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Chemistry

G. V. SAMSONOV, V. P. DZEGANOVSKII, and I. A. SEMASHKO

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Abstract

Full Text

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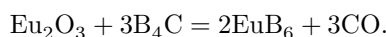
EUROPIUM HEXABORIDE

(Presented by Academician I. I. Chernyaev, 28 XI 1957)

The hexaborides of rare-earth metals, MeB_6 , have by now been studied rather well⁽¹⁾. Owing to their high thermionic-emission characteristics, these compounds find application in electronics. One of the many hexaborides that had not yet been synthesized and investigated is europium hexaboride.

Fig. 1. Line diagram of the X-ray pattern of EuB_6 .

In the present work this compound was obtained by borocarbide reduction of pure europium oxide:



The reaction was carried out in vacuum at 1650° for 2 hours. The product—a dark-gray powder—corresponded exactly to the formula of hexaboride EuB_6 , with a carbon content of less than 0.02%. An X-ray structural investigation, carried out by the powder method with copper radiation in an RKD-type camera of diameter 57.3 mm, showed that europium hexaboride has a cubic lattice with identity period $a = 4.167 \pm 0.002 \text{ \AA}$ (space group O_h^1), characteristic of all rare-earth-metal hexaborides). In Fig. 1 the line diagram of this X-ray pattern is shown, and in Table 1 the corresponding numerical data are given.

Table 1

Indexing of the X-ray pattern of europium hexaboride

hkl	ϑ	$I_{\text{expt.}}$	hkl	ϑ	$I_{\text{expt.}}$
100	$10^\circ 33'$	med.	400	$47^\circ 39'$	weak
110	$15^\circ 00'$	v. s.	410	$49^\circ 54'$	v. s.
111	$18^\circ 33'$	s.	411	$51^\circ 39'$	v. s.
200	$21^\circ 45'$	s.	331	$53^\circ 45'$	s.
210	$24^\circ 21'$	v. s.	420	$56^\circ 03'$	s.

Fig. 2. a –radii of atoms of rare-earth metals according to data (8); b –lattice periods of their hexaborides. 1 –our data, 2 –data of other authors

Figure 2: Fig. 2. a –radii of atoms of rare-earth metals according to data (8); b –lattice periods of their hexaborides. 1 –our data, 2 –data of other authors

<i>hkl</i>	ϑ	$I_{\text{expt.}}$	<i>hkl</i>	ϑ	$I_{\text{expt.}}$
211	26° 48′	s.	421	58° 09′	v. s.
220	31° 30′	med.	332	60° 18′	s.
300	33° 39′	v. s.	422	65° 15′	med.
310	35° 48′	s.	500	67° 51′	med.
311	37° 57′	s.	510 α_1	70° 39′	v. s.
320	41° 57′	s.	510 α_2	71° 06′	weak
321	43° 51′	v. s.	511 α_1	73° 57′	v. s.
			511 α_2	74° 24′	weak

The X-ray density calculated from the lattice period is 4.99 ± 0.01 g/cm³.

The obtained value of the lattice period of europium hexaboride confirms the supposition (2) concerning the correspondence between the curves of variation of the radii

of the rare-earth metal atoms and the lattice periods of the borides of these metals, as well as the conclusion, following from this, concerning the trivalent effective valence of all rare-earth elements in compounds, with the exception of europium and ytterbium, which exhibit a divalent character, marked on the curves of the atomic radii of the metals and the lattice periods of their hexaborides by sharp maxima (Fig. 2).

To construct the curve of lattice periods, in addition to the value of the period of EuB₆, we also used the values of the periods for DyB₆, HoB₆, and LuB₆ obtained by us earlier (3). The character of the position of the curve makes it possible to choose, from the available values of the lattice period of GdB₆, $a = 4.112\text{-}4.110$ Å (2,4) and $a = 4.13\text{-}4.14$ Å, the latter as the most correct from the point of view presented,

Fig. 2. a –radii of atoms of rare-earth metals according to data (8), b –lattice periods of their hexaborides. 1 –our data, 2 –data of other authors

and also to interpolate approximate values of the lattice periods of the still unknown hexaborides of promethium ($a \simeq 4.128$ Å), terbium ($a \simeq 4.12$ Å), and thulium ($a \simeq 4.11$ Å). The value of the lattice period of erbium hexaboride established by Kiessling (6) is probably somewhat underestimated.

It should be noted that the indicated regularity casts doubt on the correctness of the interpretation, in work (7), of the value of the lattice period of ytterbium hexaboride as requiring refinement. On the contrary, this quantity, just like the

value of the lattice period of EuB_6 , strictly obeys the regularity of conservation of the effective valences of rare-earth metals in their compounds.

Institute of Metal Ceramics
and Special Alloys
Academy of Sciences of the Ukrainian SSR

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