Boron Isotope Effect in Superconducting MgB$_2$.

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We report the preparation method of, and boron isotope effect for MgB$_2$, a new binary intermetallic superconductor with a remarkably high superconducting transition temperature $T_c$ of $40.2$ K. Measurements of both temperature dependent magnetization and specific heat reveal a $1.0$ K shift in $T_c$ between Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$. Whereas such a high transition temperature might imply exotic coupling mechanisms, the boron isotope effect in MgB$_2$ is consistent with the material being a phonon-mediated BCS superconductor.

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The discovery of superconductivity with $T_c \approx 39$K in magnesium diboride (MgB$_2$) was announced in January 2001. It caused excitement in the solid state physics community because it introduced a new, simple (3 atoms per unit cell) binary intermetallic superconductor with a record high (by almost a factor of two) superconducting transition temperature for a non-oxide and non-C$_{60}$-based compound. The reported value of $T_c$ seems to be either above or at the limit suggested theoretically several decades ago for BCS, phonon-mediated superconductivity. An immediate question raised by this discovery is whether this remarkably high $T_c$ is due to some form of exotic coupling. Therefore, any experimental data that can shed light on the mechanism of superconductivity in this material are of keen interest.

One probe of the extent to which phonons mediate superconductivity is the isotope effect. In the classical form of BCS theory, the isotope coefficient $\alpha$, defined by the relation $T_c \propto M^{-\alpha}$, where $M$ is the mass of the element, is equal to $1/2$. For simple metals like Hg, Pb, Sn, and Zn, the isotope coefficient is found experimentally to be close to $1/2$. More detailed and realistic theories predict slight deviations from $\alpha = 1/2$. In this Letter, we describe how to prepare high-quality powders of MgB$_2$ and, more importantly, present data on the boron isotope effect, which is consistent with phonon mediated coupling within the framework of the BCS model.

MgB$_2$ crystallizes in the hexagonal AlB$_2$ type structure, which consists of alternating hexagonal layers of Mg atoms and graphite-like honeycomb layers of B atoms. This material, along with other $3d - 5d$ transition metal diborides, has been studied for several decades, mainly as a promising technological material. The B - Mg binary phase diagram is shown in Fig. 1. As can be seen, MgB$_2$ decomposes peritectically and has no exposed liquid-solidus line. Whereas the growth of single crystals of this compound promises to be a difficult problem, high quality powders can be formed in the following manner. Elemental Mg (99.9 % pure in lump form) and isotopically pure boron (99.5 + % pure, < 100 mesh) are combined in a sealed Ta tube in a stoichiometric ratio. The Ta tube is then sealed in a quartz ampoule, placed in a 950º C box furnace for two hours, and then removed and allowed to cool to room temperature. The quartz ampoule and the Ta tubing are not attacked, but there is a distinct bowing out of the Ta tube where the MgB$_2$ powders form. The height of this bowing scales with the height of the MgB$_2$ powders and seems to be associated with an expansion of the B powder as the MgB$_2$ forms, rather than a Mg vapor pressure (which would bow out the tube over its whole length). It should be noted that if larger pieces of B are used, then this reaction scheme does not produce homogeneous material. This, combined with the phase diagram shown in Fig. 1, implies that, at least to some extent, the reaction takes place via the diffusion of Mg into the B particles.

The powder X-ray diffraction pattern of the Mg$^{10}$B$_2$ powder is shown in Fig. 2 with the peaks indexed to the hexagonal unit cell of MgB$_2$. From Fig. 2, the unit cell lattice parameters for Mg$^{10}$B$_2$ are $a = 3.1432 \pm 0.0315$ and $c = 3.5193 \pm 0.0323$ Å.

The temperature dependent magnetization of the sample was measured in a Quantum Design MPMS-7 SQUID magnetometer in an applied field of 25G. An onset criterion of 2% of the full, low temperature diamagnetic signal was used to determine $T_c$ from the zero-field-cooled $M(T)$ data that were taken on warming. In this letter we report measurements on four types of samples with the following morphologies: Mg$^{10}$B$_2$, Mg$^{11}$B$_2$ and Mg$^{10}$B$_{11}$B were all solid pieces of sample cut from the pellet that formed in the Ta reaction tubes whereas, the commercial sample was a fine powder. The three solid, isotopic samples each had $M/H > 150\%$ of $-1/4\pi$ at low temperature and the powder sample had $M/H > 200\%$ of $-1/4\pi$. By assuming spherical or slightly plate-like grains both of these values are consistent with demagnetization effects and 100% diamagnetism. The plotted magnetization data are all normalized to 1 at low temperatures for easier comparison. The specific heat data were taken using the heat capacity option of a Quantum

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Design PPMS-9 system in zero and 90 kG applied field.

The magnetization curves of a commercial (Alfa-Aesar 98% pure) MgB$_2$ powder and prepared Mg$_{11}$B$_2$ material are shown in Fig. 3. The commercial powder has a lower $T_c$ (37.5 K) and a broader superconducting transition. At present, it is not clear what causes the suppression of $T_c$, but the difference may be due to impurities present in the material.

Figure 4a presents the temperature-dependent magnetization of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$. There is a clear separation between the data of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$. Using the 2% onset of diamagnetism criterion mentioned above, the superconducting transition temperatures are 39.2 K for Mg$^{11}$B$_2$ and 40.2 K for Mg$^{10}$B$_2$. The widths of the transitions (90% – 10%) are 0.4 K and 0.5 K for Mg$^{11}$B$_2$ and Mg$^{10}$B$_2$, respectively.

In Fig. 4b the temperature-dependent specific heat data for Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ in zero and 90 kG applied field are shown. Whereas the data were collected between 2 K and 50 K, Fig. 4b presents a more limited temperature range to clearly show the shift in $T_c$ associated with the isotope effect. The transitions are shifted by the same factor of four broader than either of the isotopically pure samples. It should be noted that the Mg$^{10}$B$^{11}$B sample was made from exactly the same starting chemicals, via the same technique, and had the same morphology (a sintered lump) as the two isotopically pure samples. The origin of this broadening is not as of yet clear, but it may hint that the effect of isotopic disorder on the boron phonon modes plays a significant role.

Figure 5 presents data on a 50-50 mixture of boron isotopes: Mg$^{10}$B$^{11}$B. Also shown is the normalized sum of the pure Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ magnetization data shown in Fig. 4a. Given that the starting materials were a lump of Mg and grains of $^{10}$B and $^{11}$B, if there were no mixing between the boron particles as the MgB$_2$ was formed then one might expect the data to look like the sum plot, i.e. separate grains of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ acting independently. As can be seen, the Mg$^{10}$B$^{11}$B data does not show two steps and manifests a significantly broadened transition. Using the 2% criterion, $T_c$ = 39.9 K but, more significantly, the width of the transition is 2.1 K, a factor of four broader than either of the isotopically pure samples. It is expected that the phonon modes mediate BCS superconducting mechanism in this compound and with the possibility that boron phonon modes are playing an important role.

In conclusion, a significant boron isotope effect ($\Delta T_c = 1.0$ K, partial isotope exponent $\alpha_B \approx 0.26$) was observed in MgB$_2$. This shift is clearly seen in both magnetization and specific heat measurements. This observation is consistent with a phonon mediated BCS superconducting mechanism in this compound and with the possibility that boron phonon modes are playing an important role.

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FIG. 1. Proposed, schematic, binary phase diagram for B - Mg system (After Ref. [9]).

FIG. 2. Powder X-ray (Cu K$\alpha$ radiation) diffraction spectra of Mg$^{10}$B$_2$ (with h,k,l values) and Si standard (*).

FIG. 3. Magnetization divided by applied field as a function of temperature for Mg$^{11}$B$_2$ and natural boron sample of MgB$_2$ from Alfa-Aesar. Data are normalized to 1 at 5 K, as discussed in text.

FIG. 4. (a) Magnetization divided by applied field as a function of temperature for Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$. (b) Magnetization divided by applied field as a function of temperature for Mg$^{10}$B$^{11}$B and sum of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ data shown in panel (a). Data are normalized to $-1$ at 5 K, as discussed in text.
FIG. 5. Temperature dependent specific heat of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ in zero (filled circles) and 90 kG (open triangles) applied field for temperatures near the $T_c$. Arrows mark transition temperatures determined from the magnetization measurements shown in Fig. 4a.