EXPERIMENTAL STUDY OF THE SET OF THERMAL PROPERTIES OF CERTAIN RARE-EARTH METALS AT HIGH TEMPERATURES

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The results are given of measurements of the specific heat, thermal diffusivity and thermal conductivity of liquid lanthanum, praesodymium and dysprosium over the temperature range 1200-2000°K. The changes of these parameters on melting are discussed.

The rare-earth metals, nowadays, are finding an ever-widening application in many fields of new technology and, because of this, the need has arisen for an all-round study of their properties.

In order to investigate the set of thermal properties (thermal diffusivity, specific heat and thermal conductivity), the method of radial temperature waves [1] was used in this work. The sample being studied was a completely cylindrical cell with liquid metal, which was prepared from two thin-walled (~0.1 mm) tantalum tubes with diameters ~6 and ~14 mm. The bottom and cover of the cell was made of tantalum sheet, ~1.5 mm thickness, and welded to the tube by electron-beam welding. The height of the cell was ~70 mm. The cell was filled with beads of the material being studied to a height of ~10 mm, alternating with baffles of tantalum foil. The surface of the cavity was subjected to periodic П-shaped heating by electron bombardment and the temperature fluctuations of the surrounding surface were recorded by a non-contact method (by luminosity oscillations). The thermal diffusivity was found by the characteristic time determined by comparison of the periodic curves of the change of temperature with a known system geometry. In order to determine the specific heat and thermal conductivity, data from these same curves were used, taking account of the absolute value of the intensity and temperature changes.

The arrangement is described in detail in [1]. The distinctive feature of these recent experiments is the monitoring of the quality of filling of the working cell of the measurement device by means of γ-defectoscopy [2].

In order to solve the other procedural problem – the possible effect of convective intermixing, a new version of the measurement procedure was adopted: the method of external heating of the same sample by electron bombardment. This version was used for the setting up of control experiments with liquid Sn and Rb. The agreement of the results of the experiments with external and internal heating confirms the absence of any significant role of convection, due to a temperature gradient being constantly compared between the inside and outside surface of the sample for the usual measurement [2, 3]. The random measurement error for the thermal diffusivity amounts to 3 to 4% and 4% for the specific heat. The systematic error amounts to 4% for the thermal diffusivity and 5% for the specific heat.

The results of the investigation for the properties of La, Pr, and Dy plotted below refer to samples with the following composition: La 99.56 (Ce $2 \cdot 10^{-2}$; Pr 10^{-2}; Nd $3 \cdot 10^{-2}$; Sm 10^{-2}; Fe $3 \cdot 10^{-2}$; Ca 10^{-2}; Cu $1.6 \cdot 10^{-2}$; Cd 10^{-2}); Pr 99.76; Dy 99.9 (Hg $4 \cdot 10^{-2}$; Ho $2.5 \cdot 10^{-2}$; Y $2.5 \cdot 10^{-2}$; Er 10^{-2}; (F, Ce, Cu, Ca) $\cdot 10^{-2}$).

Up to two or three samples of different length were investigated for each substance. In calculating the molar specific heats of Pr and La, the density data from [4] were used. Experimental data on the thermal properties of Pr and Dy are shown in Figs. 1 and 2. The melting point is shown by the vertical dashed line.

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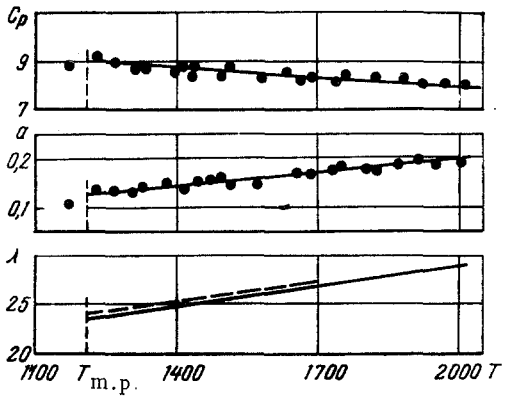

Fig. 1

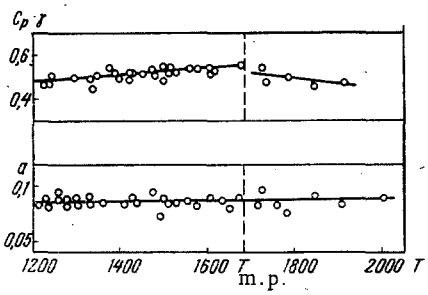

Fig. 2

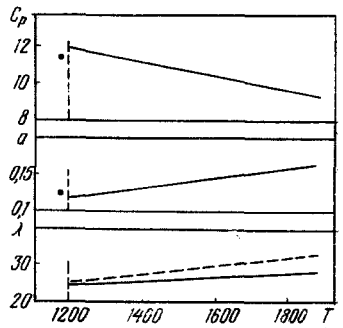

Fig. 3

Fig. 1. Thermal properties of praesodymium, λ, W/m·deg; T, °K.

Fig. 2. Specific heat of unit volume and thermal diffusivity of dysprosium in the solid and liquid states.

Fig. 3. Thermal properties of liquid lanthanum.

The temperature dependence of the specific heat and thermal diffusivity are described by the following interpolation formulas:

$$C_{p_{Pr}} = 10.44 - 1.187 \cdot 10^{-3} T,$$

$$a_{Pr} = 0.0188 + 0.0903 \cdot 10^{-3} T$$

(over the temperature range 1210-2000°K);

$$(C_p\gamma)_{Dy} = 0.314 + 0.14 \cdot 10^{-3} T,$$

$$a_{Dy} = 0.082 + 0.003 \cdot 10^{-3} T,$$

(for Dy, the specific heat per unit volume is plotted, in view of the absence of density data (1200-1680°K)):

$$(C_p\gamma)_{Dy} = 0.9693 - 0.2669 \cdot 10^{-3} T,$$

$$a_{Dy} = 0.078 + 0.0046 \cdot 10^{-3} T \ (1700 - 2000\ ^{\circ}\mathrm{K}),$$

$$C_p, \ \frac{\text{cal}}{\text{g-atm, °K}}, \ (C_p\gamma), \ \frac{\text{cal}}{\text{deg} \cdot \text{cm}^3}, \ a, \ \frac{\text{cm}^2}{\text{sec}}, \ T, \ ^{\circ}\mathrm{K}.$$

The mean-square deviation of the experimental points from the smoothed values amounts to ~3.5% for C_p and 2.5% for a.

In Figs. 1 and 3, one experimental point in the solid state is plotted for C_p and a.

In Fig. 3, we show the averaged data for liquid lanthanum from our measurements [3] and those of Atalla [8].

For La, Pr, and Dy, relatively large values of C_p (12-9 cal/g-atom·deg K) are characteristic. We observed this also for Nd and Ce [1] and Spedding also observed it for Sm, Nd, and Ce [6]. Spedding explained this by the role of the specific heat of the inner electrons added to the specific heat of the system of ions and the specific heat of the conductivity electrons. The magnitude of the sudden change of specific heat on melting is insignificant for La, Pr, and Dy and is found to be within the limits of measurement error.

The important result of this work is the small change of thermal diffusivity and thermal conductivity observed for all three of the rare-earth elements studied. This may be due to some other experimental fact – to the smallness of the change of specific electrical resistance. The latter follows from our data for these elements and also for Nd, Ce [3] and from the literature data for La, Ce, Pr, and Nd [7, 8].

The relation between the smallness of the thermal diffusivity and the thermal conductivity on melting on the one hand, and the electrical conductivity on the other hand, will be understood if the approximate practicability of the Wiedermann – Franz law is taken into account; this explains the predominance of

electron thermal conductivity over the molecular thermal conductivity. Figures 1 and 3 can serve to show the degree of fulfillment of the Wiedermann – Franz law for the liquid phase; here, data obtained from a calculation by the Wiedermann – Franz law are shown by a dashed line. (We did not do this for Dy, as the results for the liquid phase were assumed to be preliminary, because signs of interaction between the liquid metal and the material of the ampoule were detected in the experiment).

The smallness of the change of electrical conductivity according to Regel' [7] is explained by the large role of the s – d interaction, which is the principal mechanism for electron scattering in both phases.

However, another approach is possible to the explanation of this fact. As follows from a number of papers [9-11], the temperature dependence of the electrical conductivity and also the change of electrical conductivity on melting, is determined in the first place by the behavior of the specific volume of the metal. From this point of view, the smallness of the change of resistance on melting should be related with the smallness of the change of density. Unfortunately, there are no data in the literature concerning the change of density of the rare-earth elements on melting. Only the unique data of [12] for Ce confirm our hypothesis (with Ce, the change of density is less by an order of magnitude than with rare-earth metals studied by us). We assume that it would be very desirable to undertake a project to measure the changes of density of a number of rare-earth metals on heating.

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