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Superconducting properties of (formula presented)

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Structure and Superconducting Properties of "BeB_2"

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We present the crystal structure and 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 39K 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 $BeB_{2.75}$. Polycrystalline $Be(^{10.8}B)_{2.75}$ is superconducting below $T_c = 0.72$K with a critical magnetic field $H_{c2} = 0.175$T. Isotopically pure $^{10.0}$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 and may thereby produce enhanced transition temperatures. This idea is particularly well demonstrated in pure, disordered Be films, which have the highest known elemental superconducting transition temperature $T_c \approx 10$K [1]. Studies of intermetallics containing boron have been particularly interesting and fruitful [2], culminating in the recent discoveries of 39K and 9.5K superconductivity in the astonishingly simple binaries MgB_2 [3] and TaB_2 [4], respectively. 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 $M_{Mg}/M_{Be} = 2.25$. This obvious substitution was almost certainly tried by many of the groups studying MgB_2 and unfortunately proved unsuccessful. Indeed, Felner [5] has recently reported susceptibility measurements of BeB_2 that show no sign of superconductivity down to 5K. 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 [6]. As a consequence of these findings the superconducting community has abandoned its initial interest in BeB_2. In this Letter 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, $BeB_{2.75}$, is *not* isostructural with MgB_2. Indeed, $BeB_{2.75}$ forms a beautiful and surprisingly complex crystal structure, see Fig. 1, 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 calculations [6] of "BeB_2" have assumed an AlB_2-type structure and are therefore incorrect. Interestingly, we have discovered that $BeB_{2.75}$ superconducts at a transition temperature $T_c = 0.72$K. Though this is somewhat low by the standards of MgB_2, it is still very promising in that some obvious schemes to increase T_c, such as doping, may emerge once the electronic structure of the material 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 and cell dimensions of a compound purported to be BeB_2 were reported [8] to be hexagonal P6/*mmm*, a = 0.979(2) nm, c = 0.955(2) nm, but a full structure determination was not carried out. In the present study single crystals of "BeB_2" were formed by slowly cooling a *Be*-rich arcmelted boule of elemental Be and B. The crystals formed as small thin plates with a dull metallic luster and were mechanically extracted from the melt. Single-crystal intensity data were measured at 120 K on a Nonius KappaCCD diffractometer, and refinement with 606 reflections yielded a R=0.047. Our refinement resulted in a stoichiometry of $Be_{1.23}B_{3.38}$ (i.e., $BeB_{2.75}$) with a = 0.97738(7)nm and c = 0.95467(6)nm (P6/*mmm*, Z = 24).

The calculated structure is shown in Fig. 1a. It is constructed from stacked hexagonal layers of boron atoms, hexagons formed by B and Be, equilateral triangles of boron atoms, B_{12} icosahedra, and isolated Be atoms as shown in Fig. 1b. In a manner similar to what is observed in the newly-discovered superconductor MgB_2 [3], hexagonal layers of B are stacked along the c axis with hexagonal layers of sites half-occupied by boron and beryllium, as shown in

Fig. 1c. The B-B bond distances are 0.18414(19)nm, and the B-Be distances are 0.2016(2)nm. However, the layering is more complex than in MgB_2, as equilateral triangles formed by another layer of B, disordered around a sixfold axis, are also present. The interleaved stacks, Fig. 1c, described above lie in channels formed by hexagonal networks of B_{12} icosahedra, linked at the vertices by B-B bonds. These hexagonal networks of B_{12} icosahedra are in turn linked along the c-axis direction by non-icosahedral B_{12} cage polyhedra. The observed B-B distances of 0.17715(2)nm to 0.1820(2)nm in the icosahedra are similar to those in the B_{12} icosahedra in $K_2B_{12}H_{12}$ (0.1775 nm) [9] and in tetragonal boron (0.1806 nm) [10]. Be atoms lie in interstitial sites within the boron framework, including one Be site that was treated as 1/2 occupied on a site of mm symmetry, and another which was treated as 1/8 occupied on a site of $3m$ symmetry. More details of the crystal structure will be reported elsewhere [11].

Low temperature magnetotransport studies were made on samples cut from polycrystalline boules of $BeB_{2.75}$. The resistance of rectangular samples of typical dimensions 2mm x 0.5mm x 0.1mm was measured using a standard 4-probe ac technique. The samples were cooled in a dilution refrigerator down to 50mK in magnetic fields up to 6T. The polycrystalline samples had room temperature resistivities of $\sim 3000\mu\Omega$-cm that changed very little upon cooling, falling only $\sim 10\%$ from room temperature to 4K. The resistivity remained essentially unchanged at lower temperatures. We made Hall effect measurements up to 6T at 100mK 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 $N > 10^{22} cm^{-3}$. This limit is inconsistent with the high resistivity of our samples, suggesting that $BeB_{2.75}$ may be intrinsically compensated.

Shown in Fig. 2 are the resistivities as a function of temperature of two samples, one made from natural abundance $^{10.8}$B and the other from isotopically pure ^{10}B. It is evident from Fig. 2 that $BeB_{2.75}$ superconducts with $T_c(^{10.8}\mathrm{B}) = 0.72$K and that the ^{10}B sample has a slightly enhanced $T_c(^{10.0}\mathrm{B}) = 0.79$K. If the boron phonon modes are soley 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 $\alpha = 1/2$ [12,13]. $T_c(^{10.0}\mathrm{B})$ in Fig. 2 is about twice as large as the expected value $T_c(^{10.0}\mathrm{B}) \sim (1.04)\mathrm{T_c}(^{10.8}\mathrm{B})$, suggesting that $\alpha \sim 1$. The 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 non-phonon mediated superconducitivity [14].

The open symbols in Fig. 2 were data taken in a field of 1T which is above the upper critical field $H_{c2} \approx 0.18$T. Note that the normal state resistivity in Fig. 2 is temperature independent. We also found the normal state to be magnetic field independent below 1K. 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. 3 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. 4) is indicative of flux flow broadening. This suggests that the $BeB_{2.75}$ is a type II superconductor, as is MgB_2 [15]. At $T = 100$mK the upper critical field is $H_{c2} = 0.19$T, which gives a coherence length $\xi_o \sim 30$nm. In Fig. 4 we plot the upper critical field, as measured from the mid-points of the transitions in Fig. 3, as a function of the reduced temperature $1 - T/T_c$. Note the extreme linearity of the data, in contrast to the more typical quadratic dependence seen in many BCS superconductors [12]. The solid line in Fig. 4 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 conclusion, we have refined the crystal structure of "BeB_2" from single-crystal X-ray diffraction data and find that not only is BeB_2 an unstable stoichiometry but that the correct stoichiometry $BeB_{2.75}$ has an extremely complex and rare crystalline structure type. Though the superconducting transition temperature of $BeB_{2.75}$ is relatively low, one must keep in mind that virtually nothing is known about its electronic band structure. As has been the case with perovskites [16,17] and the C_{60} fullerenes [18], the rich structural framework of $BeB_{2.75}$ may afford opportunities to increase T_c once we have better understanding of its electronic properties.

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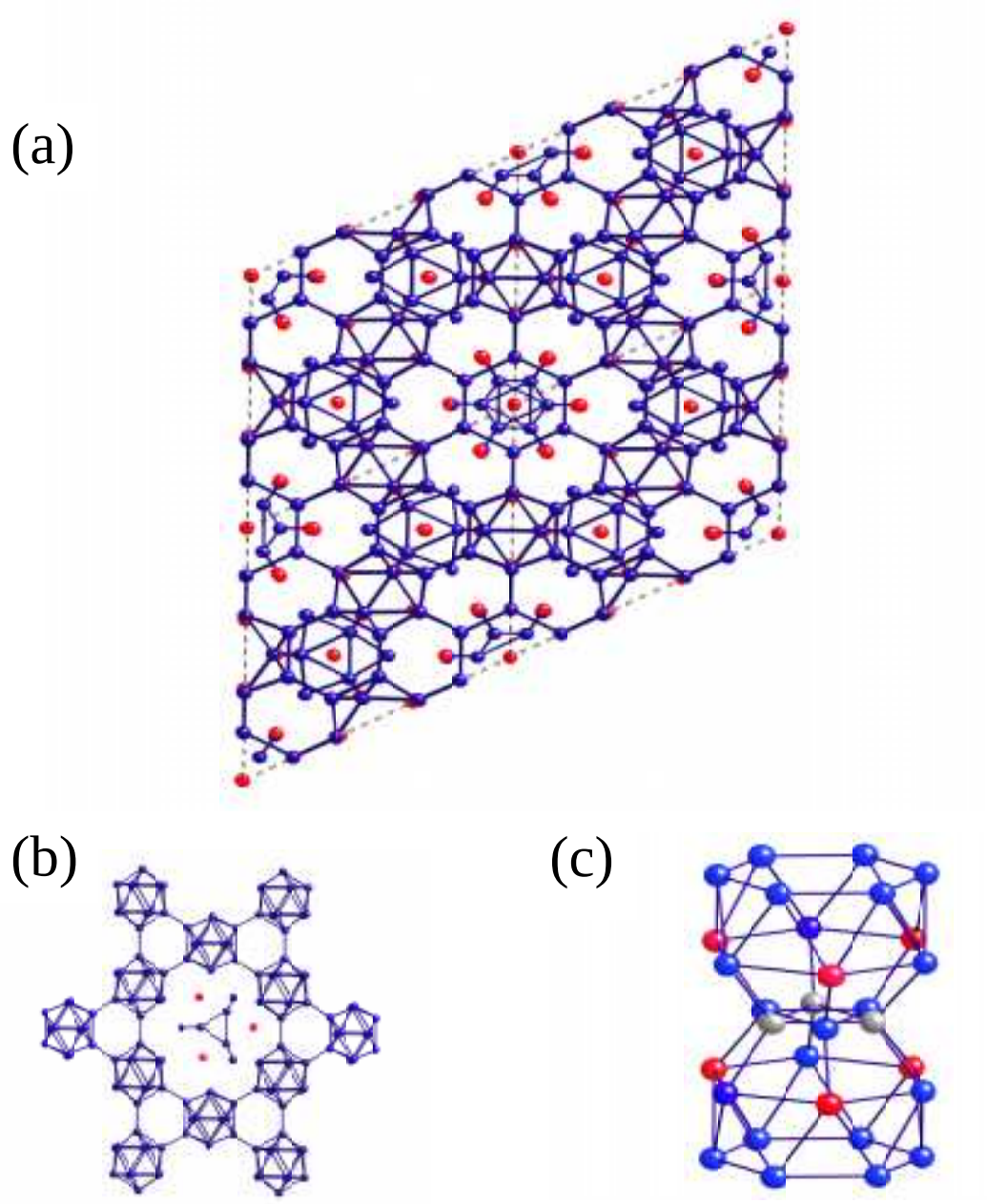

FIG. 1. a) Four unit cells of the $BeB_{2.75}$ structure are shown, where Be and B atoms are represented in red and blue, respectively. Note: The hexagonal cluster at the center of the figure is shown in greater detail in panel c). b) The hexagonal network of vertex-linked icosahedra is shown along the c direction. c) Layers of B, B/Be hexagons, and the disordered equilateral B triangles form a building block of the structure. Only one of the two possible orientations of the channel contents is shown.

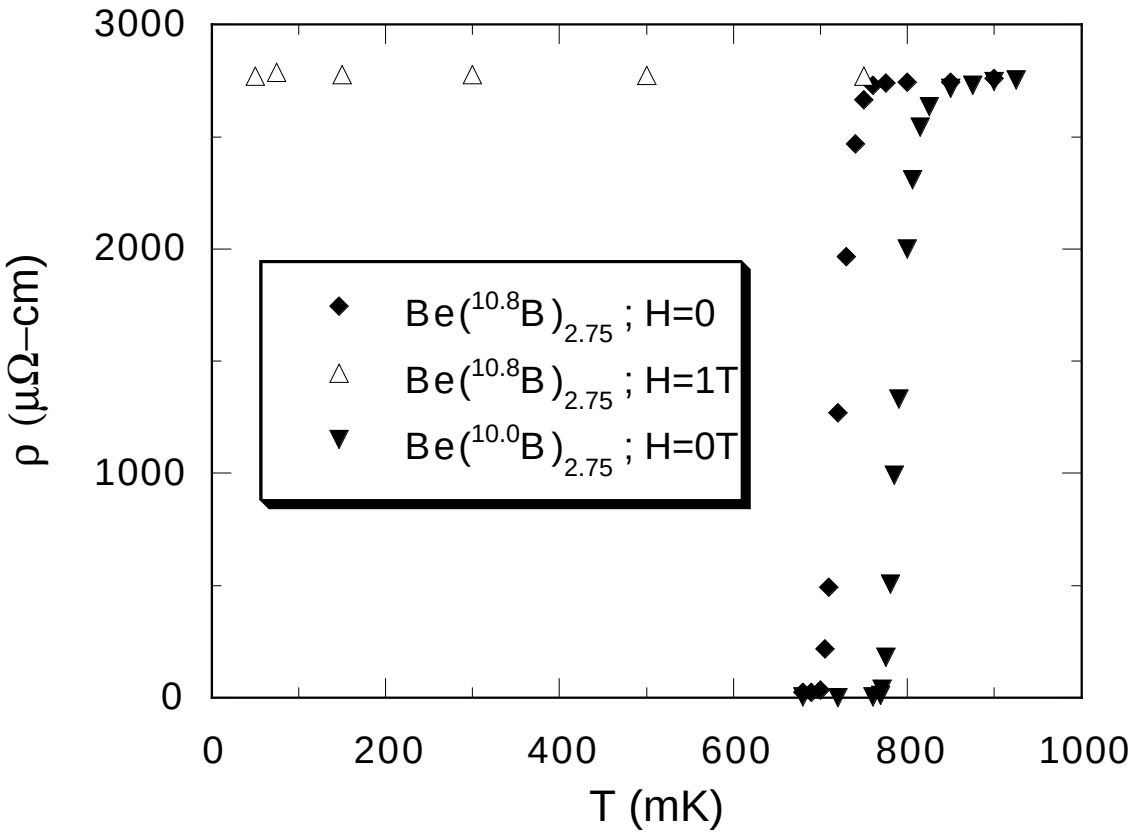

FIG. 2. Sample resistivity as a function of temperature. Solid symbols: zero field. Open symbols: H=1T. The open symbols represent the normal state.

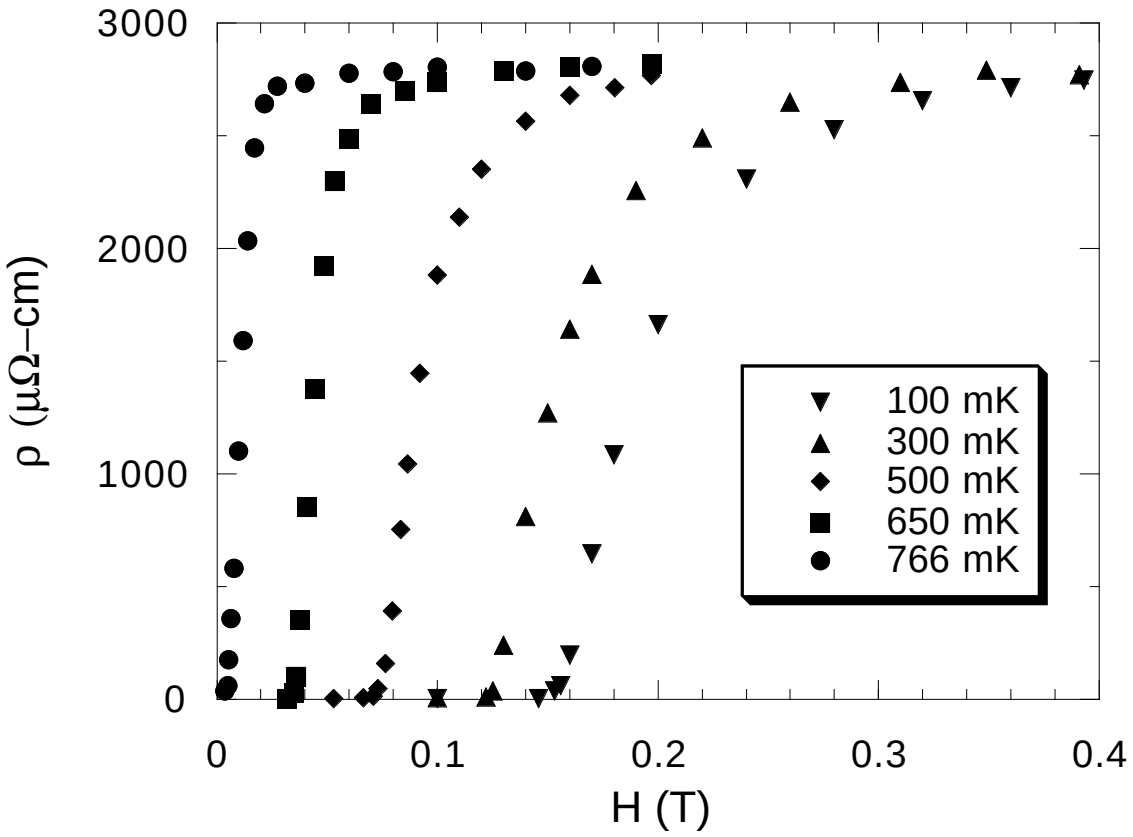

FIG. 3. Resistive upper critical field transitions for the ^{10}B sample.

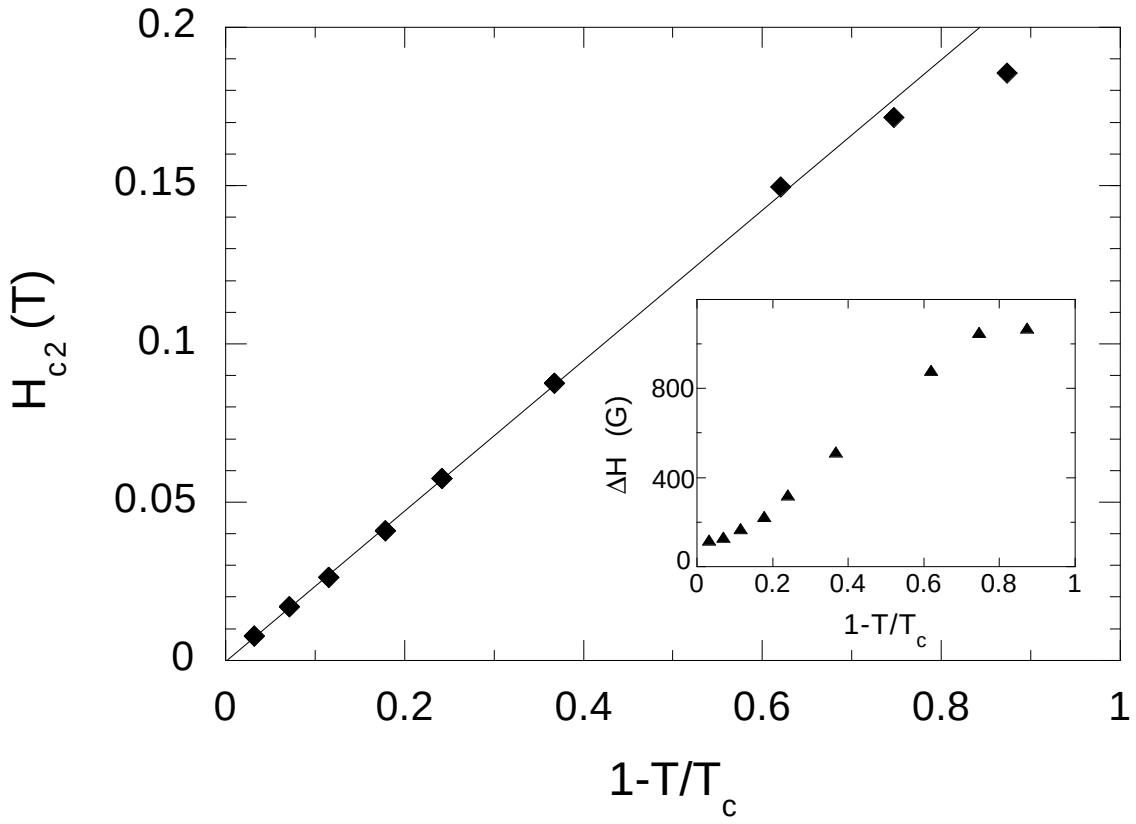

FIG. 4. Upper critical field as a function of reduced temperature. H_{c2} was taken as the midpoints of the transitions in Fig. 3. The solid line is least-squares fit to the data points near the origin. Inset: Critical field $(10\% - 90\%)$ width as function of reduced temperature.