Superconductivity in the Metal Rich Li-Pd-B Ternary Boride

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Superconductivity at about 8 K was observed in the metal-rich Li-Pd-B ternary system. Structural, microstructural, electrical, and magnetic investigations for various compositions proved that the Li_2Pd_3B compound, which has an antiperovskite cubic structure composed of distorted Pd_6B octahedrons, is responsible for the superconductivity. This is the first observation of superconductivity in metal-rich ternary borides containing alkaline metal and Pd as a late transition metal. The compound prepared by arc melting has a high density and is relatively stable in the air. The upper critical fields $H_{c2}(0)$ estimated by linear extrapolation and the Werthamer-Helfand-Hohenberg theory are 6.2 and 4.8 T, respectively.

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The search for superconductivity in boride compounds initiated in 1949 with the discovery of TaB ($T_c = 4$ K) [1]. However, most works were done in the 1970s and 1980s, resulting in the discovery of many binary and ternary superconducting borides, almost all of which involve transition metal (TM) elements, rare-earth elements, and platinum group elements of Ru, Rh, Os, Ir, and Pt as metal constituents [2]. Despite these efforts, the transition temperature T_c of binary and ternary borides remained below 12 K and could not exceed 23 K, which was the highest T_c of intermetallic compounds recorded by A15 Nb_3Ge in 1973 [3]. It is interesting that no Pd binary or ternary boride was reported in stable condition, although Pd belongs to the platinum group and gives the highest T_c in the case of the quaternary borocarbide system $(RE)(TM)_2B_2C$, where RE is a rare-earth metal and TM is Ni, Pd, or Pt [4].

The recent discovery of 39 K superconductivity in MgB_2 [5] has led to a resurgence of interest in boride compounds as possible high temperature superconductors. It is surprising that such high T_c was attained for simple binary boride with the light alkaline earth element Mg as a metallic constituent. Since then, there have been several experimental and theoretical studies to search for high T_c borides extending the metallic constituent to alkaline and alkaline earth elements. In these, of particular interest was the prediction of high temperature superconductivity in the $Li_{1-x}BC$ system [6]; however, to date, no superconductivity was reported for this system [7].

In this Letter, we report the discovery of superconductivity around 8 K in a metal-rich boride of Li_2Pd_3B compound with cubic structure. This is the first report for superconductivity in ternary borides containing alkaline metal and Pd as a platinum group element and not containing any rare-earth and transition metal elements. In addition, the compound has a unique structure containing highly distorted Pd_6B octahedrons, which form a new type of three-dimensional framework [8]. The study of the physical properties of this new antiperovskite structured superconductor, such as electronic structures, doping mechanisms, etc., attracts much interest in the investigation of the conduction mechanism of boride systems. Moreover, the investigation of superconductivity, compared to those of perovskite oxide superconductors, including high T_c superconductors, as well as to the metallic $MgNi_3C$ [9] (a cubic, antiperovskite compound composed of octahedrons, but with no distortion), is expected to provide new information to explore the occurrence of superconductivity and to identify a possible road for searching new superconductors. Considering the example of $MgNi_3C$, for which instigations are advanced, it is also of interest that, although some properties are expected to be similar to classic superconductors, structural features and other properties resemble high T_c superconductors, and the material can be probably viewed as a bridge between classic and high T_c superconductors.

The samples were prepared by an arc-melting process in order to attain high-density material that is adequate to measure electrical properties. In order to minimize the loss of Li by evaporation, we employed a two-step arc-melting process. Initially, the Pd-B binary alloy buttons were prepared by a conventional arc-melting method from the mixture of appropriate amounts of Pd (99.9%) and B (99.5%). We prepared four alloys with different Pd:B ratios of 3:2, 5:2, 3:1, and 5:1. By this alloying, the melting point of the materials can be lowered below the boiling point of Li at 1 atm. Weight loss during the first arc-melting step was negligible. The alloying of Li was done in the second arc-melting processing step. A small block of Pd-B alloy (~ 200 mg) obtained by crushing the button was placed on a small piece of Li plate (10–50 mg) freshly cut from the Li ingot ($> 99\%$). The melting was done in an ~ 1 atm argon atmosphere and the arc current was controlled to the necessary minimum; once the Pd-B alloy melted, the reaction with Li occurred and developed very fast, probably due to the self-heating generated in the exothermic-type reaction. The loss of Li was inevitable, making the control of Li concentration difficult in the final products. Therefore, the Li concentration in the obtained Li-Pd-B alloy was estimated from the weight gain of the Pd-B alloy that is considered to have a constant weight during arc synthesis.

Temperature dependence of magnetization was measured for the samples at 20–100 Oe by a superconducting quantum interference device magnetometer. A sharp drop of magnetization at around 7–8 K, which is the characteristic signature of superconductivity, was observed for a variety of compositions examined in this work. The largest diamagnetic signal (Fig. 1) was obtained for the sample with an estimated composition of approximately Li_2Pd_3B. The onset of the transition is around 8 K as shown in the inset of Fig. 1. The zero-field-cooling (ZFC) curve shows an almost full shielding effect of ~80%, while the magnetic flux exclusion fraction estimated from the field-cooling (FC) curve is as low as ~3% at 2 K.

It is usual that the FC data of bulk polycrystalline metallic superconductors shows a very low flux exclusion fraction (Meissner effect) [10,11]. This is caused by the magnetic flux trapping owing to the absence of a "weak link" problem. In order to make the flux expelling easier, the bulk sample was ground into fine powders (a few μm in size) to shorten the travel distances necessary to be expelled and subjected to the magnetization measurement. The data are included in Fig. 1. As expected, the powder sample shows a much larger FC diamagnetic signal and the estimated flux exclusion fraction is ~19% at 2 K. The reason for the broadening of the transition is not clear, but the same behavior was observed for boride nitride superconductor [10] and for MgB_2 [11]. A relatively large Meissner effect observed for the powdered sample is the hallmark of bulk superconductivity. This result is supported by the specific heat measurement addressed in the next paragraph.

The specific heat (Cp) measurement for characterization of the superconducting transition was performed by using a physical properties measuring system (Quantum Design). The measurement was done in a zero applied magnetic field and 7 T that is above H_{c2}. As shown in Fig. 2, the specific heat jump at the superconducting transition is clearly seen in zero field, although the change is broad, probably due to a small stoichiometric variation in the sample. The specific heat jump $\Delta C/T_c$ at the transition is estimated to be 20.78 mJ/mol K^2, where $\Delta C = Cp(0\ \mathrm{T}) - Cp(7\ \mathrm{T})$. This value is almost the same as that of $MgCNi_3$ ($\Delta C/T_c = 19$ mJ/mol K^2) [9], which has a similar antiperovskite structure. The observed large specific heat jump is more clear evidence for bulk superconductivity of the Li_2Pd_3B sample.

The sample has a uniform solidification microstructure (Fig. 3), composed of grains with a few hundreds μm size with cellular dendrites inside the grain. Many cracks were observed along the grain boundaries and subgrain boundaries. The powder x-ray diffraction (XRD) pattern for this sample is shown in Fig. 4. Most of the peaks can be ascribed to the Li_2Pd_3B compound, which was recently reported by Eibenstein and Jung [8]. Very small peaks are observed at $2\theta = \sim 15.0°$ and 38.6° which could not be identified. ICP (inductively coupled plasma mass spectrometry) analysis was carried out for the Li_2Pd_3B sample. The composition ratio measured by the ICP was Li:Pd:B = 1.90:2.97:1, indicating the sample has the composition close to the stoichiometric one, in spite of the difficulty in controlling the Li concentration by the arc melting. From the above results, we speculate that the amount of the impurity phases is less than a few percent. The samples with estimated compositions different from

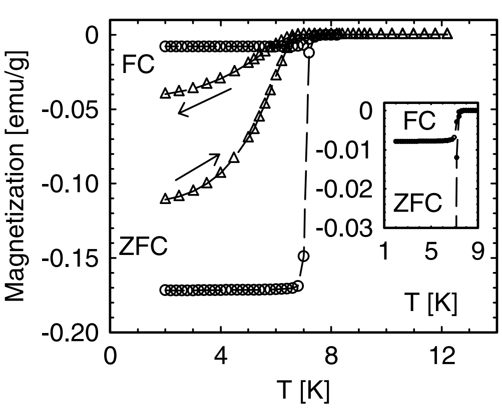

FIG. 1. Magnetization vs temperature curves for the Li_2Pd_3B sample measured in zero-field-cooling (ZFC) and field-cooling (FC) arrangements in the magnetic field of 20 Oe: circles, arc-melted bulk sample, and triangles, powdered sample. The inset shows in detail the FC curve of the arc-melted bulk sample.

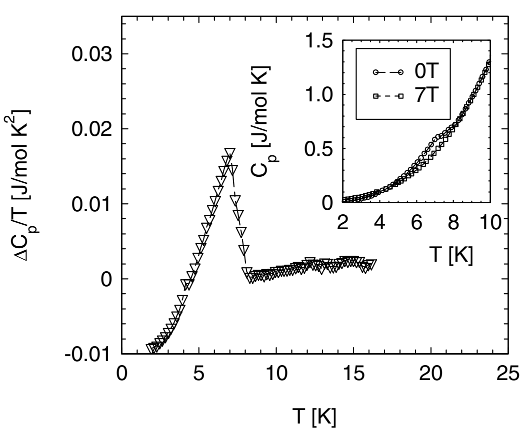

FIG. 2. $\Delta Cp/T$ plotted as a function of temperature, where $\Delta C = Cp(0\ \mathrm{T}) - Cp(7\ \mathrm{T})$. The inset shows the experimental curves of specific heat $Cp(0\ \mathrm{T})$ and $Cp(7\ \mathrm{T})$ as a function of temperature measured in the zero applied magnetic field and 7 T, respectively.

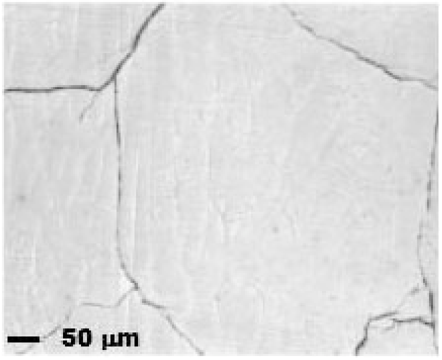

FIG. 3. Optical microstructure on the cross section of the arc-melted Li_2Pd_3B button.

Li_2Pd_3B showed a broader transition with a smaller diamagnetic signal, and at the same time extra peaks belonging to unidentified phases were clearly observed in the XRD patterns. From these results, we conclude that the Li_2Pd_3B compound is responsible for the observed 8 K superconductivity. The crystal structure is cubic and is composed of distorted Pd_6B octahedrons centered by a boron atom, which form a new type of three-dimensional network [8]. We measured the lattice constant of the Li_2Pd_3B compound down to temperatures around T_c, by using a low temperature diffractometer. The lattice constant at room temperature (300 K) is $a = 6.7523$ Å and monotonically decreases with decreasing the temperature, reaching $a = 6.7436$ Å at 7.6 K. The sample is relatively stable in the air and showed no significant difference of the diamagnetic signal after one week.

Figure 5 presents the temperature-dependent resistivity for the temperature range from 2 to 270 K measured for the Li_2Pd_3B sample using a standard four-probe method. The inset of Fig. 5 shows the superconducting transitions in applied magnetic fields up to 5 T. The sample was a bulk (a few mm size) obtained by crushing the final arc-melted product (button). The measuring applied current was 5 mA. The curve between 2 and 270 K shows the typical metallic behavior, the resistivity ratio, $\rho(270\ \mathrm{K})/\rho(10\ \mathrm{K})$, being 6.5. This relatively high value of the resistivity ratio indicates the sample has a good quality. The onset of the superconducting transition is defined by a 1% drop of the resistivity. Under zero field, the curve drops sharply with the onset temperature of 8.2 K and the transition width of 0.6 K. The onset temperature is slightly higher than that obtained from the magnetization measurement. In applied magnetic field, the curve shows the parallel shift to lower temperature, which is characteristic for the metallic superconductors. In Fig. 6 is given the onset temperature as a function of magnetic field. The curve shows a positive curvature very near T_c similar to the polycrystalline borocabides [12] and MgB_2 [11]. Except for this region, the curve is linear, whose gradient dH_{c2}/dT is -0.84 T/K. Linear extrapolation of the curve gives the upper critical field $H_{c2}(0)^{\mathrm{linear}}$ of 6.2 T. This is the upper limit for $H_{c2}(0)$, since the $H_{c2}(T) - T$ curve usually deviates from the linearity becoming parabolic at

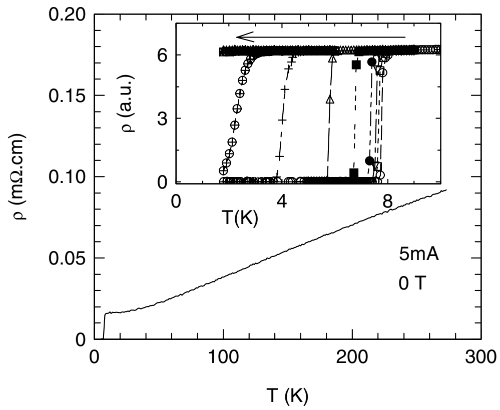

FIG. 5. Temperature-dependent resistivity measured for the Li_2Pd_3B bulk sample (a few mm size). The inset shows the resistivity transitions in applied magnetic fields H of 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, and 5 T (the arrow indicates the increase in H). The applied current was 5 mA for a 4-probe configuration.

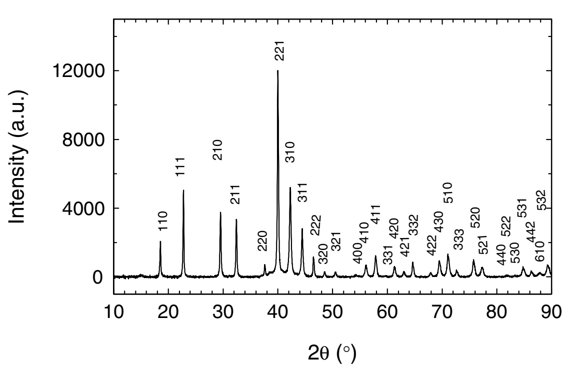

FIG. 4. XRD powder pattern of the Li_2Pd_3B sample synthesized by arc melting.

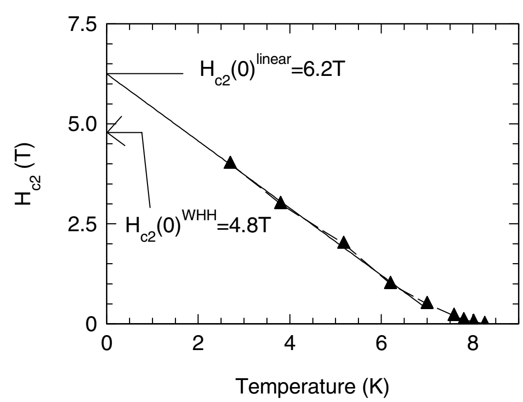

FIG. 6. $H_{c2}(T)$ plot defined by the onset temperature of the resistive transition measured in magnetic fields for the Li_2Pd_3B sample.

lower temperatures (see, e.g., [13]). By applying the Werthamer-Helfand-Hohenberg approximation of $H_{c2}(0)^{\mathrm{WHH}} = 0.691 \times H_{c2}(0)^{\mathrm{linear}}$ [14], $H_{c2}(0)^{\mathrm{WHH}}$ is estimated to be 4.8 T.

In summary, we found that the cubic Li_2Pd_3B compound is a superconductor with a critical temperature of about 8 K and an upper critical field $H_{c2}(0)^{\mathrm{WHH}}$ of 4.8 T. The compound prepared by arc melting has a uniform structure and high density, and is relatively stable in the air. This is the first observation of superconductivity in cubic, ternary metal-rich borides composed of alkaline metal, platinum group element, and boron. It also shows unique structural characteristics; in particular, the presence of the distorted octahedral units arranged in a 3D network is noteworthy. The result is expected to provide new directions for searching new types of boride or, more general, of new superconductors, as well as for understanding and improvement of the present ones.

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