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SPECIFIC HEAT OF LANTHANUM HEXABORIDE

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The specific heat of lanthanum hexaboride has been measured in the temperature ranges 2-12 and 25-298°K [1-4] and determined, with a differential equation for the temperature dependence of enthalpy, in the ranges 518-1483, 1341-2018, and 1100-2200°K [5-7]. As lanthanum hexaboride is a diamagnetic, to a first approximation its specific heat may be regarded as the sum of the specific heats of its lattice and electron gas. The temperature coefficient γ of the electronic specific heat, found by calculation, is $2.66 \cdot 10^{-3}$ J/mole-(deg K)^2 in the temperature range 2-6°K [1] and $(6.4\text{-}10.4) \cdot 10^{-3}$ J/mole-(deg K)^2 in the range 6-12°K. In the latter case the characteristic Debye temperature Θ_D = 250°K [2]. Its assessment, involving use of graphic data [1], for the range 2-6°K gives Θ_D = 210°K. Assuming the values $\gamma = 2.66 \cdot 10^{-3}$ J/mole-(deg K)^2 to be valid in a wide temperature range, for temperatures of 200-300°K we obtain, using data reported in [3, 4], Θ_D = 1110°K. Because of lack of data for the range 298-500°K, it is not possible to determine how Θ_D varies at high temperatures, and consequently in subsequent calculations the value Θ_D = 1110°K was employed.

The specific heat of lanthanum hexaboride in the temperature range 298-2200°K calculated by the usual method, employing selected values of γ and Θ_D and an equation for transition from C_v to C_p [8], is much less, particularly at high temperatures, than that obtained on the basis of results of enthalpy measurements [5-7] (Fig. 1). A linear increase in specific heat in the temperature range 500-2000°K at a mean rate of $7.5 \cdot 10^{-3}$ J/mole-(deg K)^2 cannot be attributed to gross errors in values of γ and Θ_D; it is probably linked with some contribution to specific heat which is not allowed for in the first approximation.

Hexaborides with the CaB_6 type structure, including lanthanum hexaboride, are characterized by the presence of boron atom octahedra, which exert a strong influence on the general structure of these compounds and on a number of their properties [9]. The B–B interatomic spacing in the octahedra of the hexaborides of the rare-earth metals from lanthanum through gadolinium changes but little [10], which is apparently due to strong covalent bonds in the octahedra. At elevated temperatures the vibrations of the boron atoms in the octahedra make a definite contribution to specific heat.

The magnitude of this contribution can be calculated to a first approximation by assuming that in an octahedron there are twelve (the number of shortest bonds) independent harmonic oscillators. The frequency of the vibrations of these oscillators can be assessed with Gugenheimer's formula [11],

$$\omega = 2152 \cdot z_1 z_2^{1/4} \cdot \mu^{1/2} \cdot r^{-1,23} \ (\text{cm}^{-1}), \tag{1}$$

where $z_{1,2}$ is the number of valence electrons (for boron atoms, three), μ is the reduced mass of a B–B molecule, and r is the B–B interatomic spacing in an octahedron. For the hexaborides of the rare-earth metals from lanthanum through gadolinium, this frequency is practically constant and, on the average, equal to 4385 ± 20 cm^{-1}, so that the characteristic Einstein

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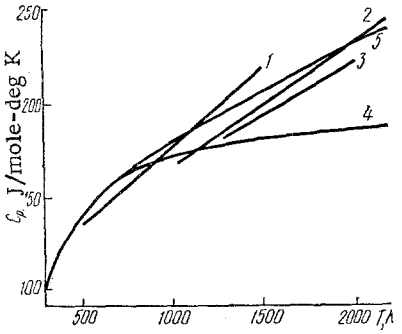

Fig. 1

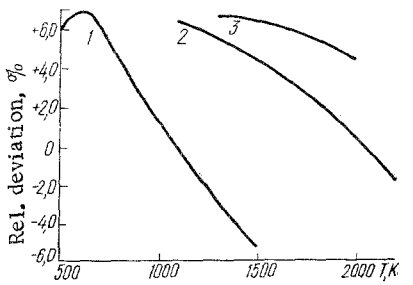

Fig. 2

Fig. 1. Specific heat of lanthanum hexaboride: 1) data from [5]; 2) [7]; 3) [6]; 4) calculated, $C_{lat} + C_{el}$; 5) calculated, $C_{lat} + C_{el} + 12C_{B-B}$.

Fig. 2. Relative deviations of experimental data from calculated values of specific heat of lanthanum hexaboride: 1) [5]; 2) [7]; 3) [6].

temperature Θ_E = 6310°K. The results of specific heat calculations for lanthanum hexaboride with allowance for the vibrations of the octahedron atoms are given in Fig. 1.

Comparison of experimental data and results of calculations (Fig. 2) leads to the conclusion that the temperature dependence of the specific heat of lanthanum hexaboride in the range 200-2200°K is described, with accuracy to within ±6 rel. %, by the expression

$$C_p = \left[7 \cdot C_D\left(\frac{1110}{T}\right) + 2.66 \cdot 10^{-3} \cdot T\right](1 + 3\alpha T/a) + 12C_E\left(\frac{6310}{T}\right), \quad (2)$$

where C_D and C_E are the Debye and Einstein specific heats, respectively, α is the coefficient of thermal expansion of lanthanum hexaboride, and a is a constant, equal, for lanthanum hexaboride, to 0.74. From Fig. 2 it follows also that, owing to the use of a simplified model, our estimate of the contribution to the specific heat of lanthanum hexaboride from the vibrations of the boron atoms in the octahedra gave only the lower limit of this quantity. Apart from this, comparison of Figs. 1 and 2 indicates that in the range 300-1000°K the Debye temperature of lanthanum hexaboride continues to rise. Use of a higher Θ_D in the calculation will give a lower rate of growth of the lattice specific heat and decrease the difference between calculated and experimental values of specific heat.

Our findings concerning the specific heat of lanthanum hexaboride would appear to apply also to the specific heats of the hexaborides of other rare-earth metals. This conclusion is based on the fact that at high temperatures (above 1000°K) the specific heats of neodymium, europium, and samarium hexaborides grow at the same rate as the specific heat of lanthanum hexaboride [12]. It is probable that an increase in specific heat is characteristic of all compounds whose structures have isolated fragments such as dumbbells, chains, prisms, and octahedra.

Thus, the specific heat of lanthanum hexaboride in the temperature range 200-2200°K can be regarded as consisting of its lattice specific heat, the heat of the electron gas, and a contribution from vibrations inside the structurally isolated fragments of its lattice — boron atom octahedra. With the hexaborides of other rare-earth metals, it is necessary to allow for the contribution from the thermal excitation of the 4f electrons of the lanthanides and magnetic ordering.

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