Superconductivity in La$_3$Pt$_4$

Yuki Kawashima*, Gaku Eguchi, Shingo Yonezawa, and Yoshiteru Maeno

Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502

KEYWORDS: superconductivity, La$_3$Pt$_4$

We found superconductivity of intermetallic La$_3$Pt$_4$ below 0.51 K, while searching for the Pt-substituted material of the noncentrosymmetric (NCS) superconductor LaNiC$_2$ ($T_c = 2.7$ K$^{1,2}$).

Superconductors with NCS crystal structures, which do not have spatial inversion symmetry, have been attracting much attention since the discovery of the absence of the Pauli limiting field in CePt$_3$Si.$^3$ Recently, some interesting superconducting properties were reported in LaNiC$_2$.\(^1\) This compound crystallizes in the CeNiC$_2$-type orthorhombic structure (space group Amm2), which lacks the inversion symmetry along the $c$-axis (see Fig. 1). A recent muon spin relaxation ($\mu$SR) result suggests unconventional superconductivity.$^4$ On the other hand, first-principle calculations for this material suggested that it is likely to be a conventional superconductor judging from its $s$-orbital-dominant electronic states near the Fermi energy.$^5$ Further confirmation of unconventional properties is needed for this material.

In NCS superconductors, antisymmetric spin-orbit interaction (ASOI) due to the absence of spatial inversion symmetry may lead to a spin singlet-triplet mixed superconducting state. A number of unconventional superconducting properties are predicted, but most of them are yet to be observed.$^6$ Since stronger ASOI is considered essential for the emergence of the unconventional superconducting properties, it is desirable to investigate NCS superconductivity in compounds containing heavy elements. For LaNiC$_2$, replacements of Ni with heavier elements such as Pd or Pt seem favorable to realize large ASOI.

We tried to synthesize La$M$C$_2$ ($M = \text{Ni, Pd, Pt}$) samples using the arc melting method. The starting materials were La (purity 99.9%), Ni (99.999%), C (99.999%), Pd (99.95%), and Pt (99.98%). These materials were melted in argon with the stoichiometric ratio of La:$M$:$C = 1:1:2$. Powder X-Ray diffraction (XRD) measurements (Bruker AXS, D8 ADVANCE) were

*E-mail address: kawashima@scphys.kyoto-u.ac.jp
carried out (Fig. 1). As represented in Fig. 1, the samples for \( M = \text{Ni} \) are almost single-phase LaNiC\(_2\). The XRD patterns of La-Pd-C and La-Pt-C samples do not resemble that of LaNiC\(_2\). Further XRD analysis revealed that carbon remains unreacted in La-Pt-C samples, and that its main constituent is actually La\(_3\)Pt\(_4\), not “LaPtC\(_2\)”. La\(_3\)Pt\(_4\) crystallizes in the rhombohedral Pu\(_3\)Pd\(_4\)-type structure (space group \( \overline{R}3 \))\(^7\) see Fig. 1). Note that its crystal structure has inversion symmetry.

New samples were synthesized by arc melting from stoichiometric mixture of La:Pt = 3:4 for La\(_3\)Pt\(_4\). As presented in Fig. 1, the XRD pattern of a La\(_3\)Pt\(_4\) sample well agrees with that of La-Pt-C. The XRD indicates that its main phase is certainly La\(_3\)Pt\(_4\) although it contains a small amount (<20\%) of LaPt\(_2\) \((T_c = 0.46 \text{ K})\) impurity. Except for LaPt\(_2\), no impurity phases are detected in this sample. The lattice parameters of La\(_3\)Pt\(_4\) obtained using the Rietveld analysis were \( a = 13.8 \text{ Å}, c = 5.83 \text{ Å} \), which agree with the literature.\(^7\)

The AC susceptibility \( \chi_{AC} \) of the synthesized La-Pt-C sample and La\(_3\)Pt\(_4\) is presented in Fig. 2. The measurements were performed by a mutual-inductance technique with a home-built first-derivative coil, mounted in a commercial \(^{3}\)He refrigerator (Oxford Instruments, Heliox). For La\(_3\)Pt\(_4\), strong magnetic shielding indicating bulk superconductivity is observed below 0.51 K. Similar shielding signal is also observed in the La-Pt-C sample, indicating
Fig. 2. (Color online) Temperature dependence of the real and imaginary parts of the AC magnetic susceptibility $\chi_{AC}$ of the samples of La-Pt-C and $\text{La}_3\text{Pt}_4$ down to 0.3 K. The AC magnetic field $H_{AC}$ was $1 \mu$T-rms, and its frequency was 887 Hz for the La-Pt-C sample and 3011 Hz for the $\text{La}_3\text{Pt}_4$ sample.

that $\text{La}_3\text{Pt}_4$ is indeed the majority phase in this sample. In addition, weak magnetic shielding below 1.6 K is observed only in the La-Pt-C sample. The shielding is presumably a superconducting impurity phase, but the origin is unclear. Note that $\text{LaC}_2$ is known to exhibit superconductivity below 1.6 K, although the corresponding XRD peaks are not detected.

The resistivity of $\text{La}_3\text{Pt}_4$ under 0 T and 0.1 T is presented in Fig. 3(a). It was measured by a conventional DC four-probe technique with Heliox as well. The zero-resistivity temperature 0.5 K well agrees with the onset temperature of $\chi_{AC}$. The residual resistivity ratio $RRR \equiv \rho_{300K}/\rho_{1K}$ is approximately 30 (not shown) for the present polycrystalline samples.

The specific heat $c_p$ divided by temperature in several magnetic fields is presented in Fig. 3(b). The heat capacity was measured using a relaxation-time-method with a commercial apparatus (Quantum Design, PPMS) down to 0.35 K. The molar specific heat are evaluated assuming single-phase $\text{La}_3\text{Pt}_4$. The clear and large specific heat jump at 0.5 K in 0 T due to the transition indicates the bulk superconductivity.

Superconductivity is suppressed by a magnetic field of 0.1 T, as evidenced by both $\rho$ and $c_p/T$ measurements. The normal state $c_p/T$ is independent of the applied magnetic field within the experimental resolution. Thus $c_p/T$ at 0.1 T can be used to evaluate specific-heat coefficients: $c_p/T$ in the normal state is fitted by the relation $c_p/T = \gamma + \beta T^2$, where $\gamma$ and $\beta$ are the electronic and the phononic specific-heat coefficients, respectively. The value of $\gamma$ is evaluated to be 15.5 mJ/(f.u.mol·K$^2$). We also calculated $\gamma$ based on the first-principle calculation using the WIEN2k package$^{13}$ as 3.0 mJ/(f.u.mol·K$^2$). Thus, the electronic mass
Fig. 3. (Color online) (a) Temperature dependence of $\rho$ of $\text{La}_3\text{Pt}_4$ under 0 T and 0.1 T at low temperatures. (b) Temperature dependence of $c_p/T$ of $\text{La}_3\text{Pt}_4$ at low temperatures. The dotted line is a fit of $c_p/T = \gamma + \beta T^2$ to the normal state data up to 2.0 K. The obtained parameters are $\gamma = 15.5$ mJ/(f.u.mol·K$^2$) and $\beta = 2.40$ mJ/(f.u.mol·K$^4$). The curve based on the conventional BCS theory deduced from $\gamma$ and $T_c = 0.47$ K is also presented.$^{11}$ The inset shows the upper critical field $H_{c2}(T)$ determined from the onset $T_c$ of $c_p/T$ (red circles) and the resistive midpoint (blue stars). The dashed line is the WHH curve for $H_{c2}(T)$ in the dirty limit,$^{12}$ giving $\mu_0 H_{c2,WHH}^{\text{onset}}(0) = -0.693 T_c d(\mu_0 H_{c2})/dT)|_{T=T_c} = 11$ mT.

The specific-heat jump height $\Delta c_p$ divided by $\gamma T_c$ is smaller than that of the weak-coupling BCS theory: 1.43. The fact suggests existence of residual density of states that does not contribute to the superconductivity. The residual density of states is attributable to impurity phases that were detected in the X-ray spectrum in Fig. 1. Improvement of sample quality as well as measurements down to a lower-temperature region is necessary for further investigation.

The superconducting $H - T$ phase diagram based on the onset $T_c$ of $c_p/T$ and the resistive midpoint is presented in the inset of Fig. 3(b). The conventional Werthamer-Helfand-Hohenberg (WHH) curve$^{12}$ with the onset $T_c = 0.5$ K and the initial slope
\[ \frac{d(\mu_0 H_{c2})}{dT} \bigg|_{T=T_c} = 32 \text{ mT/K} \] is also shown. The WHH upper critical field is estimated to be 11 mT. From this value, we crudely estimate the zero-temperature GL coherence length \( \xi(0) \) as 170 nm, using the orbital depairing relation \( \mu_0 H_{c2}^{WHH}(0) = \Phi_0/[2\pi\xi^2(0)] \).

In summary, we found that centrosymmetric La\(_3\)Pt\(_4\) exhibits superconductivity below 0.51 K, while trying to synthesize LaPdC\(_2\) and LaPtC\(_2\) using arc melting.

**Acknowledgment**

We thank Y. Yamaoka, T. Iye, S. Kitagawa, K. Ishida, and H. Sawa for fruitful discussion. This work is supported by a Grant-in-Aid from the Global COE program “The Next Generation of Physics, Spun from Universality and Emergence” from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan, and by the “Topological Quantum Phenomena” Grant-in Aid for Scientific Research on innovative Areas from MEXT of Japan. G.E. is also supported by JSPS.
References

1) W. Lee, H. Zeng, Y. Yao, and Y. Chen: Physica C **266** (1996) 138.

2) V. K. Pecharsky, L. L. Miller, and K. A. Gschneidner: Phys. Rev. B **58** (1998) 497.

3) E. Bauer, G. Hilscher, H. Michor, C. Paul, E. W. Scheidt, A. Gribanov, Y. Seropegin, H. Noël, M. Sigrist, and P. Rogl: Phys. Rev. Lett. **92** (2004) 027003.

4) A. D. Hillier, J. Quintanilla, and R. Cywinski: Phys. Rev. Lett. **102** (2009) 117007.

5) A. Subedi and D. J. Singh: Phys. Rev. B **80** (2009) 092506.

6) S. Fujimoto: J. Phys. Soc. Jpn. **76** (2007) 051008.

7) A. Palenzona: J. Less-Common Met. **53** (1977) 133.

8) T. H. Geballe, B. T. Matthias, V. B. Compton, E. Corenzwit, G. W. Hull, Jr., and L. D. Longinotti: Phys. Rev. **137** (1965) A119.

9) R. W. Green, E. O. Thorland, J. Croat, and S. Legvold: J. Appl. Phys. **40** (1969) 3161.

10) K. Momma and F. Izumi: J. Appl. Crystallogr. **44** (2011) 1272.

11) B. Mühlenschlegel: Z. Phys. **155** (1959) 313.

12) N. R. Werthamer, E. Helfand, and P. C. Hohenberg: Phys. Rev. **147** (1966) 295.

13) K. Schwarz and P. Blaha: Comput. Mater. Sci. **28** (2003) 259.