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SUPERCONDUCTING ISOTOPE EFFECT IN ZrB$_{12}$

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The Zr isotope effect appears to be much stronger in ZrB$_{12}$ than in elemental Zr (the B isotope effect in ZrB$_{12}$ is known to be small). The superconductivity of ZrB$_{12}$ is apparently caused by optical phonon modes associated with the internal motion of Zr atoms inside boron cages.

ZrB$_{12}$ belongs to an interesting group of superconductors in which transition metal atoms are embedded in a light atom matrix of high Debye temperature. The small boron isotope effect on the superconducting transition temperature of ZrB$_{12}$ ($\alpha = d \log T_c/d \log m = -0.09 \pm 0.05$, $m =$ mass of boron isotope) [1] shows either that the acoustic phonon modes which determine the high Debye temperature ($\Theta_D = 945$ K) [2] are not responsible for the relatively high superconducting transition temperature ($T_c = 5.9$ K), or that Coulomb repulsion effects between the electrons are strong enough to strongly reduce the isotope effect which one might expect on the basis of the BCS theory. The latter situation is believed to occur, for example, in elemental Zr and Ru. The Zr isotope effect in ZrB$_{12}$ is therefore of interest for understanding the superconductivity of these curious compounds.

Zr isotopes 90, 91, 92 and 94 were obtained from Oak Ridge National Laboratories in the form of 10 mil sheet. The $T_c$ values for these isotopes did not agree with those published. The isotopes were purified by heating several minutes under He in an arc-furnace. ZrB$_{12}$ was then prepared from this material by arc-melting together with high purity B under argon. All superconducting transition widths were 30 ± 5mdeg. There is no correlation between the $T_c$ of the Zr isotope starting material and that of the corresponding ZrB$_{12}$. This makes us confident that the isotope effect observed is not due to any impurities present. Only Sc, Y, rare earths and actinides are expected to be at all soluble in ZrB$_{12}$, and the spectrographic analyses supplied with the Zr isotopes show these not present.

* Work was done at Bell Telephone Laboratories while a consultant for Department 1112.

Fig. 1. Logarithm of $T_c$ of ZrB$_{12}$ versus logarithm of Zr isotopic mass in ZrB$_{12}$. Our measured $T_c$ for natural abundance Zr in ZrB$_{12}$ is 5.940 K.
Fig. 1. is a (base 10) log $T_c$ versus log $M$ plot, where $M$ is the Zr atomic weight appropriate for the isotopic abundance of Zr in each specimen. We prepared three specimens of ZrB$_{12}$ for each Zr isotope, and the points in the figure give the average value of the midpoint of the transitions for each isotope, the error bars indicating the spread of mid-points observed. Only one specimen of ZrB$_{12}$ with natural abundance of Zr was measured, the transition width for this being 40 mdeg.

The slope of the straight line in the figure gives $\alpha = -0.32 \pm 0.02$, somewhat larger, but comparable, to $\alpha = -0.23$ for Mo in MoBe$_{22}$ [3]. It is interesting that the isotope effect in elemental Zr is zero [4]. Our result contrasts with Engelhardt's on the isotope effect of Mo in Mo$_2$B [5]: Zr in ZrB$_{12}$ behaves very differently from elemental Zr, while the behavior of Mo in MoBe$_{22}$ and Mo$_2$B does not differ much from that of elemental Mo.

The fact that a large $\alpha$(Zr) exists in ZrB$_{12}$ shows that Coulomb repulsion effects are not responsible for the small $\alpha$(B). Then it is clear that if acoustic phonon modes are responsible for the superconductivity, one would expect a value for $\alpha$(B) which is much larger than that observed. We conclude that in ZrB$_{12}$ the superconductivity is caused by the optical phonon modes associated with the internal motion of Zr atoms inside their boron cages.

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