Superconducting Properties of Noncentrosymmetric Li$_2$(Pt$_{1-x}$Pd$_x$)$_3$B Superconductors

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Abstract. Superconductivity has been found in two Li-containing compounds, Li$_3$PtB and Li$_3$PdB, which show superconducting transition at temperatures 2.5 K and 7.2 K, respectively, and have the same cubic structure ($P4_{3}32$) without mirror or inversion symmetry. Because the compounds are noncentrosymmetric, it is interesting to study the symmetries of the superconducting gap function and Cooper pairs. The specific heat of Li$_2$(Pt$_{1-x}$Pd$_x$)$_3$B ($x$ = 0, 0.5, 1) was measured. The Pd-concentration ($x$)-dependent electronic specific heat ($C_{es}$) of Li$_2$(Pt$_{1-x}$Pd$_x$)$_3$B at low temperatures $<<T_c$ showed distinctly different features on varying $x$. The temperature dependence of $C_{es}$ for one end member, Li$_2$PdB, follows an exponential behavior as in conventional superconductors, while those of Li$_2$Pd$_{1.5}$Pt$_{1.5}$B and Li$_2$Pt$_3$B follow a quadratic one, suggesting the existence of line nodes in the superconducting gap. This contrasting result conceivably originates from the difference in the strengths of the spin-orbit coupling of the Pt- and Pd-based compounds.

1. Introduction

The discovery of and research into new metal boride superconductors have been encouraged since the discovery of MgB$_2$. Some electronic band structure calculations suggest that higher superconducting transitions are possible in materials composed of light elements. For example, LiB$_2$, BeB$_2$ [1], and LiBC [2] are the first natural candidates since lighter atoms may help in providing larger phonon frequencies. They have been investigated experimentally and theoretically, but extensive research into these new materials with light elements has not produced positive results. However, some new superconductors have been found in recent years, including MgNi$_3$ ($T_c = 7.6$ K) [1], Y$_2$C$_3$ ($T_c = 18$ K) [2], W$_5$Re$_{13}$X ($X$=B, $T_c = 7.1$ K and X=C, $T_c = 7.3$ K) [3], La$_3$Pd$_4$Ge$_4$ ($T_c = 2.75$ K) [4], and B-doped diamond ($T_c = 4$ K) [5].

We have long been interested in multinary borides such as RRh$_3$B$_4$, RM$_3$B, and RNi$_3$B$_2$C (R=Y, Lanthanoid Elements, M=Rh, Pd, Pt), which show rich and interesting phenomena arising out of the competition between superconductivity and magnetism at low temperatures. In the recent years, we have also been searching for new superconducting materials containing lithium and boron that lead to the discovery of superconductivity in Li$_3$Pt$_3$B and Li$_2$Pd$_3$B at around 2.5 K and 7.2 K, respectively [6,7]. These superconductors crystallize in a cubic structure with a space group of $P4_{3}32$ that lacks both mirror and inversion symmetry-operations. In particular, the Pt and Pd atoms are situated in...
noncentrosymmetric sites. Since these compounds are non-magnetic, they may be ideal for studying the influence of this type of broken symmetry, in contrast to a novel heavy fermion (magnetic) superconductor CePt$_3$Si [8] that lacks a mirror symmetry only along the c-axis. The higher atomic numbers of Pt(Z$_{Pt}$) and Pd(Z$_{Pd}$), together with their ratio (Z$_{Pt}$/Z$_{Pd}$)$^{2-3}$, emphasize the importance of spin-orbit coupling (SOC), which, as evident, is much stronger for the Pt-based compound than its Pd-based isomorph. According to the results of a penetration depth study by H. Q. Yuan et al. [9] and NMR measurements by M. Nishiyama et al. [10,11], Li$_3$Pd$_3$B behaves as a full-gap superconductor, while Li$_3$Pt$_3$B has line nodes in the energy gap. In this study, we have investigated the symmetry of the superconducting gap function in Li$_2$(Pt$_{1-x}$Pd$_x$)$_3$B $[x = 0, 0.5, 1]$ by using specific-heat measurements.

2. Experimental

Samples of Li$_2$(Pt$_{1-x}$Pd$_x$)$_3$B $[x = 0, 0.5, 1]$ were prepared from an Li lump (Kanto Kagaku Co., above 99%), Pd plate (Rare Metallic Co., 99.95%), Pt wire (Furuya Metal Co., 99.99%), and B flake (Rare Metallic Co., 99.8%). Initially, stoichiometric ratios of Pt/Pd and B were melted together by an arc-furnace in a pure argon atmosphere. Then the ingot of (Pt/Pd)$_3$B and the lump of Li with a 15% excess were melted together to produce stoichiometric Li$_3$(Pt/Pd)$_3$B. The internal textures of the reacted materials were observed using a scanning electron microscope (SEM, JEOL JSM-6301F). The microstructural observation was carried out for powdered samples using transmission electron microscopy (TEM, JEOL FX-2000). X-ray powder diffraction (XPD) analyses were performed using a diffractometer equipped with a rotating anode and a graphite monochrometer (JEOL JDX-3500). The composition of Li$_2$Pt/PdB was determined by chemical analysis using the induced coupled plasma (ICP) method. The magnetic properties were measured using a SQUID magnetometer (MPMS-XL, Quantum Design Co., Ltd.). Polycrystalline samples of Li$_2$PtB, Li$_2$Pd$_3$Pd$_{1.5}$B and Li$_2$Pd$_3$B were cut into rectangular shapes with dimensions of approximately 1.7 $\times$ 3.0 $\times$ 0.4 mm$^3$. Their resistivity was measured by a conventional four-probe method using the MPMS-XL system between 1.8 K and room temperature. The lower temperature dependence of the resistivity was implemented using $^3$He cryostat set-ups operating within the range of 0.4 K to 20 K, up to 50 kOe. The four samples of Li$_2$PtB (#1, #2), Li$_2$Pt$_{1.5}$Pd$_{1.5}$B, and Li$_2$Pd$_3$B with weights of 9.1 (#1), 4.4 (#2), 6.5, and 11.1 mg, respectively, were used for the specific-heat measurements using a relaxation-type calorimeter (Oxford Instruments) operated with a $^3$He refrigerator in the range of 0.4 K to 15 K. The samples were kept in a vacuum or argon gas atmosphere for storage and handling.

3. Results and discussion

The temperature dependence of the resistivity of Li$_3$(Pt$_{1-x}$Pd$_x$)$_3$B $[x = 0, 0.5, 1]$ was measured in magnetic fields up to 50 kOe. The upper critical field $H_{c2}(T)$ vs. temperature is shown in Fig. 1, and three of the $H_{c2}(T)$ curves of $x = 0, 0.5,$ and 1 were well fitted by the Werthamer-Helfand-Hohenberg (WHH) formula $H_{c2}(0) = 0.691 \times (dH_{c2}/dT)_{T_c} \times T_c$. Consequently, $H_{c2}(0)$ was estimated to be 19, 25, and 45 kOe for Li$_3$(Pt$_{1-x}$Pd$_x$)$_3$B $[x = 0, 0.5,$ and 1], respectively. According to the Ginzburg-Landau (G-L) theory, $H_{c2}$ near $T_c$ is given by the following equation:

\[ H_{c2}(T) = H_{c2}(0) - T \frac{dH_{c2}(T)}{dT} \]

Fig. 1 Upper critical field $H_{c2}$ vs temperature and $H_{c2}(0)$ estimated by the WHH fitting formula for the studied three compositions are shown.
\[ H_{c2}(T) = \frac{\Phi_0}{2\pi^2\xi^2} = \frac{\Phi_0}{2\pi^2\xi^2(0)}(1 - \frac{T}{T_c}), \]  

\( \Phi_0 \) : the fluxoid quantum, \( \xi \) : the G-L coherence length, and \( T_c \) : the superconducting transition temperature. The coherent length \( \xi(0) \) was calculated to be 11.8, 9.9 and 7.6 nm, respectively.

The bulk superconducting transitions were observed at 2.5 K, 3.9 K, and 7.2 K for Li\(_2\)(Pt\(_{1-x}\)Pd\(_x\))\(_3\)B \( [x = 0, 0.5, \text{and} 1, \text{respectively}] \) by the zero field specific-heat measurements. They were completely suppressed at the magnetic fields of 15, 30, and 50 kOe, respectively. These specific-heat temperatures \( C \) are the sum of an electron contribution \( (C_e) \) and a lattice contribution \( (C_l) \). \( C_l \) is described by \( \beta T^3 + \delta T^5 + \epsilon T^7 \) in the harmonic-lattice approximation for an adequate fit. In the normal state, \( C_e \) is described by the Sommerfeld term of \( \gamma_n T \), where \( \gamma_n \) is proportional to the electron density of states. Estimates of \( \gamma_n = 9.6, 9.7, \text{and} 9.8 \text{ mJmol}^{-1}\text{K}^{-2} \) and \( \beta = 0.80, 0.81, \text{and} 0.90 \text{ mJmol}^{-1}\text{K}^{-4} \) for \( x = 0, 0.5, \text{and} 1, \text{respectively} \), were obtained from the normal state data at the magnetic fields described above with fitting at temperatures below 2.5 K, 3.9 K, and 7.2 K, respectively.

The electronic specific heat within the superconducting phase \( (C_{es}) \) at low temperatures is calculated by subtracting \( C_l \) from \( C \). The \( C_{es}/\gamma_n T_c \) of the three compounds is shown in Fig. 2 as a semilogarithmic plot with \( T_c/T \). To evaluate the superconducting gap function in these compounds, \( C_{es} \) was analyzed by exponential and quadratic fittings in the low temperature range below \( T_c/3 \) \( (T_c/T > 3) \). The plot (c) of \( C_{es}/\gamma_n T_c \) in Li\(_2\)Pd\(_3\)B follows an exponential, activated process, but the fitting is not good at \( C_{es}/\gamma_n T_c \) lower than 0.01. However, any quadratic fitting is impossible. Li\(_2\)Pd\(_3\)B is estimated to be a conventional BCS superconductor with a fully opened isotropic gap. On the other hand, from the electronic specific heat of Li\(_2\)Pt\(_3\)B in (a), it is not clear if it follows an exponential or a quadratic behavior in a low temperature range below \( T_c/3 \). However, the exponential fitting formula is very different from the calculations of the BCS theory, \( C_{es}/\gamma_n T_c = 8.5 \exp (-1.44 T_c/T) \) for \( 2.5 < T_c/T < 6 \) [12]. This result suggests that Li\(_2\)Pt\(_3\)B is an unconventional superconductor, consistent with independent experiments of the penetration depth study [9] and the NMR.

**Fig. 2 Reduced electronic specific heat \( C_{es}/\gamma_n T_c \) vs. \( T_c/T \) of Li\(_2\)(Pt\(_{1-x}\)Pd\(_x\))\(_3\)B \( [x = 0, 0.5, 1] \). The broken and solid lines are the calculated curves fitted by the exponential and quadratic formulas, respectively.**
measurements [11]. In the case of Li2Pt1.5Pd1.5B in plot (b), surprisingly, the 50% Pd-diluted solid-solution still shows the same behavior of the electronic specific heat as that in Li2Pt3B.

In the discussion above, $C$ is assumed to be the sum of $C_{es}$ and $C_{I}$ in the superconducting state. However, in a number of superconductors, notably heavy-fermion compounds and high-$T_C$ cuprates, the total specific heat ($C$) possibly includes an additional sample-dependent, $T$-proportional contribution, which is probably associated, at least in part, with residual normal material. Its origin is not entirely clear, however. The specific heat of another Li2Pt3B sample (#2) with a different $T_C$ (2.6 K) and transition width was also measured, and the $C_{es}$ was calculated. The low-temperature behaviors of $C_{es}$ in the two samples coincide in the temperature range of $T_c/T > 3$ even though their $T_c$'s are different, which supports the notion that the $C_{es}$ of Li2Pt3B shown in Fig. 2 is sample-independent.

In summary, we have investigated the low-temperature specific heat of Li2(Pt1-xPdx)3B [x = 0, 0.5, 1]. The electronic specific heat ($C_{es}$) in the superconducting state behaves as a BCS-type conventional superconductor for Li2Pt3B but not for Li2Pt1.5Pd1.5B and Li2Pd3B. The physical parameters for the superconductivity in Li2(Pd1-xPtx)3B [x = 0, 0.5, and 1] are listed in Table 1 below.

### Table 1. Normal and superconducting parameters of Li2(Pt1-xPdx)3B [x=0, 0.5, and 1].

| Compound | $T_c$ [K] | $\gamma$ [mJ/mol K$^2$] | $\theta_D$ [K] | $\Delta C/\gamma T_c$ [KJ/mol K$^2$] | $H_{c2}(0)$ [kOe] | $\xi(0)$ [nm] |
|----------|----------|--------------------------|----------------|---------------------------------|-----------------|-------------|
| Li2Pt3B  | 2.6      | 9.6                      | 240            | 0.75                            | 19              | 11.8        |
| Li2Pt1.5Pd1.5B | 3.9    | 9.7                      | 242            | 1.1                             | 25              | 9.9         |
| Li2Pd3B  | 7.2      | 9.5                      | 228            | 1.7                             | 45              | 7.6         |

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