Non-magnetic impurity and defect doping in superconductors
Li$_2$Pd$_3$B with noncentrosymmetric crystal structures

G Bao$^{1}$, Y Inada$^{1,2,*}$, S Harada$^{1}$ and G-q Zheng$^{1}$

$^1$Department of Physics, Okayama University, Okayama 700-8530,
$^2$Graduate School of Education, Okayama University, Okayama 700-8530

E-mail: y-inada@okayama-u.ac.jp

Abstract. The spin singlet and spin triplet superconducting states can coexist in noncentrosymmetric crystal structures like Li$_2$T$_3$B (T: Pd, Pt), while it is prohibited in ordinary crystal structures. In this study, we focused our research on non-magnetic impurity effect in Li$_2$Pd$_3$B. The nature of the pair breaking by non-magnetic impurity in the parity mixing superconducting state is still unclear. We investigated the effect of non-magnetic impurity on $s$-wave dominant parity mixing superconductor Li$_2$Pd$_3$B by substituting B with Al. In this substitution process, we controlled the quality of the samples and showed their quality deteriorations through the measurement of residual resistivity at $T_c$. Furthermore, we checked the relations of residual resistivity and $T_c$ as well as its superconducting phase diagram. Our results showed that $s$-wave dominant parity mixing superconductor Li$_2$Pd$_3$B exhibits the small $T_c$ suppression attributed by the non-magnetic impurities and defects, while the $H_{c2}$ value clearly increased about 1.5 times in the poor quality samples. Such behaviours are similarly observed in ordinary $s$-wave superconductors.

1. Introduction
The superconductors with noncentrosymmetric crystal structures has been a hot topic in condensed matter physics. In ordinary centrosymmetric crystal structures, Cooper-pair symmetry was classified into either spin singlet or spin triplet state, however, the broken inversion symmetry in the crystal causes finite antisymmetric spin orbit coupling (ASOC) [1-3], which causes the parity mixing. The first discovery of noncentrosymmetric heavy fermion unconventional superconductor CePt$_3$Si [4] opened the new physics in superconductivity.

Li$_2$Pd$_3$B and Li$_2$Pt$_3$B crystallize with same noncentrosymmetric crystal structures ($P4_332$ in space group [5]). They have attracted much attention because they exhibit completely different superconducting properties [6-10]. Previous studies of NMR [8] and penetration depth measurements [9] suggested that Li$_2$Pt$_3$B is a spin triplet dominant superconductor with the ratio of singlet to triplet order parameter of 0.6, with the inclusion of sufficiently large amount of spin-singlet order parameter components, while Li$_2$Pd$_3$B is an $s$-wave spin singlet dominant superconductor with the ratio of 4. We expect they are candidate to study the purity mixing superconductors. Furthermore, no strong electron correlation is observed in Li$_2$Pd$_3$B and Li$_2$Pt$_3$B, as contrasted with CePt$_3$Si. CePt$_3$Si has a tetragonal crystal structure with no inversion center due to the lack of the mirror plane perpendicular to the only

* To whom any correspondence should be addressed.
one axis (c-axis), while Li$_2$T$_3$B (T: Pd, Pt) is in a cubic structure composed of distorted octahedral units of BP$_6$ or BP$_{d6}$. There is no mirror plane in all directions and no inversion center. These differences may be important in the discussion of superconductivity in nonentrosymmetric crystal structures with ASOC without strong electron correlation.

It is known that $s$-wave superconductor is not affected by non-magnetic impurity and defects doping in contrast to that of a non $s$-wave superconductor. It is caused by the sign inversion of the order parameter on the Fermi surface, although the nature of the pair breaking by non-magnetic impurity in the parity mixing superconducting state is still unclear. We expect that parity mixing ratio can be controlled by non-magnetic impurity effect. At this point, we investigate that the non-magnetic impurity and defect doping effect in Li$_2$T$_3$B (T: Pd, Pt). In this paper, our experimental results are presented in detail on the spin-singlet dominant superconductor of Li$_2$Pd$_3$B. We prepared the different quality samples by substituting B with Al, and the sample quality is checked by the residual resistivity.

2. Experimental Details
Polycrystalline samples of Li$_2$Pd$_3$(B$_{1-x}$Al$_x$) were prepared by two-step arc melting method [6]. In the first step, Pd$_3$(B$_{1-x}$Al$_x$) was synthesized by using Pd (99.95%), B (99.5%), Al (99.999%). In the second step, excess Li (99.9%) by 10% was added to Pd$_3$(B$_{1-x}$Al$_x$) alloys. The powder XRD measurements showed that there was no other phase in all samples. Measurements of electrical resistivity vs. temperature have been done by standard four-probe method under magnetic fields by using the PPMS (Quantum Design). Temperature dependence of magnetization was measured by the MPMS (Quantum Design). All samples showed more than 90% of the perfect shielding effect and the bulk superconductivity.

3. Results and Discussion
Figure 1(a) shows the temperature dependence of the electrical resistivity in the four different quality samples of Li$_2$Pd$_3$(B$_{1-x}$Al$_x$). Sharp transitions and clear zero resistivity are observed. The aluminum content of this samples are $x = 0$ (#4), 0.01 (#2), 0.05 (#1), 0.1 (#3), respectively. Their quality deteriorations are shown through the measurement of residual resistivity (RR). The #1 with smallest RR is expected to include the least impurities and defects. Contrary to expectations, The #4 (no aluminum content) does not show the smallest RR. In synthesis process of these compounds, sufficient repetitional melting process is difficult to prevent Li loss, so it is difficult to control the homogeneity of samples. It is probably a reason why the #4 does not show the smallest RR, although the sample qualities (non-magnetic impurities and defects) can be estimated by the residual resistivity. The critical temperatures $T_c$ were determined at the mid point between normal and zero resistivity. Figure 1(b) shows the $T_c$ values plotted against the RR. Small $T_c$ suppression was observed by non-magnetic impurities and defects. This is similar behaviour in ordinary $s$-wave superconducting state.

Figure 2(a) shows the temperature dependence of the upper critical field $H_{c2}(T)$ in four samples. The values of $T_c$ are almost same (10% reduction in worse sample #4), while the $H_{c2}(0)$ value clearly increased about 1.5 times in worse sample #4. This is similar behaviour in ordinary $s$-wave superconducting state explained by nonlocal generalization of the London equation introduced by Pippard [11]. The coherence length $\xi_0$ in the presence of scattering were assumed to be related to that of pure material $\xi_0$ by

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\alpha l},$$

where $l$ is the mean free path and $\alpha$ is a numerical constant. From the relation of $H_{c2}(0) = \phi_0/2\pi\xi^2$ ($\phi_0 = h/2e$ is the quantum fluxoid), we can expect $H_{c2}(0)$ to increase when $l$ becomes short.
Figure 1. (a) Temperature dependence of resistivity in the four different quality samples, and (b) the critical temperature $T_c$ plotted against the RR. The aluminum content of this samples are $x = 0$ (#4), 0.01 (#2), 0.05 (#1), 0.1 (#3), respectively. It is expected that the #1 will contain the least defects and impurities meanwhile, the #4 will contain the larger defects. Small $T_c$ suppression is observed.

Figure 2. (a) H-T phase diagram of the four different quality samples, and (b) $1/\xi$ and the mean free path $l$ plotted against residual resistivity (RR) in the four different quality samples. The $\xi_0$ represents the coherence length in pure material, which is estimated from Eq.(1). The mean free path $l$ is obtained from Eq.(2). The $H_{c2}(0)$ value clearly increased about 1.5 times in worse sample #4.

We can estimate the coherence length of $\xi_0$ in an ideally pure material from Fig.2 (b) under the assumption of $(\alpha l)^{-1} \propto \rho_{RR}$. The value of $\xi_0^{-1}$ is obtained from the y-intercept of the $1/\xi$ vs. $\rho_{RR}$ graph in Fig.2 (b). The estimated value of $\xi_0$ is 11.6 nm. The mean free path $l$ is obtained from

$$l = 1.00965 \times 10^{-21} (\xi_0 T_c \rho_{RR})^{-1}$$

(2) [12],

where $\xi_0$ is the BCS coherence length of $1.16 \times 10^{-10}$ m as mentioned above, $\gamma$ is the electronic
specific heat coefficient of $1.94 \times 10^{2} \text{Jm}^{-3}\text{K}^{-2}$ in Li$_2$Pd$_3$B [10]. The values of $T_c$ (K) and $\rho_{\text{RR}}$ (\Omega m) are critical temperature and residual resistivity in four different samples, respectively. The values of $\xi_0$ are plotted in Fig.2(b). The values of $\xi$ are 11.0 nm (#1), 9.2 nm (#2), 8.2 nm (#3) and 7.7 nm (#4), respectively. The values of $l$ are 63.7 nm (#1), 16.2 nm (#2), 8.9 nm (#3) and 8.4 nm (#4), respectively. As the sample quality deteriorates, the mean free path $l$ and $\xi$ shortens. In this system, superconductivity is gradually deviating from the clean limit condition in the poor quality sample (#3 or #4).

The $\alpha$ in Eq.(1) is a numerical constant of order unity in ordinary superconductors. In our results, the value of $\alpha$ is about 0.3, and it is smaller compared to the experimental value of $\text{tin}$, which is 0.8 [11]. The small value of $\alpha$ brings differences between the values of $\xi$ and $\xi_0$ (pure material) regardless of the enlargement of the value of $l$. The small $\alpha$ may be attributed by ASOC.

4. Conclusion

Our results showed that s-wave dominant parity mixing superconductor Li$_2$Pd$_3$B exhibits the small $T_c$ suppression attributed by the non-magnetic impurities and defects, while the $H_c$ value clearly increased about 1.5 times in the poor quality samples. They are similar behaviour of ordinary s-wave superconductor. The $\xi_0$ (a coherence length in an ideal pure sample) was estimated in Li$_2$Pd$_3$B at 11.6 nm.

Li$_2$Pt$_3$B is a spin-triplet dominant superconductor with the inclusion of sufficiently large amount of spin-singlet order parameter components. It is interesting how non-magnetic impurity influences superconducting nature of the material. It is expected that non-magnetic impurities have the ability to selectively influence the spin-triplet order parameter components in the parity mixing superconducting state.

This work was supported by the "Topological Quantum Phenomena" (No. 22103004) Grant-in-Aid for Scientific Research on Innovative Areas from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References

[1] Dresselhaus G 1955 Phys. Rev. Lett. 100 580
[2] Rashba E and Tverd Fiz (Leiningrad) Tela, 1959 Sov. Phys. Solid State 1 368
[3] Gorkvand L P and Rashba E I, 2001 Phys. Rev. Lett. 87 037004
[4] Bauer E, Hilscher G, Michor H, Paul Ch, Scheidt E W, Grivanov A, Seropegin Y, Noel H, Sigrist M, and Rogl P, 2004 Phys. Rev. Lett. 92 027003
[5] Eibenstein U and Jung W J 1997 Solid State Chem. 133 21
[6] Badica P, Kondo T, Orimo and Togano K 2005 J. Phys. Soc. Jpn. 74 1014-1019
[7] Nshiyama M, Inada Y and Zheng Guo-qing 2005 Phys.Rev. B 71, 220505
[8] Nshiyama M, Inada Y and Zheng Guo-qing 2007 Phys. Rev. Lett. 98, 047002
[9] Yuan H Q, Agterberg D F, Hayashi N, Badica P, Vadervelde D, Togano K, Sigrist K and Salmon M B 2006 Phys. Rev. Lett. 97 017006
[10] H. Takeya, M. ElMassalami, S. Kasahara and K. Hirata, 2007 Phys. Rev. B 76, 104506.
[11] Pippad A B, 1953 Proceedings the Royal Society A. 216 547-568
[12] e.g., the appendix in T. P. Orlando et.al., 1979 Phys.Rev.B19 4545