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REMARKS ON THE MUTUAL SOLUBILITIES AND SUPERCONDUCTIVITY OF HEXABORIDES

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ABSTRACT

X-ray diffraction and electron microprobe data indicate that the mutual solubility of LaB_6 and YB_6 depend strongly on the method of alloy preparation. Superconducting transition temperatures of these alloys are reported.

The hexaborides of yttrium, thorium and the light rare earths all crystallize in a cubic structure which can be visualized as a CsCl arrangement of metal atoms and B_6 octahedra. We give our values of a_o measured on single crystals in a Gandolfi camera in Table 1. Because of the small variations of the lattice constant, one expects, on the basis of the Hume-Rothery rules, complete solid solution between these hexaborides.

In a study of superconductivity in the YB_6-LaB_6 system, we found that arc-melting of YB_6-LaB_6 mixtures invariably produced

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TABLE 1

Compound	a_o (Å) Experiment	Literature[1]
LaB_6	4.156	4.154
CeB_6	4.141	4.141
PrB_6	4.133	4.130
NdB_6	4.126	4.126
SmB_6	4.133	4.133
GdB_6	4.109	4.108
ThB_6	4.110	4.113
YB_6	4.102	4.113

material with two distinct cubic lattice parameters, as well as tetraboride contamination. Metallurgical examination showed that three phases were present. Further examination in an electron-beam microprobe showed that a nominal $(La_{.5}Y_{.5})B_6$ arc-melted button contained two distinct B_6 phases, the LaB_6-rich phase containing 15 ± 5 a/o YB_6, and the YB_6-rich phase containing no LaB_6 within counting statistics. Microprobe scans for La L_α- and Y L_α-radiation are shown in Fig. 1.

This lack of solubility of LaB_6 in YB_6 is surprising, especially in view of the rapid quenching on the water-cooled arc-furnace hearth and the almost identical lattice parameter. Attempts were also made to prepare LaB_6-YB_6 solid solutions by sintering a pressed pellet of the mixed oxides and boron at 1600°C in vacuum. A possible reaction is:[2]

$$(Y, La)_2O_3 + 14B \rightarrow 2(Y, La)B_6 + B_2O_3$$

Initially, we prepared YB_6 via this reaction. X-ray diffraction analysis showed both YB_4 and YB_6 present, and the material was not superconducting to 1.5°K, although arc-melted YB_6 is superconducting at 6.8°K. The results of increasing the B/Y_2O_3 ratio on T_c are given in Table 2. It appears from these results that there is some

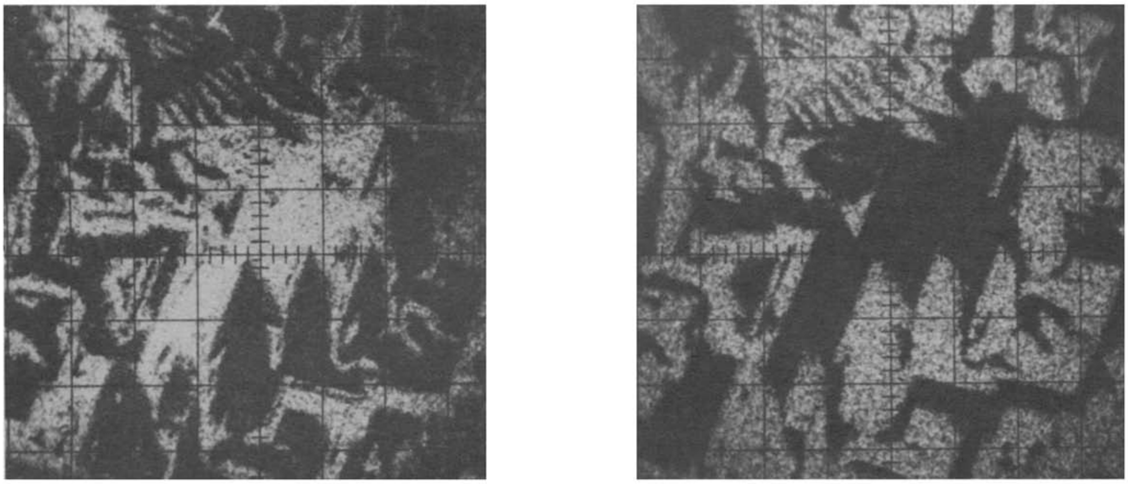

FIG. 1

Microprobe scans of $La_{.5}Y_{.5}B_6$. Left, LaL_α radiation; right Y L_α radiation. The field of view is approximately $150\mu \times 150\mu$. Regions of inexact registry contain tetraboride.

variation in the stoichiometry which has a marked effect on T_c. A very slight variation in a_o ($\Delta a_o \sim 0.001$ Å) was observed on varying the B/Y_2O_3 ratio.

The T_c and lattice parameter data for YB_6-LaB_6 mixtures prepared from oxides as above are given in Fig. 2. These data indicate the formation of a solid solution and the fact that the T_c extrapolates to zero near 25 a/o YB_6. X-ray analysis indicates that now only one cubic phase is present and that Vegard's law is reasonably well obeyed.

TABLE 2

moles B/moles Y_2O_3	Phases Present	T_c(°K)
14	YB_4, YB_6	None to 1.5°K
20	YB_4, YB_6, YB_{12}	6.8 0.1
26	YB_4, YB_6, YB_{12}	6.3 ± 0.3

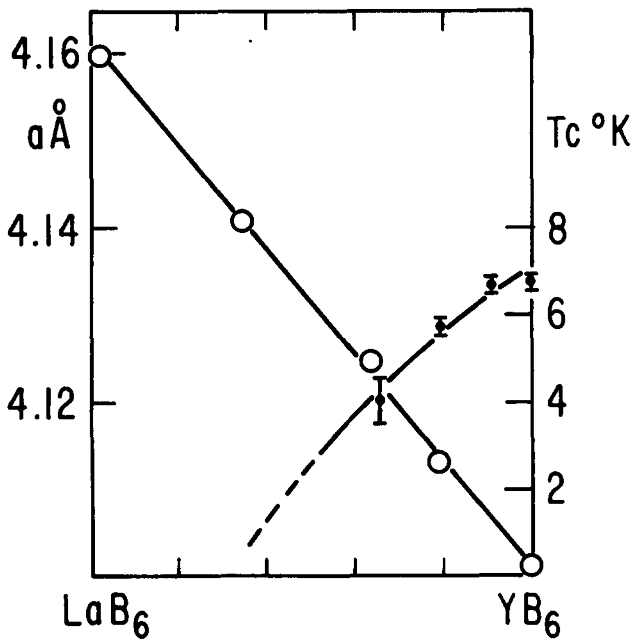

FIG. 2

Lattice parameters and superconducting transition temperatures of (La, Y)B_6 solid solutions.

Since LaB_6 is congruently melting and YB_6 is incongruently melting, a possible explanation for the observed insolubility of La in YB_6 in arc-melted material is that the morphology of the appropriate ternary diagram is such that LaB_6 solidifies first from the (La, Y)B_6 melt, and that the liquidus-solidus separation is large enough to result in nearly complete fractionation.

Finally, we note that ThB_6 dissolves readily in both YB_6 and LaB_6 in the arc-furnace. The size factor certainly favors ThB_6-YB_6 solid solution, and our low temperature electrical resistivity measurements suggest that ThB_6 and LaB_6, but not YB_6, are electronically very similar. Insufficient data on the Th-B phase diagram exist to conclude whether ThB_6 melts congruently.

References

1. See compilation by J. L. Hoard and R. E. Hughes in The Chemistry of Boron and Its Compounds [ed. E. L. Muetterties; New York, 1967], p. 118.

2. See discussion in G. V. Samsonov, High-Temperature Compounds of Rare Earth Metals with Nonmetals (New York: 1965), p. 56.

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