

Superconducting properties of $\text{BeB}_{2.75}$

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We present the low-temperature electronic transport properties of the intermetallic commonly known as BeB_2 . In contrast to the much simpler AlB_2 -type structure of the 39-K superconductor MgB_2 , BeB_2 forms a complex structure-type that is nearly unique in nature. The structure has 110.5 atoms per unit cell and a stoichiometry $\text{BeB}_{2.75}$. Polycrystalline $\text{Be}^{(10.8\text{B})}_{2.75}$ is superconducting below $T_c=0.72$ K with a critical magnetic field $H_{c2}=0.175$ T. Isotopically pure $^{10.0\text{B}}$ samples have an enhanced $T_c=0.79$ K. Hall-effect measurements suggest that the material is intrinsically compensated.

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Over the last few years there has been a renewed interest in intermetallic superconductors that incorporate relatively low-mass elements. In the framework of BCS theory the lighter elements result in higher frequency phonon modes that may in turn produce enhanced transition temperatures. This idea is particularly well demonstrated in pure, disordered Be films, which have one of the highest known elemental superconducting transition temperatures $T_c \approx 10$ K.¹ Studies of intermetallics containing boron have been particularly interesting and fruitful,² culminating in the recent discovery of 39-K superconductivity in the relatively simple binary MgB_2 .³ Naively one would hope to obtain even higher transition temperatures by substituting Be for the Mg in MgB_2 given that the atomic mass ratio of Mg to Be is $M_{\text{Mg}}/M_{\text{Be}}=2.25$. Felner⁴ has recently reported susceptibility measurements of BeB_2 that show no sign of superconductivity down to 5 K. Recent band-structure calculations of BeB_2 , in which the AlB_2 -type structure of MgB_2 was assumed, indicate that the Fermi-surface topology of BeB_2 is sufficiently modified from that of MgB_2 so as to preclude the possibility of medium- T_c superconductivity.⁵ In this paper we demonstrate that the compound commonly referred to as BeB_2 is much more interesting than expected. Our single-crystal x-ray refinement of the structure not only shows that the BeB_2 stoichiometry does not exist but that the correct stoichiometry, $\text{BeB}_{2.75}$, is *not* isostructural with MgB_2 . Indeed, $\text{BeB}_{2.75}$ forms a complex crystal structure⁶ that is almost unique in nature—only two other compounds are known to have the same structure.⁷ To our knowledge all previous electronic band calculations⁵ of “ BeB_2 ” have assumed an AlB_2 -type structure and are therefore nonphysical.

Interestingly, we have discovered that $\text{BeB}_{2.75}$ superconducts at a transition temperature $T_c=0.72$ K. Though this is somewhat low by the standards of MgB_2 , the fact that this

proposed structure-type supports superconductivity is interesting in itself. The interplay between crystal structure, electron correlations, and disorder in a wide variety of superconducting systems remains an outstanding issue in the field. Indeed, some insight into how to raise T_c should emerge once the electronic structure of $\text{BeB}_{2.75}$ is known.

Though beryllium diboride has been known and studied for more than 40 years, there has been no firm evidence that this phase exists with stoichiometry BeB_2 . The space group of a compound reported to be BeB_2 (Ref. 8) was hexagonal $P6/mmm$ with lattice constants $a=0.979(2)$ nm and $c=0.955(2)$ nm, but a full structure determination was not carried out. In the present study Be plate (Alfa, 99.8%) and B pieces (Alfa, 99.5%) were arc-melted together on a water-cooled copper hearth under ultra-high-purity argon gas. The starting ratio of Be to B was 4:1. Approximately 5% of the Be mass was lost during the melting process due to volatilization. Small plateletlike single crystals, which were dull silver in color, formed near the top of the button. These were mechanically extracted, and single-crystal x-ray diffraction determined the stoichiometry of the crystals to be $\text{BeB}_{2.75}$. The remainder of the button was copper in color, and powder x-ray diffraction determined this polycrystalline material to be Be_4B . Transport measurements were carried out on bars cut from polycrystalline samples that were arc-melted at the $\text{BeB}_{2.75}$ stoichiometry with an excess of 5% Be. These samples were characterized by x-ray powder diffraction and found to be single phase, to within the limits of the sensitivity of the method. The polycrystalline samples had lattice constants that were identical to those of the $\text{BeB}_{2.75}$ single-crystal samples. Single-crystal intensity data were measured at 120 K on a Nonius Kappa charge coupled device diffractometer. The refinement was carried out with 606 unique reflections up to $2\theta=64^\circ$ and yielded a $R=0.047$. The re-

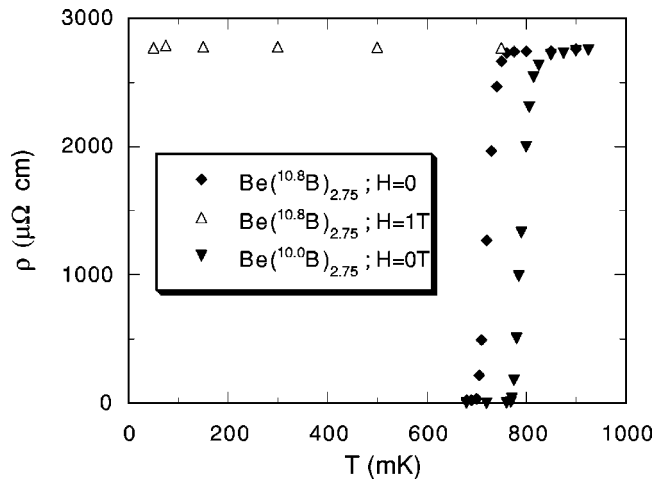


FIG. 1. Sample resistivity as a function of temperature. Solid symbols: zero field. Open symbols: $H=1$ T. The open symbols represent the normal state.

finer structure produced a stoichiometry of $\text{Be}_{1.23}\text{B}_{3.38}$ (i.e., $\text{BeB}_{2.75}$) with $a=0.97738(7)$ nm and $c=0.95467(6)$ nm. The structure has 81 B atoms and 29.5 Be atoms per unit cell. Details of the structure refinement have been reported elsewhere.⁶

Low-temperature magnetotransport studies were made on samples cut from polycrystalline buttons of $\text{BeB}_{2.75}$. The resistance of rectangular samples of typical dimensions $2\text{ mm}\times 0.5\text{ mm}\times 0.1\text{ mm}$ was measured using a standard four-probe ac technique. The samples were cooled in a dilution refrigerator down to 50 mK in magnetic fields up to 6 T. The polycrystalline samples had room-temperature resistivities of $\sim 3000\ \mu\Omega\text{ cm}$ that changed very little upon cooling, falling only $\sim 10\%$ from room temperature to 4 K. The resistivity remained essentially unchanged at lower temperatures. We made Hall-effect measurements up to 6 T at 100 mK in order to determine the carrier density N but could not extract a measurable Hall voltage. Assuming single carrier conduction, our Hall measurements indicate a lower bound on the carrier density of $N > 10^{22}\text{ cm}^{-3}$. This limit is inconsistent with the high resistivity of our samples, suggesting that the resistance was dominated by microstructural defects such as grain boundaries and/or microcracks. It is also possible that the resistance is high due to a low carrier density. This can be reconciled with a small Hall effect, if $\text{BeB}_{2.75}$ is intrinsically compensated with roughly equal densities of mobile electron and hole carriers. Preliminary band-structure calculations suggest that this is, in fact, the case.⁹

Shown in Fig. 1 are the resistivities as a function of temperature of two samples, one made from natural abundance $^{10.8}\text{B}$ and the other from isotopically pure ^{10}B . It is evident from Fig. 1 that $\text{BeB}_{2.75}$ superconducts with $T_c(^{10.8}\text{B})=0.72$ K and that the ^{10}B sample has a slightly enhanced $T_c(^{10.0}\text{B})=0.79$ K. If the boron phonon modes are solely responsible for mediating the superconductivity, then BCS theory predicts that the ^{10}B transition temperature should be enhanced by the factor $(10.8/10.0)^\alpha$ where $\alpha=1/2$.^{10,11} $T_c(^{10.0}\text{B})$ in Fig. 2 is about twice as large as the expected value $T_c(^{10.0}\text{B})\sim(1.04)T_c(^{10.8}\text{B})$, suggesting that $\alpha\sim 1$. The

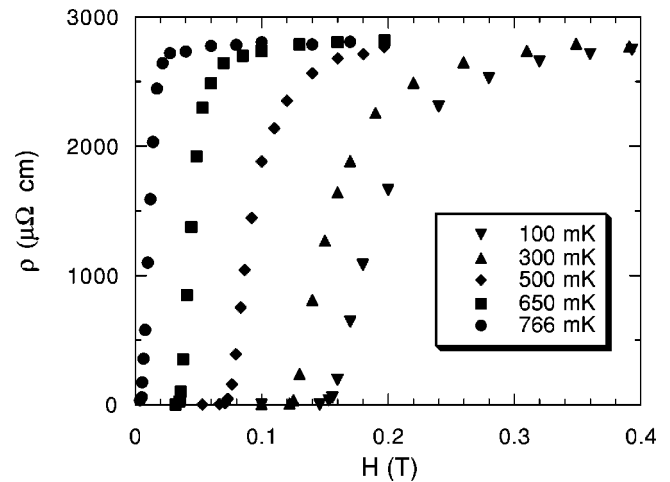


FIG. 2. Resistive upper critical field transitions for the ^{10}B sample.

deviation from $\alpha=1/2$ may be due to the complexity of the BCS state in this material. It is also possible that it is representative of nonphonon mediated superconductivity.¹²

The open symbols in Fig. 1 were data taken in a field of 1 T that is above the upper critical field $H_{c2}\approx 0.18$ T. Note that the normal-state resistivity in Fig. 1 is temperature independent. We also found the normal-state resistivity to be magnetic-field independent below 1 K. This leads us to believe that the relatively high resistivity of our samples is a consequence of a low carrier concentration and not disorder. In Fig. 2 we show the resistive upper critical-field transitions at several temperatures of the ^{10}B sample. The increase of the transition width with decreasing temperature (see inset of Fig. 3) is indicative of flux flow broadening. This suggests that the $\text{BeB}_{2.75}$ is a type II superconductor, as is MgB_2 .¹³ At $T=100$ mK the upper critical field is $H_{c2}=0.19$ T, which gives a coherence length $\xi_0\sim 30$ nm. In Fig. 3 we plot the upper critical field, as measured from the midpoints of the transitions in Fig. 2, as a function of the reduced temperature

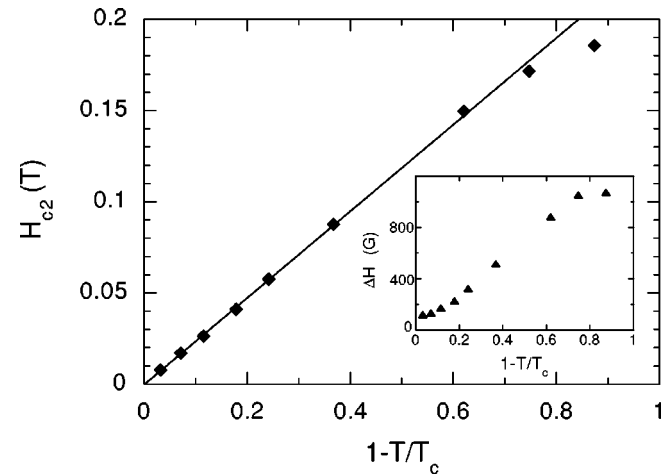


FIG. 3. Upper critical field as a function of reduced temperature. H_{c2} was taken as the midpoints of the transitions in Fig. 2. The solid line is least-squares fit to the data points near the origin. Inset: Critical field (10%–90%) width as function of reduced temperature.

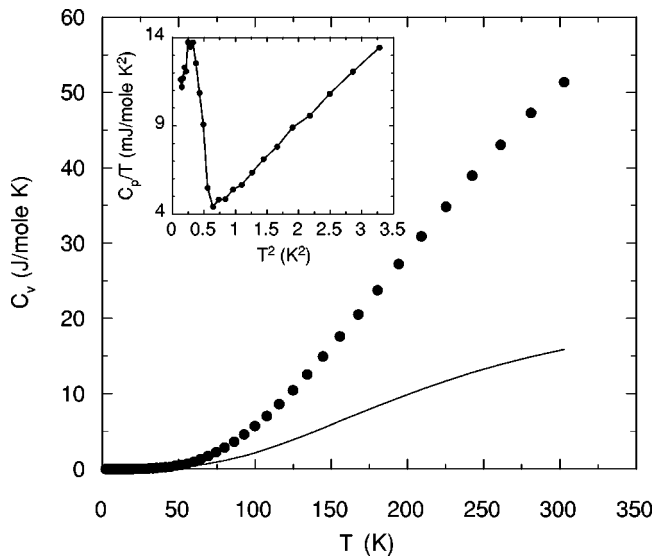


FIG. 4. Circles are the specific heat of $\text{Be}^{10.8}\text{B}_{2.75}$ as a function of temperature in zero field. The line is an estimation of the Debye contribution using $\Theta_D \sim 1000$ K, which was extracted from data between 10 K and 20 K. Inset: Specific-heat jump associated with the superconducting transition at $T_c \sim 0.72$ K.

$1 - T/T_c$. Note the linearity of the data, in contrast to the more typical quadratic dependence seen in many BCS superconductors.¹⁰ The solid line in Fig. 3 is a linear least-squares fit to the data points near the origin, and has a slope $dH_{c2}/dT \approx 0.2$ T/K. Similar linearity was also obtained from critical fields determined by an onset criterion.

In the main body of Fig. 4 we show measurements of the

zero-field specific heat from 0.3 to 300 K, which were made using a heat-pulse decay method. Using data between 10 and 20 K to extract the phonon contribution, we find a Debye temperature $\Theta_D \sim 1000$ K. Shown as a solid line in Fig. 4 is the expected high-temperature Debye specific heat. It is evident that there is a comparable contribution to the specific heat from an optical phonon. Fits to the data gave an Einstein temperature of 700 K for this mode. Low-temperature C_p/T measurements are plotted as a function of T^2 in the inset Fig. 4. The normal-state electronic contribution to the specific heat γ was determined to be 0.6 mJ/mole K^2 . Note the well defined jump in specific heat at the superconducting transition. The magnitude of specific-heat discontinuity at T_c is $\Delta C_p/C_p \sim 2.3$ that is somewhat larger than the BCS value $\Delta C_p/C_p = 1.4$.¹⁰

In conclusion we find that the compound commonly referred to as BeB_2 superconducts below $T_c \sim 0.72$ K if made from natural abundance boron. However, x-ray analysis reveals that BeB_2 is unstable, and that the correct stoichiometry $\text{BeB}_{2.75}$ has a complex and rare crystalline structure-type. Both the isotope effect and the specific-heat discontinuity at T_c are significantly larger than predicted by BCS theory. Like the perovskites^{14,15} and the C_{60} fullerenes,¹⁶ the structural framework of $\text{BeB}_{2.75}$ may be playing an important role in its superconducting behavior. At this point we do not know which specific components of the structure are responsible for the superconductivity.⁶

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