Reports

Boron Isotope Effect in Superconducting Zirconium Dodecaboride

Abstract. *The boron isotope effect in ZrB_{12} has been determined to be* $T_c \propto M^{\alpha}$, *where* α *is equal to* -0.09 ± 0.05, M *is the boron mass, and* T_c *is the superconducting transition temperature.*

The superconductivity of several cubic hexa- and dodecaborides has been discovered by Matthias *et al.* (*1*). After comparing the electronic specific heats of ZrB_{12} and YB_6 they suggested that the superconductivity of these compounds might be indicative of the behavior of a hypothetical cubic, metallic boron (*1*). The superconducting transition temperature T_c of ZrB_{12} is 5.85°K, and that of YB_6 is 6.5° to 7.1°K (*1*). Elemental boron is not metallic and exists in several complicated, noncubic forms (*2*). A determination of the boron isotope effect in these compounds might serve to establish the degree of participation of boron in their superconductivity.

Since "metallic" boron would be expected to exhibit the isotope effect of an *sp*-superconductor, $T_c \propto M^{\alpha}$, with $\alpha = -0.5$, where M is the isotopic mass (*3*), a shift in T_c of some 0.3°K might be anticipated as the boron mass in the compounds changes from 10 to 11. This would be an unusually large effect, easily resolvable in the case of ZrB_{12}, which exhibits a relatively sharp superconducting transition (*1*). We prepared the compound ZrB_{12} with natural boron (atomic mass 10.81) and with boron isotopes of average masses 10.04 and 10.98. The purities of the zirconium and the boron lots used are given in Table 1.

Below 1860°C, ZrB_{12} is not an equilibrium phase (*4*), but it may be retained at room temperature as a metastable phase by rapid cooling from the melt. We prepared our samples by compressing zirconium and boron powders together into cylindrical pills and melting the pills several times on the water-cooled copper hearth of an arc furnace. We were not successful in obtaining homogeneous, single-phase samples by this method, but were able, for the samples made with B^{10} and natural boron, to ascertain the transition temperatures appropriate to ZrB_{12} to a precision of ± 10 millidegrees Kelvin. The other phases present in the pills were ZrB_2 and, presumably, elemental boron (*4*); ZrB_2 is not superconducting down to 1.8°K (*5*). Our better samples were ≧ 80 percent ZrB_{12}, as determined by x-ray examination.

Superconductivity was detected at 140 hz by monitoring an output voltage proportional to the change in mutual inductance between a secondary coil containing the sample and a surrounding primary coil. Bulk superconductivity in ZrB_{12} has been established by specific heat measurements (*1*). The transition temperatures are displayed as a function of boron isotopic mass in Fig. 1. The vertical bars show the widths of the linear portions of the transition curves. Dashed lines indicate "tails" that follow the main transitions. These usually constituted some 20 to 40 percent of the total signal.

Scatter in the data is more pronounced for the various samples made with the isotope B^{11} than for those made with the other isotopic compositions, although only one lot of B^{11} was used in preparing the B^{11} samples. Two lots, differing in purity, were used in preparing the various B^{10} and natural boron samples (Table 1). The reason for our problems with the B^{11} samples is thus not readily apparent. These samples were prone to exhibit "tails," and their transition temperatures are generally higher than those of the natural boron samples, which is unexpected. Several samples (not shown) were prepared by mixing B^{10} and B^{11} isotopes to achieve intermediate masses. There was no indication of a minimum in T_c.

The general scatter in the data in Fig. 1 is probably due to stresses in the samples. This characteristic of the samples was reflected by their tendency, on occasion, to shatter in the arc furnace. Those samples which shattered are indicated by open circles in Fig. 1. Two of these, made with natural boron, exhibited double transitions, as shown. The appreciable scatter among the B^{11} samples and the lesser scatter among the B^{10} and natural B samples may be reduced somewhat if we choose the midpoints of the transition curves to be the proper measure of the transition temperatures

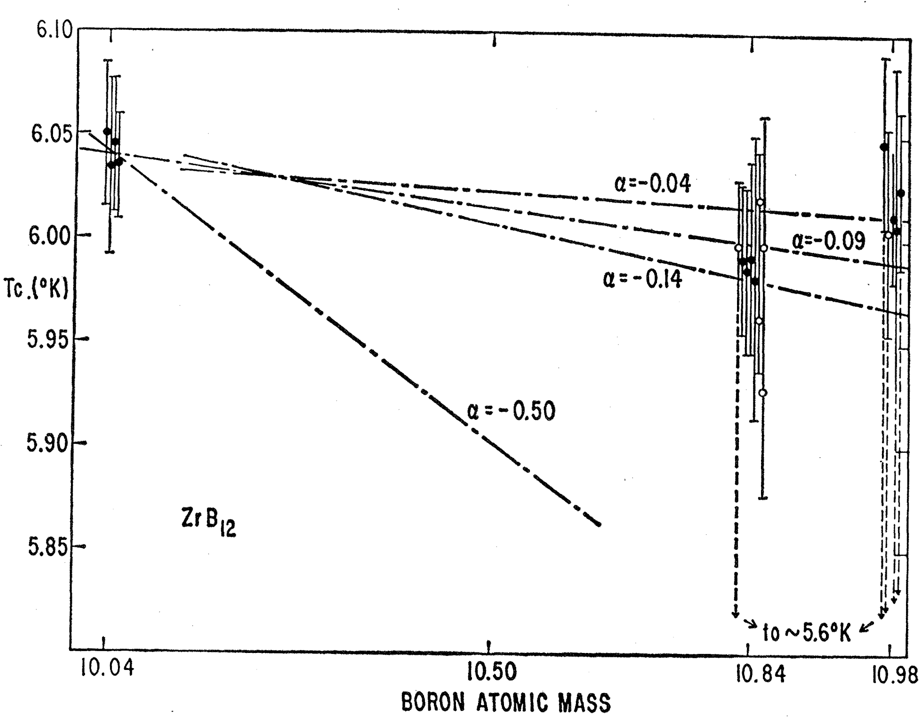

Fig. 1. Superconducting transition temperatures of ZrB_{12} samples as a function of boron isotopic mass M. The widths of the transition curves were determined by extending the linear portion of each curve to horizontal lines corresponding to zero and total superconducting signal. Curves composed of two distinct transitions are shown with double midpoints. "Tails" of reduced signal strength and following the main transitions are indicated by dashed vertical lines. Open circles represent samples which shattered during preparation. The slanted lines indicate the slopes of T_c plotted against M which approximate the exponential dependence $T_c \propto M^{\alpha}$ for the values of α shown.

Table 1. Materials used in preparing superconducting ZrB_{12} samples. Boron lots are listed in their order of appearance (left to right) in Fig. 1.

Material	Isotopic comp. (av. atomic mass)	Chemical purity (%)*	Impurities (ppm)†			No. of samples
B^{10}						
Lot 1	10.04	97.6	Ca, 1000 K, 100 Ni, <500 C, 7500	Cu, 500 Mg, 200 Si, 5000	Fe, 1000 Mn, <200 Ta, 500	2
B^{10}						
Lot 2	10.04	99.97	Si, 200 Ca, 4	Mg, 5	Fe, 53	2
Natural B						
Lot 1	10.81	99.75	C, 1100	Fe, 1400		4
Lot 2	10.81	99.9995				3
B^{11}	10.98	99.89	Si, 1100	Mg, 4		5
Zr	91.22	99.2	C, 175 Hf, 190 O, 980 Ti, 70	Cr, 150 N, 119 Ta, <200	H, 125 Nb, <100 Si, 75	

* By weight. † Oxygen content in boron lots unknown.

and if we give greater consideration to samples which neither shattered nor exhibited "tails." We may then express the isotope effect as $T_c \propto M^\alpha$, $\alpha = -0.09 \pm 0.05$, where M is the boron mass, assuming the usual exponential dependence of T_c upon M. A value of $\alpha = -0.16 \pm 0.09$ is obtained if the total mass is used.

These values of α would seem to demonstrate that the superconductivity of the compound ZrB_{12} is not readily identifiable with that due to a hypothetical metallic boron. It is apparent, however, that phonon modes involving boron atoms are pertinent. Further interpretation is difficult for several reasons, particularly the fact that any zirconium contribution to the superconductivity of ZrB_{12} would be likely to strongly influence the boron isotope effect, since elemental zirconium itself shows a vanishing isotope effect (*6*). Little detailed theoretical work has been done on the significance of isotope effects measured in compounds, and few, if any, isotope effects have been determined in systems analogous to ZrB_{12}. Engelhardt *et al.* (*7*) found the boron isotope effect in W_2B to be $\alpha = -0.090 \pm 0.016$, using the boron mass only for calculation, but in Mo_2B the same measurement gives (*7*) $\alpha = -0.004 \pm 0.016$, making the results difficult to interpret in relation to elemental boron. If the molybdenum mass alone is used for calculation, the molybdenum isotope effect in Mo_2B ($\alpha = -0.42 \pm 0.02$) (*7*) is approximately the same as in the element ($\alpha = -0.37 \pm 0.04$) (*8, 9*). In $MoBe_{22}$, which has cubic symmetry and may be more analogous to ZrB_{12} (*1*), the molybdenum isotope effect is changed to $\alpha = -0.23 \pm 0.10$ (*8*). This is close to the value for molybdenum in Mo_3Ir (*9*) ($\alpha = -0.20$), again if the molybdenum mass alone is used for calculation. On this basis, the transition-metal character of the superconductivity of molybdenum is retained completely in Mo_2B, where the boron isotope effect vanishes, and is as evident in $MoBe_{22}$ as in Mo_3Ir.

Perhaps a clear-cut demonstration of any tendency of a hypothetical cubic boron [or cubic beryllium (*1*)] toward superconductivity can only be accomplished in the absence of transition elements, which have always been essential so far for the superconductivity of boron (and beryllium) compounds (*1, 5, 8, 10*). The hexa- and dodecaborides formed with the rare earths produce only magnetic compounds (*1, 11*).

Aluminum and gallium, which are in the same column in the periodic table as boron, form high T_c compounds with niobium isomorphous with Nb_3Sn (*5*) ($T_c = 18°K$). In Nb_3Sn, the tin isotope effect is very small (*12*) ($\alpha = -0.02$, -0.08, depending on the mass used for calculation), although tin in its elemental form exhibits a normal isotope effect ($\alpha = -0.5$) (*13*). Thus the superconductivity of the compound is not characteristic of the nontransition metal. It would seem that, under favorable conditions, nontransition elements in compounds with transition elements either enhance the *sd*-interactions responsible for superconductivity in the transition metals, which show reduced isotope effects, or introduce phonon modes conducive to high T_c's for which the effect of isotopic mass has not been studied.

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References and Notes

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14. We thank Dr. B. T. Matthias for stimulating conversations and for informing us of his results before publication. We thank J. Engelhardt for providing us with the high-purity boron isotopes and for guidance in their use and evaluation; D. Wohlleben and G. W. Webb for rewarding discussions and H. L. Luo for the x-ray studies. Research supported by AFOSR grant 631-67.
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Venera 4 Probes Atmosphere of Venus

Abstract. *The atmospheric data and information on trajectory received from Venera 4 together provide consistent and firm evidence of its success in reaching the surface of Venus.*

On 18 October 1967 a Russian probe entered the atmosphere of Venus and transmitted the first measurements ever made *in situ* of the atmosphere of a planet other than Earth. When the complete results of this major accomplishment are reported they should provide a firm basis for a major advance in understanding of the lower atmosphere of Venus. Only a limited amount of information is yet available through Russian radio and press releases on the direct measurements of atmospheric properties. One can, however, use the information on Venera 4's entry and descent trajectory to provide further insight into those atmospheric data. After summarizing briefly the information