Superconducting Transition in the $\beta$-Pyrochlore AOs$_2$O$_6$ (A=Cs, Rb, K) under Pressure

Kiyotaka MIYOSHI, Yuta TAKAICHI, Yusuke TAKAMATSU, Motonobu MIURA and Jun TAKEUCHI

Department of Material Science, Shimane University, Matsue 690-8504

Pressure dependence of superconducting transition temperature $T_c$ has been determined through the DC magnetic measurements under pressure up to $P=10$ GPa for $\beta$-pyrochlore oxides AOs$_2$O$_6$ with $A$=Cs ($T_c$=3.3 K), Rb (6.3 K) and K (9.6 K). Both for $A$=Rb and Cs, $T_c$ increases with increasing $P$ and shows a saturation at $T_{cm}$$\sim$8.8 K, which is considered as the upper limit of $T_c$ inherent in AOs$_2$O$_6$. In contrast, the $T_c$–$P$ curve for KOs$_2$O$_6$ shows a sharp maximum of $\sim$10 K at $P$=0.5 GPa, and $T_c$ is higher than $T_{cm}$ for $0$$\leq$$P$$\leq$1.5 GPa, suggesting the enhanced superconductivity due to the rattling of K ions.

KEYWORDS: $\beta$-pyrochlore, high pressure, KOs$_2$O$_6$, RbOs$_2$O$_6$, CsOs$_2$O$_6$, superconductivity, DC magnetization, diamond anvil cell

In recent years, there has been a great deal of interest in pyrochlore or spinel oxides, in which a variety of remarkable low-temperature properties e.g., metal-insulator transition or superconducting transition, the exotic magnetic ground state such as spin ice, and heavy mass Fermi-liquid behavior have been found, exploring new types of electronic behavior on the geometrically frustrated lattice. Among these, the recent discovery of the $\beta$-pyrochlore superconductor AOs$_2$O$_6$ (A=Cs, Rb, K) and K$^{+}$ may stimulate renewed interest in superconductivity on geometrically frustrated structures, as in LiTi$_2$O$_4$, Cd$_2$Re$_2$O$_9$. Indeed, the superconductivity in AOs$_2$O$_6$ has been the subject of intensive research and several experiments suggest the conventional s-wave superconductivity.\(^{15-20}\)

One of the characteristic features of AOs$_2$O$_6$ is the anharmonic rattleing motion of A ions in an oversized cage of Os-O network,\(^{21}\) which has been experimentally inferred from the specific heat data showing the existence of low frequency Einstein mode contribution,\(^{22,23}\) and also demonstrated by the recent NMR experiments.\(^{24}\) Especially for KOs$_2$O$_6$, the superconducting transition at $T_c$=9.6 K is followed by a second transition concerning to the rattling freedom of K ion at $T_p$$\sim$7.5 K, and a field-independent specific heat anomaly of first order transition has been observed at $T_p$.\(^{25,26}\) The measurements of electrical resistivity $\rho$ as a function of temperature $T$ in high magnetic fields have revealed that $\rho(T)$ changes the curvature from a concave-downward one at high temperatures to a Fermi-liquid behavior $\rho(T)$=$AT^2$ below $T_p$, suggesting that the electron-rattling phonon scattering disappears below $T_p$.\(^{27,28}\) In RbOs$_2$O$_6$ and CsOs$_2$O$_6$, such a crossover of $\rho(T)$ has been observed at $T^*$$\sim$15 K and $\sim$20 K, respectively, suggesting that the rattling motion is frozen below $T^*$.\(^{28}\) Moreover, a strong coupling between the rattling motion of K ions and quasiparticles has been evidenced through the recent microwave penetration depth study, where it is suggested that the rattling phonons help to enhance superconductivity and K sites freeze to an ordered state below $T_p$.\(^{19}\) Also, the ordering of K ions at $T_p$ has been suggested from the theoretical side.\(^{29}\) Thus, there exists an intriguing possibility that novel superconductivity enhanced by the rattling phonons is realized between $T_p$ and $T_c$ in KOs$_2$O$_6$.

To gain more insight into the mechanism of the superconductivity in KOs$_2$O$_6$, it is important to clarify the intrinsic $T_c$ inherent in AOs$_2$O$_6$ by the application of physical pressure $P$, which elevates $T_c$ as expected from the relation between $T_c$ and lattice constant ranging from 10.099 Å ($A$=K) to 10.148 Å ($A$=Cs), and examine whether or not $T_c$ for KOs$_2$O$_6$ is really enhanced compared with that for other members. In this view, to establish the $T_c$–$P$ relations for AOs$_2$O$_6$ is of significant importance. In the present work, we have performed DC magnetization measurements for AOs$_2$O$_6$ ($A$=Cs, Rb, K) under high pressure up to $P=10$ GPa and determined the precise $T_c$–$P$ relations. It has been found that the $T_c$–$P$ curve both for A=Rb and Cs saturates at $T_{cm}$=8.8 K, which is thought of to be the upper limit of $T_c$ inherent in AOs$_2$O$_6$. On the other hand, $T_c$ for A=K is higher than $T_{cm}$=8.8 K for $0$$\leq$$P$$\leq$1.5 GPa, suggesting the enhanced superconductivity in KOs$_2$O$_6$.

The polycrystalline samples of AOs$_2$O$_6$ ($A$=Cs, Rb, K) used in this study were synthesized by the solid-state reaction technique similar to that described in the literatures.\(^{11,12,14}\) For the products, powder X-ray diffraction measurements were examined and most of the diffraction peaks were indexed as a pyrochlore structure with a lattice parameter consistent with earlier results.\(^{11,12,14}\) A small amount of OsO$_2$ was also detected as an impurity. $T_c$ at ambient pressure for all samples was confirmed to agree with literatures.\(^{11,12,14}\) For the magnetic measurements under high pressure up to 10 GPa, a miniature diamond anvil cell (DAC) with an outer diameter of 8 mm was used to generate high pressure and combined with a sample rod of a commercial SQUID magnetometer. The details of the DAC are given in elsewhere.\(^{30}\) The AOs$_2$O$_6$ sample was loaded into the gasket hole together with a small piece of high purity lead (Pb) to realize in situ observation of pressure by determining the pressure from the $T_c$ shift of Pb. Daphne oil 7373 was used as a pressure transmitting medium.
To investigate the $T_c$–$P$ relations, zero-field-cooled DC magnetization $M$ versus temperature data were collected at each pressure and the diamagnetic onset temperature was defined as $T_c$. For all samples, the $M$–$T$ curve at ambient pressure was confirmed to remain unchanged after pressure cycling. First, we show the $M$–$T$ curves for KOs$_2$O$_6$ under various pressures in Fig. 1. In the figure, the $M$–$T$ curve at ambient pressure exhibits a sudden decrease indicating the superconducting transition in KOs$_2$O$_6$ at $T_c$~9.6 K in addition to a sharp drop at ~7 K corresponding to the diamagnetic onset of Pb for the pressure calibration. Both of the $M$–$T$ curves at $P$=0.35 and 0.53 GPa shows a diamagnetic onset at $T_c$~10 K, higher than $T_c$ at ambient pressure. However, the $M$–$T$ curve at $P$=1.1 GPa indicates a lower $T_c$ of ~9.4 K, and $T_c$ appears to be systematically decreased as the pressure is increased as $P$≥0.53 GPa in Fig. 1. These results indicate that $T_c$ for KOs$_2$O$_6$ exhibits a maximum of ~10 K at $P$≥0.4~0.5 GPa, consistent with the results of the magnetic measurements under pressure $P$≤1.2 GPa by Muramatsu et al. The $M$–$T$ curves at $H$=20 Oe does not show an anomaly corresponding to the transition at $T_p$, different from those at $H$≥1 T.\textsuperscript{26,27}

Next, we show typical results of the $M$–$T$ measurements under pressure for RbOs$_2$O$_6$ and CsOs$_2$O$_6$ in Figs. 2 and 3, respectively. As seen in Fig. 2, the $M$–$T$ curve at $P$=0 GPa for RbOs$_2$O$_6$ exhibits a two-step decrease with decreasing temperature corresponding to the superconducting transition in Pb at ~7 K and RbOs$_2$O$_6$ at ~6.3 K. $T_c$ for RbOs$_2$O$_6$ shifts toward higher temperature side as increasing $P$ and reaches ~8.8 K at $P$=3.0 GPa. For the further increase of pressure, $T_c$ becomes pressure independent but appears to be decreased for $P$>4.7 GPa. For $P$≥4.7 GPa, the decreasing rate of $M$ below $T_c$ becomes smaller, suggesting that the superconducting transition is more gradual in connection with the decrease of $T_c$. On the other hand, the superconducting transition for CsOs$_2$O$_6$ is almost overlapped with that for Pb at $P$=2.7 GPa in Fig. 3. In the figure, $T_c$ appears to be monotonically increased by the application of pressure and is achieved to ~8.8 K at $P$=6.2 GPa but appears to be independent of pressure for 6.2 GPa<$P$<8.2 GPa. Since the diamagnetic onset was unclear due to the broadening of the superconducting transition for $P$>8.2 GPa, it is uncertain whether or not $T_c$ for CsOs$_2$O$_6$ is lowered from ~8.8 K under high pressure as in RbOs$_2$O$_6$.

In Fig. 4(a), $T_c$ versus pressure data for AOs$_2$O$_6$ are summarized. In the figure, the $T_c$–$P$ curve for RbOs$_2$O$_6$ displays a monotonic increase for $P$<3 GPa and a plateau between $P$~3 GPa and 5 GPa. The $T_c$–$P$ curve for CsOs$_2$O$_6$ also shows a monotonic increase and a saturation for $P$>6 GPa. The $T_c$–$P$ curve both for A=Rb and Cs saturates at the same temperature $T_{cm}$=8.8 K. The increasing rate of the $T_c$–$P$ curve for $T_{cm}$<$T_c$ is 0.9~1.0 K/GPa for both materials. The shapes of the $T_c$–$P$ curves are similar to each other although a decrease from $T_{cm}$ at high pressure was not observed for CsOs$_2$O$_6$. In striking contrast, the $T_c$–$P$ curve for KOs$_2$O$_6$ exhibits a sharp maximum of ~10 K which is nearly 1 K higher than $T_{cm}$. The $T_c$–$P$ curves previously reported by Mu-
ramatsu et al. are also described in the figure for comparison. They have determined $T_c$ through the $\rho$–$T$ measurements for polycrystalline samples under pressure up to 10 GPa using a cubic anvil press except for $P\leq1.2$ GPa. They have adopted the diamagnetic onset of the $M$–$T$ curve as $T_c$ for $P\leq1.2$ GPa. For KOs$_6$, the $T_c$–$P$ curve coincides with that by Muramatsu et al. for $P<2$ GPa but not for $P>2$ GPa. The $T_c$–$P$ curve based on the $\rho$–$T$ measurements for RbOs$_2$O$_6$ (CsOs$_2$O$_6$) displays a broad maximum of $\sim8$ K at $P=2$ GPa ($\sim7.5$ K at $P=6$ GPa), different from that based on the $M$–$T$ measurements, but is coincident with each other for $P\leq2$ GPa ($P<4$ GPa). The inconsistency is mainly coming from the difficulty to determine $T_c$ from the $\rho$–$T$ curve, which shows a resistive drop over wide temperature range of $\Delta T=1$–5 K under high pressure. Muramatsu et al. has determined $T_c$ as the midpoint of the resistive drop. The onset of the resistive drop would be rather close to the diamagnetic onset in the present work.

As seen in Fig. 4(a), our magnetic measurements under pressure reveal the characteristic $T_c$–$P$ curves, although the evolution of the overall band structures for the physical compression is known to be rather small. Particularly for KOs$_6$, the $T_c$–$P$ curve takes a maximum of $\sim10$ K higher than those for other members ($T_{cm}=8.8$ K) indicating the enhanced superconductivity or the extension of the superconducting region in the $T$–$P$ phase diagram. An enhancement of superconductivity in KOs$_6$ is also suggested by Shimono et al. through the measurements of microwave surface impedance. They have shown that the temperature dependence of superfluid density exhibits a step-like change near $T_p$ and extrapolates to zero at $T_0=8.7$ K. $T_0$ is the effective $T_c$ estimated from the behavior below $T_p$ where the rattling motion freezes, and $T_c(=9.6$ K) is surely higher than $T_0$, suggesting the enhanced superconductivity and the importance of the rattling motion for the enhancement. In a similar context, the recent Hall-sensor magnetometry has revealed that the lower critical field versus temperature data below $T_p$ extrapolates to zero at 9.2 K, lower than $T_c$, suggesting that the superconducting gap is reduced below $T_p$. Indeed, $T_0(=8.7$ K) is considered as the original $T_c$ in the absence of the rattling of K ions, and is in good agreement with the upper limit of $T_c$ for A=Rb and Cs ($T_{cm}=8.8$ K) inferred from the saturation of the $T_c$–$P$ curve. This suggests that the upper limit
of \( T_c \) is basically \( T_{cm}=8.8 \) K in AOs\(_2\)O\(_6\) superconductor but \( T_c \) for KO\(_2\)O\(_6\) is markedly enhanced from the upper limit probably due to the rattling motion of K ions. It is expected that, in case of the absence of the rattling motion in KO\(_2\)O\(_6\), the maximum of \( T_c \) would be limited to 8.8 K, and then a plateau of the \( T_c-P \) curve would be realized for \( 0\leq P \leq 1.5 \) GPa.

In Fig. 4(b), \( T_c \) versus unit cell volume \( V \) data are plotted. We obtained the \( T_c-V \) data by transforming the \( T_c-P \) data using the relation \( \Delta V/V_0=-\alpha P+\beta P^2 \), where \( \alpha=0.00726 \) (GPa\(^{-1}\)) and \( \beta=0 \) for KO\(_2\)O\(_6\), \( \alpha=0.00777 \) (GPa\(^{-1}\)) and \( \beta=0 \) for RbO\(_2\)O\(_6\), and \( \alpha=0.00756 \) (GPa\(^{-1}\)) and \( \beta=0.000198 \) (GPa\(^{-2}\)) for CsO\(_2\)O\(_6\). Since \( T_c \) systematically changes with A ion radius or lattice constant in AOs\(_2\)O\(_6\), one may expect that the \( T_c \) versus cell volume data for all members are interpolated by a universal curve indicating that \( T_c \) is determined by lattice constant independently on whether the lattice is compressed by chemical or physical pressure, such as the lattice constant \( \approx \) by a universal curve indicating that

Acknowledgements

This work is financially supported by a Grant-in-Aid for Scientific Research (No. 17740229) from the Japanese Ministry of Education, Culture, Sports, Science and Technology.

1) Y. Shimakawa, Y. Kubo and T. Manako: Nature 379 (1996) 53.
2) D. Mandrus, J. R. Thompson, R. Gaal, L. Forro, J. C. Bryan, B. C. Chakoumakos, L. M. Woods, B. C. Sales, R. S. Fishman and V. Keppens: Phys. Rev. B 63 (2001) 195104.
3) K. Miyoshi, T. Yamashita, K. Fujiwara and J. Takeuchi: J. Phys. Soc. Japan 72 (2003) 1855.
4) A. Yamamoto, P. A. Sharma, Y. Okamoto, A. Nakao, H. A. Katori, S. Niitaka, D. Hashizume and H. Takagi: J. Phys. Soc. Japan 76 (2007) 043703.
5) M. Hanawa, Y. Muraoka, T. Tayama, T. Sakakibara, J. Yamaura and Z. Hiroi: Phys. Rev. Lett. 87 (2001) 187001.
6) H. Sakai, K. Yoshimura, H. Ohno, H. Kato and S. Kambe, R. E. Walstedt, T. D. Matsuda, Y. Haga, Y. Onuki: J. Phys. Condens. Matter 13 (2001) L785.
7) D. C. Johnston: J. Low Temp. Phys. 25 (1976) 145.
8) M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske and K. W. Godfrey: Phys. Rev. Lett. 79 (1997) 2554.
9) S. T. Bramwell and M. J. P. Gingras: Science 294 (2001) 1495 and references therein.
10) S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem and J. D. Jorgensen: Phys. Rev. Lett. 78 (1997) 3729.
11) S. Yonezawa, Y. Muraoka and Z. Hiroi: J. Phys. Soc. Japan 73 (2004) 1655.
12) S. Yonezawa, Y. Muraoka, Y. Matsushita and Z. Hiroi: J. Phys. Soc. Japan 73 (2004) 819.
13) M. Brühwiler, S. M. Kazakov, N. D. Zhigadlo, J. Karpinski and B. Batlogg: Phys. Rev. B 70 (2004) 020503(R).
14) S. Yonezawa, Y. Muraoka, Y. Matsushita and Z. Hiroi: J. Phys. Condens. Matter 16 (2004) L9.
15) R. Khasanov, D. G. Eshchenko, J. Karpinski, S. M. Kazakov, N. D. Zhigadlo, R. Britsch, D. Gavillet, D. Di Castro, A. Shengelaya, F. La Mattina, A. Maisuradze, C. Baines and H. Keller: Phys. Rev. Lett. 93 (2004) 157004.
16) K. Magishi, J. L. Gavilano, B. Pedrini, J. Hinderer, M. Weller, B. H. Ott, S. M. Kazakov and J. Karpinski: Phys. Rev. B 71 (2005) 024524.
17) M. Brühwiler, S. M. Kazakov, J. Karpinski and B. Batlogg: Phys. Rev. B 71 (2005) 214517.
18) Y. Kasahara, Y. Shimono, T. Shibauchi, Y. Matsuda, S. Yonezawa, Y. Muraoka and Z. Hiroi: Phys. Rev. Lett. 96 (2006) 247004.
19) Y. Shimono, T. Shibauchi, Y. Kasahara, T. Kato, K. Hashimoto, Y. Matsuda, J. Yamaura, Y. Nagao and Z. Hiroi: Phys. Rev. Lett. 98 (2007) 257004.
20) T. Shimojima, Y. Shibata, K. Ishitake, T. Kus, A. Chainani, T. Yokoya, T. Togashi, X.-Y. Wang, C. T. Chen, S. Watanabe, J. Yamaura, S. Yonezawa, Y. Muraoka, Z. Hiroi, T. Saitoh and S. Shin: Phys. Rev. Lett. 99 (2007) 117003.
21) J. Kuneš, T. Jeong and W. E. Pickett: Phys. Rev. B 70 (2004) 174510.
22) Z. Hiroi, S. Yonezawa, T. Muramatsu, J. Yamaura and Y. Muraoka: J. Phys. Soc. Japan 74 (2005) 1255.
23) M. Brühwiler, S. M. Kazakov, J. Karpinski and B. Batlogg: Phys. Rev. B 73 (2006) 094518.
24) M. Yoshida, K. Arai, R. Kaido, M. Takigawa, S. Yonezawa, Y. Muraoka and Z. Hiroi: Phys. Rev. Lett. 98 (2007) 197002.
25) Z. Hiroi, S. Yonezawa, J. Yamaura, T. Muramatsu and Y. Muraoka: J. Phys. Soc. Japan 74 (2005) 1682.
26) Z. Hiroi, S. Yonezawa and J. Yamaura: J. Phys. Condens. Matter 19 (2007) 145283.
27) Z. Hiroi, S. Yonezawa, Y. Nagao and J. Yamaura: Phys. Rev. B 76 (2007) 014523.
28) Z. Hiroi, J. Yamaura, S. Yonezawa and H. Harima: Physica C 460-462 (2007) 20.
29) J. Kuneš and W. E. Pickett: Phys. Rev. B 74 (2006) 0940302.
30) M. Mitroy, M. Hitaka, T. Kawae, K. Takeda, T. Kitai and N. Toyoshima: Jpn. J. Appl. Phys. 40 (2001) 6641.
31) T. Muramatsu, S. Yonezawa, Y. Muraoka and Z. Hiroi: J. Phys. Soc. Japan 73 (2004) 2912.
32) T. Muramatsu, N. Takeshita, C. Terakura, H. Takagi, Y. Tokura, S. Yonezawa, Y. Muraoka and Z. Hiroi: Phys. Rev. Lett. 95 (2005) 167004.
33) R. Saniz and A. J. Freeman: Phys. Rev. B 72 (2005) 024522.
34) T. Shibauchi, M. Konczykowski, C. J. Van der Beek, R. Okazaki, Y. Matsuda, J. Yamaura, Y. Nagao and Z. Hiroi: Phys. Rev. Lett. 99 (2007) 257001.
35) K. Miyoshi, Y. Takamatsu and J. Takeuchi: J. Phys. Soc. Japan 75 (2006) 065001.