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Abstract

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THERMAL CONDUCTIVITY OF HEXABORIDES OF ALKALINE-EARTH AND RARE-EARTH METALS

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Compounds of rare-earth metals have recently been attracting increasing attention from researchers in connection with the expansion of the areas of their practical use. Among such compounds, the hexaborides of alkaline-earth and rare-earth metals are of definite interest; some of them are used as thermionic emitters in electronic devices.

The physical properties of these compounds, despite a number of extensive studies on this question ([1–4]), have not been fully clarified. In particular, the literature contains no data on their thermal conductivity (with the exception of gadolinium hexaboride ([5])), whose magnitude is of not only theoretical but also practical importance.

Table 1

Some physical characteristics of metals and their hexaborides

Element	Hexaborides: electrical conductivity, $\Omega^{-1}\cdot cm^{-1}$	Hexaborides: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_{tot}	Hexaborides: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_e	Hexaborides: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_{ph}	Hexaborides: mean-square amplitude of vibrations, $\sqrt{\overline{u^2}}$, Å	Metals: electrical conductivity, $\Omega^{-1}\cdot cm^{-1}$	Metals: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_{tot}	Metals: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_e	Metals: thermal conductivity $\cdot 10^3$ cal/cm·sec·deg, λ_{ph}	Metals: mean-square amplitude of vibrations, $\sqrt{\overline{u^2}}$, Å	$\lambda_{MeB6}/\sqrt{\overline{u^2}}_{Mea}/\sqrt{\overline{u^2}}_{MeB6}$
Ca	4500	55$±4	7078	0.050	26300	40000	—	7.228	64	4.523	Sr | 9000 | 63±3 | 14 | 29 | 0.049 | 43500 | — | — | — | 0.180 | — | 3 | 35 | 14 | 0.045 | 7120 | 21 | 11 | 10 | 0.133 | 2.3 | 2.9 | | Tb | 26700 | 48±3 | 42 | 6 | 0.047 | 7380 | — | — | — | 0.133 | — | 2.8 | | Yb | 2

* According to the data of work ([5]), the thermal-conductivity coefficient of CdB_6 is $47 \cdot 10^{-3}$ cal/cm · sec · deg.

In connection with this, we have for the first time systematically measured the thermal-conductivity coefficients of hexaborides of most alkaline-earth and rare-earth metals at room temperature. The measurements were made by the steady-state method on the apparatus described in work ([6]), on samples on which a number of other physical properties had previously been investigated ([7]). The chemical composition of the samples corresponded sufficiently well to the stoichiometric composition. The obtained thermal-conductivity coefficients are given in Table 1. The values of the specific electrical conductivity of the hexaborides in this table are given according to the data of work ([7]). The thermal-conductivity coefficients and the specific electrical conductivity of the metals were taken from work ([8]). The same table also gives the calculated values of the electronic λ_e and phonon λ_{ph} parts of the thermal conductivity of the metals and hexaborides. The calculation was made from experimental data on thermal and electrical conductivity on the basis of the Wiedemann–Franz law:

$$\lambda_{ph} = \lambda - L_0 \sigma T,$$

where λ is the experimental value of the thermal-conductivity coefficient, σ–

specific electrical conductivity, L_0 is the theoretical value of the Lorenz number, and T is the absolute temperature (in our experiments 300°C).

From consideration of the data in Table 1 it follows that the thermal conductivity of the hexaborides of the metals under consideration is approximately three times higher than that of the metals themselves. The high thermal conductivity of hexaborides is due to higher values of both the electronic and the phonon components in comparison with the corresponding values for the initial metals. However, the relative share of phonon thermal conductivity in hexaborides is generally higher than in metals (Table 1). The share of lattice thermal conductivity is especially noticeably increased in the hexaborides of samarium, europium, ytterbium, and alkaline-earth elements, in which it is even higher than the electronic component.

The Lorenz number, both for the metals themselves and for their hexaborides, owing to the greater role of phonon thermal conductivity, is substantially higher than the theoretical value. The high thermal conductivity of hexaborides, in comparison with metals, can be explained by features of the structure of hexaborides. It is known that compounds of metals with boron of the type MeB_6 are characterized by strong covalent bonds between boron atoms, which form their own spatial lattice, centering the simple cubic lattice of metal atoms. The presence of this lattice of boron atoms has a decisive influence on the increase in thermal conductivity. First, it causes an increase in the share of phonon thermal conductivity, and second, the strong covalent bonds between boron atoms determine the high rigidity of the hexaboride lattice. As a result, the magnitude

of the root-mean-square amplitudes of the vibrating atoms and their complexes $\sqrt{\overline{u^2}}$ decreases, which reduces scattering of conduction electrons and leads to an increase in the electrical conductivity and the electronic share of thermal conductivity in comparison with those in metals; this is clearly seen from the data of Table 1. In the borides of divalent metals (Ca, Sr, Ba, Eu, Yb) and samarium (with intermediate valence), as should be expected from their electronic structure ([4]), the electronic component of thermal conductivity is reduced in comparison with the borides of trivalent metals.

Table 1 gives the averaged values of the root-mean-square amplitudes of vibrating complexes in the metals considered and their hexaborides, calculated from the coefficients of thermal expansion in work ([9]). As follows from the data of this table, the ratio of the thermal conductivity of hexaborides to the thermal conductivity of the corresponding metals is approximately equal to the inverse ratio of the indicated amplitudes. This indicates the decisive influence of the lattice rigidity of the compounds considered on the magnitude of their thermal conductivity.

Thus, from the results of the measurements and their analysis it follows that the thermal conductivity of the hexaborides of alkaline- and rare-earth metals is substantially higher than the thermal conductivity of the corresponding metals, which is due to the presence of strong covalent bonds between boron atoms in the hexaborides.

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Note: Figure translations are in progress. See original paper for figures.