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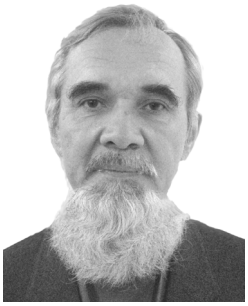

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THERMOELECTRIC POWER OF RARE-EARTH METAL ROW OVER A WIDE RANGE OF PRESSURES

The results of investigations of thermoelectric properties of rare-earth metals under high pressure application up to 20 GPa at room temperature are reported. This study has experimentally confirmed that a high-pressure behavior of thermoelectric power of lanthanide metals follows a general trend due to the electron s → d transfer. A distinctive behavior of thermopower of divalent europium and ytterbium has been found under pressure application. Possible influence of valence change as well as the variation of the occupancy of s-, p-, d-electronic states under pressure on the behavior of the thermoelectric power of europium and ytterbium is discussed.

Key words: thermopower, high pressure, rare-earth metals.

Introduction

Thermoelectric effect (Seebeck effect, *S*) is a very efficient tool to study the electronic structure modification of materials at the variations of temperature (*T*) [1, 2] or pressure (*P*) [3]. The *S*(*P*) data allow studying phase transitions as well as thermoelectric properties of high-pressure phases. The study of *S*(*P*) of the rare-earth metals group allows summarizing the contribution of *f*- and *d*-states to the electron structure near the Fermi level over a wide range of pressures.

The range of applications of rare-earth metals is extraordinarily wide, from the petroleum cracking catalysts and pigments for glass and ceramics to the miniature nuclear batteries, superconductors and miniature magnets. So the knowledge of their electronic properties under stress application is critically important for technologies.

Rare-earth metals include the fifteen lanthanides as well as yttrium and scandium. Under high pressure most rare-earth metals suffer a sequence of phase transformations as follows: hcp → *Sm*-type → dhcp → fcc → distorted-fcc (*d*-fcc) [4-6]. This tendency involves the majority of rare-earth metals (*Sc*, *Y*, *La*, *Pr*, *Nd*, *Pm*, *Sm*, *Gd*, *Tb*, *Dy*, *Ho*, *Er*, *Tm*, and *Lu*). While some of them (*Ce*, *Eu*, and *Yb*) demonstrate very peculiar behavior.

The purpose of the present work is the investigation of the thermoelectric power of the rare-earth metal row under high pressure up to 20 GPa. The results of investigations of thermoelectric properties of typical lanthanides (*Gd*, *Tb*, *Dy*) that follow a commonly accepted sequence of structural transformations as well as peculiar ones: lanthanum (*La*), europium (*Eu*) and ytterbium (*Yb*) are presented. The latter metals have also peculiar electronic configurations: trivalent *La* has empty *f*-band and divalent *Eu* and divalent *Yb* possess one-half filled and completely filled 4*f* electron shell, respectively.

Experimental details

The experiments were carried out on pure polycrystalline samples of the rare-earth metals. Purity of the samples was as follows: *Sc* (99.9 %), *Y* (99.9 %), *La* (99.9 %), *Ce* (99.84 %), *Pr* (99.81 %), *Nd* (99.65 %), *Sm* (99.77 %), *Eu* (99.89 %), *Gd* (99.91 %), *Tb* (99.79 %), *Dy* (99.85 %), *Ho* (99.90 %), *Er* (99.91 %), and *Yb* (99.85 %). The measurements were performed on disk-shaped samples of ~ 200 μm in the diameter and ~ 30 μm in the thickness cut from the bulk ingots. Several samples of each element were examined one by one in the same conditions for verification of data reproducibility [7].

$S(P)$ measurements were carried out using the automated setup operating with high-pressure cells with synthetic diamond anvils [3]. A sample was loaded in a container made of the lithographic stone (soft $CaCO_3$ based mineral) that served both as a gasket and a pressure-transmitting medium. The ratio of container thickness (h) to a diameter of the top of diamond anvils d = 600 μm·h/d < 0.055 provides the quasi-hydrostatic condition of pressure created [3, 8, 9]. The automated measurements permit obtaining high-quality data on pressure evolution of the thermoelectric properties. A good agreement has been obtained between the values of S at ambient pressure [2] and those measured on high-pressure setup at $P \approx 0$ GPa. The details of high-pressure experiments are described in the previous works [3, 7-9].

Results

A representative set of the data obtained is shown in Figure 1. Tables 1 and 2 summarize structural and thermoelectric data for the investigated rare-earth metals.

Table 1

Structural and thermoelectric properties of the selected rare-earth metals in the pressure range below 20 GPa

Element	Z	Electronic configuration	Ambient structure	Phase transition pressures (GPa) from Refs. [4, 10-40]					
				Sm-type	dhcp	fcc	*d*-fcc	hcp	bcc
La	57	$4f^0(5d6s)^3$	dhcp	–	–	2 – 3	5.3 – 7	–	–
Eu	63	$4f^7(5d6s)^2$	bcc	–	–	–	–	12 – 14	–
Gd	64	$4f^7(5d6s)^3$	hcp	1 – 3.5	6.5 – 10	–	–	–	–
Tb	65	$4f^9(5d6s)^3$	hcp	3 – 5	12 – 16	–	–	–	–
Dy	66	$4f^{10}(5d6s)^3$	hcp	5 – 7.5	15 – 19	–	–	–	–
Yb	70	$4f^{14}(5d6s)^2$	fcc	–	–	–	–	–	3.5 – 4.5

Gadolinium, terbium and dysprosium crystallize in hcp lattice at ambient conditions. They show the standard transformation sequence: hcp → *Sm*-type → dhcp (Table 1). For gadolinium phase transitions occur at 1 – 3.5 and 6.5 – 10 GPa, respectively [4, 10-16] (Table 1). For terbium the same phase transitions occur at higher pressures 3 – 5 and 12 – 16 GPa [4, 10-12, 17, 18] (Table 1). And in dysprosium similar transition pressures are shifted to higher magnitudes, 5 – 7.5 and 15 – 19 GPa, respectively [4, 10, 12, 19-21] (Table 1). At room temperature, *Gd* exhibits also a ferromagnetic transition near 3.5 – 5 GPa [12, 22]. Ambient thermopower values were reported to be $S \sim -(0.7 \div 2)$ μV/K,

~ –(0.9 ÷ 1.4) μV/K, and ~ –(0.55 ÷ 2) μV/K for *Gd*, *Tb* and *Dy*, respectively [2, 41] (Table 2). They agree well with our experimental data (Figs. 1, 2). Peculiarities detected on pressure dependence of thermoelectric power were referred to the above mentioned structural transitions. The Seebeck effect in gadolinium, terbium and dysprosium subjected to compression demonstrates similar behavior: monotonic rising from small negative values, –(1 ÷ 2) μV/K to magnitudes of ~ + (8 – 10) μV/K beyond ~ 5 GPa (Figs. 1, 2).

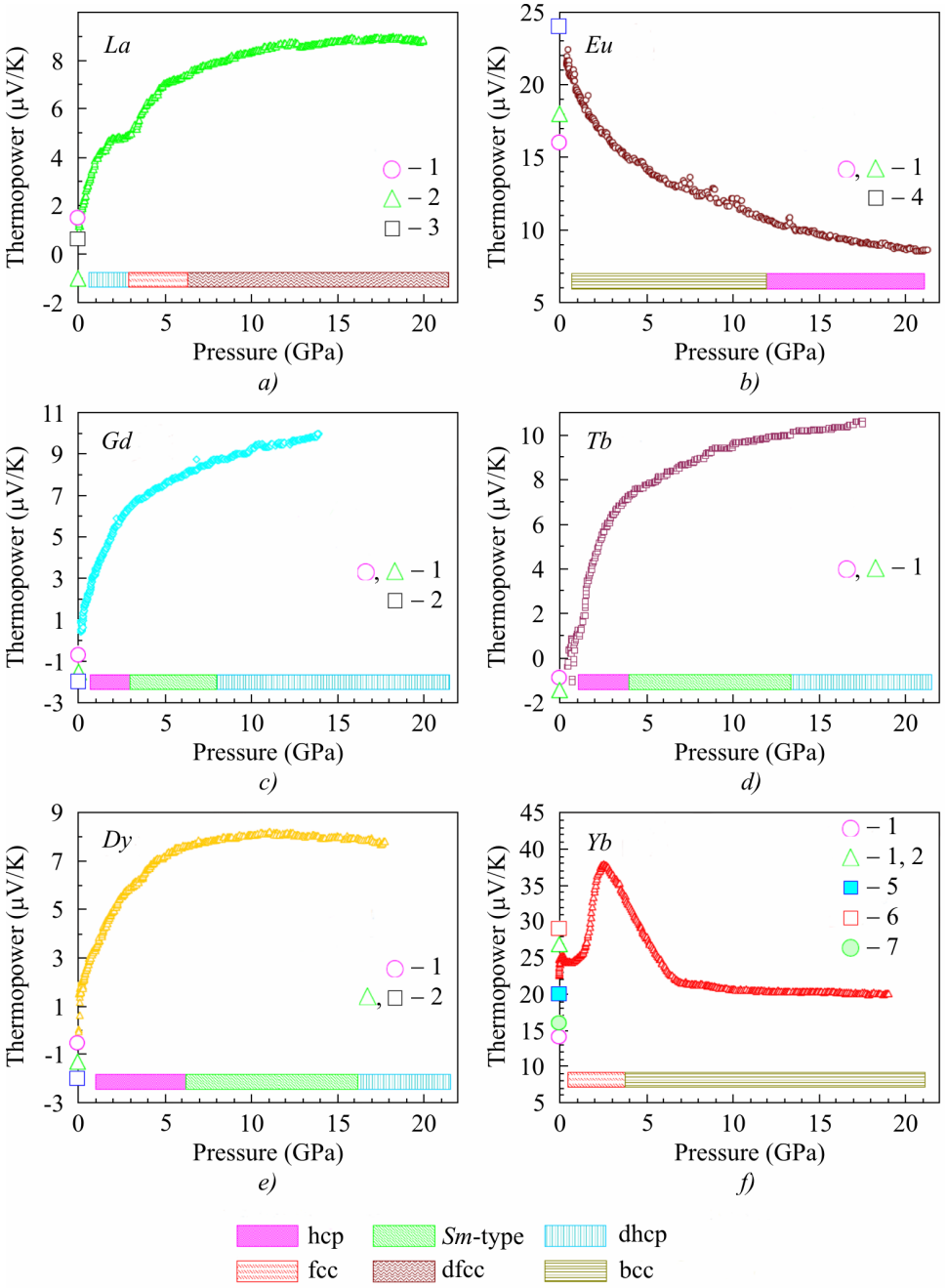

Fig. 1. Pressure dependencies of thermoelectric power of the selected lanthanides: (a) lanthanum, (b) europium, (c) gadolinium, (d) terbium, (e) dysprosium and (f) ytterbium. The dashed rectangles schematically show the stability regions of different phases, summarized in Table 1. The points 1 – 7 at ambient pressure label data taken from the literature: 1 – [2], 2 – [41], 3 – [42], 4 – [43], 5 – [39], 6 – [44], and 7 – [40]. Data for Gd, Tb and Dy have been taken from [7].

Table 2

Thermoelectric properties of the selected rare-earth metals in the range of pressures below 20 GPa

Element	Thermoelectric power (μV/K)	
	Ambient	at 16 – 20 GPa
La	+1.5[a], –1[b], +0.6[c]	+8.9
Eu	+16[a],+18[a], +24[d]	+8.5
Gd	–0.7[a], –1.5[a], –2[b]	+(9.5 ÷ 10)
Tb	–0.9[a], –1.4[a], –1.2[b]	+(10 ÷ 10.5)
Dy	–0.55[a], –1.3[b], –2[b]	+8
Yb	+14[a], +27[a, b], +20[e], +29[f], +16[g]	+20

[a] – [2], [b] – [41], [c] – [42], [d] – [43], [e] – [39], [f] – [44], [g] – [40]

Lanthanum has $4f^0(5d6s)^3$ electronic configuration and at ambient conditions it crystallizes in a dhcp lattice (space group $P6_3/mmc$). It shows a phase transformation path: dhcp → fcc → distorted-fcc at 2 – 3 GPa and 5.3 – 7 GPa, respectively [4, 10, 23-26]. Ambient thermopower values determined in our experiments $S \cong (-1 \div +1.7)$ μV/K (Figs. 1(*a*) and 2) agree well with the literary data [2, 41, 42]. Pressure behavior of thermopower in *La* resembles those of most of the lanthanides [7], *Sc* and *Y* [45]. But on $S(P)$ dependence for *La* one can see a pronounced kink near 3 GPa related probably to the dhcp → fcc transition [4, 10, 23-26]. A smooth bend in the thermopower curve near 5.5 – 6 GPa (Fig. 1 (*a*)) could be due to the structural transition into the distorted-fcc phase [4, 10, 23-26].

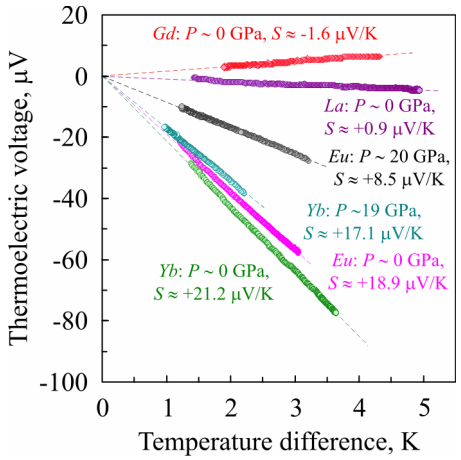

Fig. 2. Examples of dependences of thermoelectric signal U on applied temperature difference ΔT between sample edges. The values of thermopower S correspond to a linear coefficient between thermoelectric voltage (U) and temperature difference (ΔT) as follows: $S = -U/\Delta T$.

Europium is a divalent metal having an electron configuration of $4f^7(5d6s)^2$ and at ambient conditions, it adopts a body-centered cubic (bcc) lattice (space group $Im\bar{3}m$). At pressure of 12 – 14.5 GPa at room temperature, *Eu* transforms to hcp phase [4, 10, 27-32]. Previous studies have reported *Eu* to transform from the hcp structure to a new phase, *Eu*-III, at 18 GPa [4, 10, 30, 32]. However, recent *X*-ray diffraction investigations show a sluggish transition above 18 GPa to a mixture

of hcp and a monoclinic phase with space group *C*2/*c* [29]. In [28, 30] it is illustrated that this *Eu*-III phase consists of hcp-*Eu* plus a rhombohedral phase (perhaps a hydride EuH_x), the atomic volume of which suggests that it is an impurity [28, 30]. At ambient pressure the thermopower values of *Eu* were found to be within a range of $S \sim (+17, +23)$ μV/K (Figs. 1 (*b*) and 2) close to previously reported values [2, 43]. The Seebeck effect decreases with pressure and reaches $S \sim +(8 \div 9)$ μV/K near 22 GPa (Figs. 1 (*b*) and 2). The pressure dependence of thermopower for this element (Fig. 1 *b*) is completely opposite to similar dependences for the majority of lanthanides [7].

Ytterbium is a divalent semimetal having an electron configuration of $4f^{14}(5d6s)^2$. At room and elevated temperatures, *Yb* has a fcc lattice (β-phase) of the $Fm\bar{3}m$ space group [10, 46-47]. With pressure application, it suffers fcc → bcc phase transition at 3.5 – 4.5 GPa [4, 10, 33-40]. Near 2 GPa, *Yb* shows a semimetal-semiconductor electronic transition [39, 48-52]. A huge peak on the thermopower curve near 2.6 GPa (Fig. 1 (*f*)) is probably due to this electronic transition [39, 48-52]. With transition to the bcc lattice, *Yb* is reported to be metallized under pressure [10, 35, 36]. Ambient thermopower values were found to be $S \sim +(20 \div 25)$ μV/K (Figs. 1 (*f*) and 2), that is close to previously reported values [2, 39-41, 44].

Discussion

Similar thermopower behavior under pressure of lanthanides that follows a commonly accepted sequence of structural transformations [4] was observed in previous investigation [7]. For *Sc*, *Y* and *La* as well as for most of the lanthanides [7] the pressure applied tends to rising of the Seebeck effect to relatively high positive values of $S \sim 10$ μV/K beyond ~ 3 – 10 GPa (not shown at Fig. 1). Divalent elements *Eu* and *Yb* do not follow a commonly observed sequence of structural transformations for lanthanides and also demonstrate pressure evolution of thermoelectric properties (Fig. 1) distinguishing from the above mentioned trend. Both metals have much higher initial values of $S \sim +25$ μV/K which are strongly decreased under pressure in the bcc crystal structure (for *Yb* above ~ 3 GPa).

Under high pressure, a population of *s*-electrons in general decreases and that of *d*-electrons increases due to $s \rightarrow d$ electron transfer [4-6]. For a description of the thermopower behavior the expression ought to be used that takes contributions of both *s*- and *d*-bands into consideration [53]

$$S_d^s = -\frac{\pi^2 k^2 T}{3|e|}\left(\frac{3}{2\varepsilon} - \frac{1}{N_d(\varepsilon)}\frac{dN_d(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_F}, \quad (1)$$

where S_d^s is the diffusion thermoelectric power, k is the Boltzmann constant, T is the absolute temperature, e is the electron charge, ε is the electron energy, N_d is the density of states in the *d*-band and ε_F is the Fermi energy. Due to high concentrations of charge carriers in metals, the first term in Eq. 1 usually gives contributions to thermopower values of about ~ 1 μV/K. Thus, the higher thermopower values can not be explained by the first term and therefore they could come out from the second one. Similar behavior of thermoelectric properties of *Gd*, *Tb*, *Dy* and *La* under compression indeed can originate from pressure-enhanced scattering of the *s*-electrons by the carriers of *d*-band (the second term in Eq. 1). Most of lanthanides (except for *Ce*, *Eu* and *Yb*) demonstrate behavior of thermopower under pressure similar to *La* [7]. The contribution of the *f*-band to the values of *S* in view of similarity of *S*(*P*) dependences for these rare-earth metals row seems to be not very essential [53].

The second term in Eq. 1 gives a positive contribution to *S* for almost empty *d*-band [53] that agrees well with our experiments (Figs. 1, 2)

The anomalous behavior of *Eu* and *Yb* thermopower under pressure may be due to several reasons. First, it may be partial delocalization of *f*-electrons and the corresponding increase of valence from 2 to 3. The second reason may be the variation of occupancy of *s*-, *p*-, *d*-electronic bands, and in particular the filling of almost empty *d*-bands. Peculiar electronic properties of *Yb* under pressure are believed to be determined by partial delocalization of the *f*-electrons [4-6, 14]. At higher pressures the narrow *f*-bands overlap and their interatomic interactions increase, finally leading to *f*-delocalization [14]. The fcc to bcc transition at *Yb* was proposed to occur when the 4*f* electrons start to delocalize varying the valence of *Yb* from 2+ to 3+ [39].

Experimental investigation of *X*-ray absorption near-edge spectroscopy (XANES) at Eu's L_3 edge to pressures as high as 34 GPa [54], the ^{151}Eu Mössbauer spectroscopy studies to 14 GPa at 44 K [55] and synchrotron Mössbauer experiment at ambient temperature [56] have shown that the valence of *Eu* increases sharply under pressure, reaching the valence of ~ 2.5 at 10 – 12 GPa. A more recent XANES, *X*-ray magnetic circular dichroism, and synchrotron Mössbauer spectroscopy experiments have shown *Eu* metal to remain nearly divalent to the highest pressures reached (87 GPa) with magnetic order persisting to at least 50 GPa [57]. An analysis based on ab initio calculations indicates that the pressure-induced changes in XANES spectra in the 10 – 20 GPa range, which were previously interpreted as indicative of a marked change in *Eu* valence, result from significant changes in the electronic and crystal structure at the bcc → hcp structural phase transition. However, this increase may originate from pressure-induced changes in the properties of the *s*-, *p*-, and *d*-electrons, and so is not related to a significant change in 4*f*-electron occupation. Thus, *Eu* metal probably remains divalent or nearly divalent to 87 GPa [57]. Using the second approach of change in the occupancy of electronic *s*-, *p*-, *d*-states, the strong decrease of *S* in *Eu* with a rise in pressure is attributable to considerable increase of *s*-electron states density (and hence the electron concentration) or to filling of empty *d*-band; with certain occupancy of *d*-band the second term in Eq.1 is reduced indeed [53].

Conclusions

The measurements of thermoelectric power of rare-earth metals over a wide range of pressures have revealed the similarity of *S*(*P*) behavior for most members of the row (except for *Ce*, *Eu* and *Yb*) corresponding to similarity of the sequence of structural transformations under pressure of these metals. For divalent *Yb* and *Eu* the inverse pressure dependence of *S* (decrease) in bcc phase as compared to the rest of rare-earth metals can be attributed to several possible reasons: the partial delocalization of *f*-states (most probably it occurs at *Yb*) [4-6, 14, 39] and the variation of occupancy of *s*-, *p*-, *d*-electron bands [57]. The second term in Eq. 1 indeed has a sharp maximum at certain position of the Fermi level [53] that may tend to decrease in *S* with a rise in pressure. The second approach also allows explaining the high values of $S \sim +25$ μV/K for *Yb* and *Eu* as compared to the rest of rare-earth metals.

The work was done within RAS Program (Project no. 01.2.006 13394), by UD RAS as part of Program ''Matter at high energy densities'' of the Presidium of RAS (project 12-P-2-1004), by the Ministry of Education and Science of the Russian Federation (Contract 14.518.11.7020), and by the Oriented Basic Research Project of the Ural Branch of the Russian Academy of Sciences.

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Submitted 16.05.2013.