contribution was subtracted from the full effect in order to reveal these anomalies (see Section 2). So, the values near y-axis at the insets are relative.
Here, $f$ is the distribution function; $E_F$ the Fermi energy; $k_0$ the Boltzmann’s constant; $e$ the electron charge; $T$ the temperature; $E$ is the electron energy. In case of metallic conductivity, Eq. (1) transforms to the well-known formula: $S \approx -(k_0/e)(\pi^2/3)(k_0T)\left[d\ln\sigma(E)/dE\right]_{E=E_F}$ [36,37].

In Ce and Pr the electrons of $s$-, $d$- and $f$-bands may contribute into total electrical conductivity $\sigma$, so the thermopower of these metals may be described by a formula for two-band metal with carriers of $s$- and $d$-bands, $S \approx -(k_0/e)(\pi^2/3)(k_0T)\left[3(2E_F) - 1/N_0(E) \partial N_0(E)/\partial E\right]_{E=E_F}$, where $N_0(E)$ the density of states in d-band [36,37]. The second term in the square bracket is due to scattering of electrons by carriers of the d-band; that brings a significant contribution both in value and sign of thermopower [36,37]. For the almost empty d-band, the last expression explains the positive sign of thermopower [36,37]. In case of Ce and Pr, there is one more almost empty band (f-band) where the main changes may happen influencing on thermopower under pressurisation [14]. For Pr, an influence of f-band on $S$ seemed to be weaker comparatively with Ce. The behaviour of $S(P)$ for Pr (Fig. 2b) is more similar to one of La [38] possessing an empty 4f band [6–8], than to one of Ce (Fig. 2a). Both in Pr and La the structural transitions under pressure are thought to be associated with the transfer of s electrons into d-bands [6,38].

According to the calculation of the density of electron states for the high-pressure phases of Ce [14], the Fermi level of $\alpha$-phase lies near van Hove peak, while in the other phases one lies in a pseudo-gap region that corresponds to higher structural stability. The density of states calculated may explain the strong pressure dependence of $S$ observed for Ce. So, according to Ref. [14], the structural instability of Ce is related to degeneration of hybridized $pd$-states near the Fermi level, and Peierls distortion of lattice was supposed to be a mechanism of these transitions. From the symmetry analysis [4] the same phonon instability was proposed to induce the transitions into the monoclinic phases of Ce and Pr.

The bulk modulus $B_0$ in the monoclinic phase of Ce and Pr were found to be approximately equal (~30.7 and 30.5 GPa, respectively) [4], as well as in the fcc one (24.4 and 25.1 GPa, respectively) [4]. This similarity permits to attribute the monoclinic structure of Pr to a one with itinerant 4f electrons [4]. The almost continuous pressure dependence of volume of Pr at phase transition points gave an evidence of electronic shell modification, which transforms the “compressibility” of atom itself [4].

Our curves of sample contraction for Ce and Pr (Fig. 2, insets) qualitatively agreed with the above diffraction volumetric results [4].

4. Conclusion

From the results, obtained it follows that thermopower values of Ce and Pr where electrons of the $s$, $d$-, and $f$-band play an active role, respond to changes of electron subsystem both at the phase transitions and in the phase stability regions. Such changes were poorly seen at the electrical resistance curves. This circumstance points at high potential of the thermopower technique in investigation of phase transitions and electron structure of high-pressure phases.

Acknowledgements

The authors are grateful to Drs. I.F. Begrer and V.I. Voronin (IMP) for neutron diffraction testing of the samples as well as to Prof. Y. Uwatoko (ISSP) for the interest in the research. The work was partly supported by the Russian Foundation for Basic Research (Gr. Nr. 04-02-16178), and by the Japan Society for the Promotion of Science (ID no. P 05312).

References