Anomalous Pressure Dependence of the Superconducting Transition Temperature of β-Pyrochlore AOs$_2$O$_6$ Oxides

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High-pressure effects on the superconducting transitions of β-pyrochlore oxide superconductors AOs$_2$O$_6$ (A = Cs, Rb, K) are studied by measuring resistivity under high pressures up to 10 GPa. The superconducting transition temperature T_c first increases with increasing pressure in every compound and then exhibits a broad maximum at 7.6 K (6 GPa), 8.2 K (2 GPa), and 10 K (0.6 GPa) for A = Cs, Rb, and K, respectively. Finally, the superconductivity is suppressed completely at a critical pressure near 7 GPa and 6 GPa for A = Rb and K and probably above 10 GPa for A = Cs. Characteristic changes in the coefficient A of the T^2 term in resistivity and residual resistivity are observed, both of which are synchronized with the corresponding change in T_c.

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A new family of transition metal oxide superconductors AOs$_2$O$_6$ (A = Cs, Rb, K) called β-pyrochlore oxides was found recently [1–4]. They exhibit superconductivity at T_c = 3.3, 6.3, and 9.6 K, respectively. Extensive studies are now in progress in order to elucidate the mechanism of the superconductivity. μSR experiments by Koda *et al.* on KOs$_2$O$_6$ suggested the presence of an anisotropic order parameter [5], which is in contrast to previous experimental results on Cd$_2$Re$_2$O$_7$ revealing an isotropic gap [6]. In NMR experiments on ^{39}K and ^{87}Rb nuclei, Arai *et al.* found a tiny coherence peak in $1/(T_1T)$ below T_c for RbOs$_2$O$_6$, while no peaks were found for KOs$_2$O$_6$, which strongly suggests that unconventional superconductivity is realized, particularly in KOs$_2$O$_6$ [7]. In contrast, there are a few reports insisting on conventional BCS-type superconductivity in RbOs$_2$O$_6$ [8,9].

Concerning the normal-state properties, the temperature dependence of resistivity shows T^2 behavior at low temperature for every compound, suggesting that either electron-electron correlations or electron-phonon interactions are significantly strong. The coefficient A of the T^2 term in resistivity is larger in KOs$_2$O$_6$ than in CsOs$_2$O$_6$ and RbOs$_2$O$_6$. Moreover, it is found that the Sommerfeld coefficient γ from specific heat measurements is nearly equal for the Cs and Rb compounds, $\gamma = 20$ mJ/K^2 mol Os [10], while it is much larger for KOs$_2$O$_6$ [11]. Hence there is a large mass enhancement toward KOs$_2$O$_6$, which may be related to the increase in T_c.

The superconducting transition temperature of the β-pyrochlore oxides increases with decreasing the ionic radius of A-site alkali metals from Cs to K at ambient pressure (AP). Accordingly, the lattice volume is decreased by the positive chemical pressure. This fact implies that the reduction of the lattice volume by applying physical pressure would further enhance T_c. It was confirmed in fact in two previous high-pressure (HP) experiments by measuring magnetization up to 1.2 GPa for all the members [12] and up to 0.8 GPa for RbOs$_2$O$_6$ [8]. Another interesting finding in the former study is that only in the case of KOs$_2$O$_6$ does the T_c exhibit a saturation around 0.6 GPa and then decrease slightly with pressure, suggesting a complicated pressure dependence at higher pressures. Thus, it is important to investigate the pressure dependence of T_c and other properties in a wider pressure range. It is also intriguing to search for another ground state which could exist next to the superconducting state under very high pressure, as often found in other unconventional superconductors [13]. In this Letter, we report on resistivity measurements under high pressures up to 10 GPa on all the three members of the β-pyrochlore oxide superconductors. A characteristic pressure-temperature phase diagram has been obtained, where in general the T_c exhibits a dome-shaped change as a function of pressure.

Polycrystalline samples of AOs$_2$O$_6$ were prepared as reported previously [1–3]. For the Cs and Rb samples, they were nearly pure including a small amount of Os metal. For the K sample, 10 mol% of Cd$_2$Os$_2$O$_7$ was contained as another phase, which was necessary to obtain a sufficiently hard pellet for reliable resistivity measurements. The coexistence of Cd$_2$Os$_2$O$_7$ may not affect the determination of T_c, because it becomes insulating below 230 K [14]. Electrical resistivity measurements were performed by the four-probe method in a cubic-anvil press apparatus [15] at high pressures from 2 to 10 GPa and temperatures from 3 to 300 K. A fluorinert liquid, which was a one-to-one mixture of FC-70 and FC-77 (3M$^{\text{TM}}$), was used as a pressure transmitting medium. Each run of measurements was carried out at a constant pressure on cooling and then heating with adjusting the load to the anvils automatically.

The temperature dependence of resistivity shows a systematic change under high pressure, as shown in Fig. 1. In

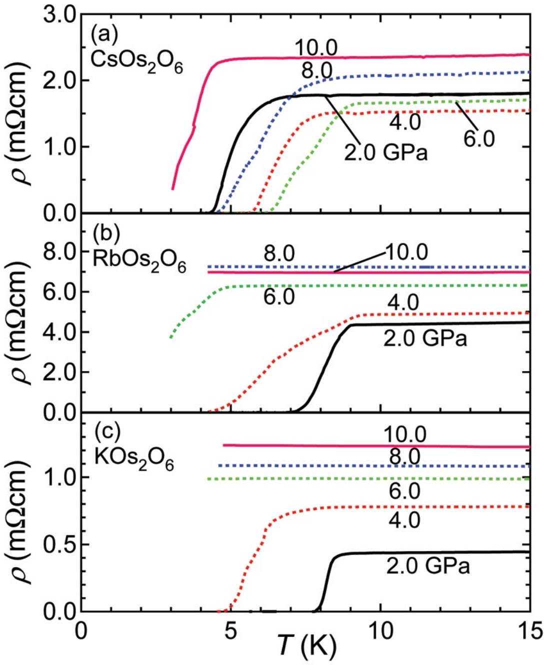

FIG. 1 (color). Superconducting transitions of β-pyrochlore oxides $A\mathrm{Os}_2\mathrm{O}_6$ (A = Cs, Rb, K) detected by resistivity measurements under high pressures from 2 to 10 GPa. The T_c at ambient pressure is 3.3, 6.3, and 9.6 K, respectively.

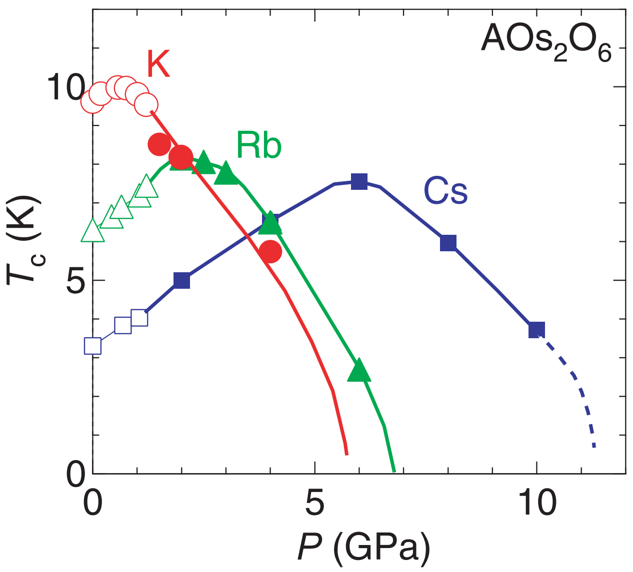

FIG. 2 (color). Pressure dependence of superconducting transition temperature T_c for the three β-pyrochlore oxides. Open marks below 1.2 GPa are the data from previous magnetization measurements [12] and solid marks represent T_c determined in the present resistivity measurements. Squares, triangles, and circles correspond to Cs, Rb, and K, respectively. Solid and dashed lines are guides to the eye.

each compound a drop in resistivity due to the superconducting transition is clearly observed at low pressures. T_c is defined as the midpoint of the transition. The most dramatic change in T_c with pressure is observed in Fig. 1(a) for $\mathrm{CsOs}_2\mathrm{O}_6$ with the lowest $T_c = 3.3$ K at AP. The T_c is already raised to 5.0 K at 2 GPa and further increased to 7.6 K at 6 GPa. Then, it turns to decrease at higher pressures and finally reaches to 3.7 K at 10 GPa. It is also to be noted that the resistivity just above T_c varies markedly with pressure: It first decreases and then increases with increasing pressure.

In the case of $\mathrm{RbOs}_2\mathrm{O}_6$, as shown in Fig. 1(b), the T_c at 2 GPa is 8.2 K, raised from 6.3 K at AP. It is reduced gradually with further increasing pressure, and at last no drops in resistivity are observed above 7 GPa down to 4.2 K. Probably, the superconducting transition is suppressed above a critical pressure $P_c \sim 7 \pm 0.5$ GPa. In the case of $\mathrm{KOs}_2\mathrm{O}_6$ with the highest T_c of 9.6 K at AP [Fig. 1(c)], the T_c is reduced to 8.2 K at 2.0 GPa, 5.7 K at 4.0 GPa, and disappears above that. In both cases, the resistivity above T_c is enhanced enormously with increasing pressure.

The pressure dependences of T_c are summarized in Fig. 2. Data points below 1.2 GPa were determined by magnetization measurements reported in our previous study [12] and those from 2 to 10 GPa are from the present study. Note that they are connected smoothly to each other. In each compound, T_c initially increases, exhibits a broad maximum, and then decreases with increasing pressure; that is, a dome-shaped variation as a function of pressure. However, the positions of the maximum are quite different among them: $(P^*/\mathrm{GPa}, T_c^*/\mathrm{K}) = (6.0, 7.6)$, $(2.0, 8.2)$, and $(0.6, 10.0)$ for Cs, Rb, and K, respectively. The critical pressures, where superconductivity is suppressed, are also different; $P_c \sim 6 \pm 1$ GPa, 7 ± 0.5 GPa, and 12 ± 1 GPa for K, Rb, and Cs, respectively. These differences in P^* and P_c must come from differences in the lattice constant and its compressibility under high pressure. The lattice constant becomes smaller from Cs to K, and the compressibility also becomes smaller in the same direction [16]. Therefore, it is plausible to assume that the T_c of $A\mathrm{Os}_2\mathrm{O}_6$ exhibits a general dome-shaped dependence on the lattice volume. The enhancement in T_c at AP from Cs to K is ascribed to the smaller lattice volume. On the other hand, the observed differences in T_c^* among the three compounds must come from another degree of freedom. Possibly, it is related to the only one variable crystallographic parameter of the β-pyrochlore structure, which is the x parameter of the $48f$ oxygen. This parameter determines the magnitude of a trigonal distortion for OsO_6 octahedra and thus may influence the band structures of the β-pyrochlore oxides.

Among the three compounds, $\mathrm{RbOs}_2\mathrm{O}_6$ would provide us with a suitable playground to study the pressure dependence of resistivity in detail, because the entire range of the T_c dome, as well as a nonsuperconducting regime, can be examined in one system. The temperature dependences of resistivity for $\mathrm{RbOs}_2\mathrm{O}_6$ under various pressures are shown in Fig. 3. In the pressure range below 4 GPa [Fig. 3(a)], where T_c exhibits a broad maximum, the overall temperature dependence of resistivity is rather similar to each other. Resistivity near room temperature decreases with pressure, while that at low temperature above T_c increases slightly. This reduction of resistivity near room temperature is probably not intrinsic but may come from the compression of grains in the polycrystalline sample used in this work. In contrast, the enhancement of the low-temperature resistivity must be intrinsic and implies that the residual resistivity is increased with pressure.

On the other hand, in the pressure range between 4 and 7 GPa which corresponds to the right half of the T_c dome, a remarkable change in resistivity is observed as shown in Fig. 3(b). The room temperature resistivity becomes now almost independent of pressure, while the residual resistivity is further increased enormously. As a result, the resistivity at 7 GPa becomes almost temperature independent. Applying further pressure, the overall resistivity shifts upward uniformly at 8 GPa, and surprisingly at 10 GPa the resistivity starts to decrease steeply below 100 K, implying that metallic behavior is recovered. However, it is to be noted that this temperature dependence of resistivity at 10 GPa is apparently different from that at low pressure in the superconducting regime. Very recently, we carried out another HP experiment on a different sample of $RbOs_2O_6$ with better purity and larger residual resistivity ratio and obtained essentially the same results, indicating that the above changes are intrinsic and reproducible. We found substantially the same behavior in resistivity under HP for $CsOs_2O_6$ and KOs_2O_6, except for differences in the pressure range.

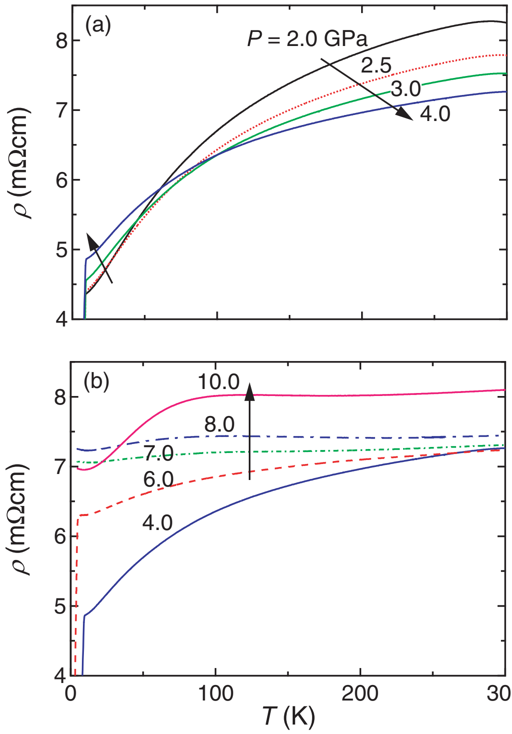

FIG. 3 (color). The evolution of temperature dependence of resistivity ρ for $RbOs_2O_6$ in the pressure ranges of 2–4 GPa (a) and 4–10 GPa (b).

It is known that the low-temperature resistivity of the β-pyrochlore oxides generally exhibits T^2 behavior, indicative of large electron correlations. The coefficient A of the T^2 term is much larger in KOs_2O_6 than in $CsOs_2O_6$ and $RbOs_2O_6$, suggesting that the coefficient correlates with T_c. Here, we demonstrate how pressure affects A as well as residual resistivity ρ_0 (Fig. 4). In order to deduce a general trend, each quantity has been normalized by the value at the maximum of the T_c dome. Pressure is also normalized as $P_n = (P - P^*)/(P_c - P^*)$, where P^* is a pressure at the T_c maximum and P_c is a critical pressure where superconductivity disappears; that is, $P_n = 0$ for $P = P^*$ and $P_n = 1$ for $P = P_c$. For KOs_2O_6, only T_c is plotted, because we could not obtain reliable data due to the presence of impurities. As shown Fig. 4(a), it becomes apparent now that normalized T_c falls on a universal curve. Either normalized A and ρ_0 are connected smoothly between $RbOs_2O_6$ and $CsOs_2O_6$ to show a general curve [Fig. 4(b)]: normalized A exhibits a broad maximum near the T_c maximum and a minimum near P_c, while normalized ρ_0 does a minimum near P^* and a maximum near P_c. Thus, the close correlation between T_c and A is confirmed

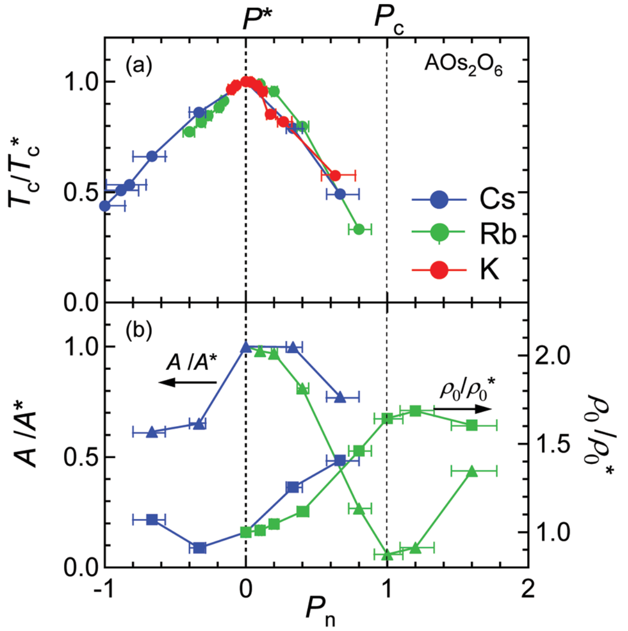

FIG. 4 (color). Pressure dependence of T_c (a), coefficient A, and residual resistivity ρ_0 (b). In order to deduce general features, normalized pressure P_n is used, which is given by the equation $P_n = (P - P^*)/(P_c - P^*)$, where P^* and P_c are pressures with the maximum T_c and $T_c \rightarrow 0$, respectively. A and ρ_o are also normalized by the corresponding values at the maximum T_c. Error bars for P_n come from experimental ambiguity in determining P_c.

unequivocally. The observed enhancement of A toward the T_c maximum must imply that carriers become heavy due to some correlation which may be relevant to the pairing mechanism of superconductivity in the β-pyrochlore oxides.

On the other hand, residual resistivity is generally expressed by the equation $\rho_0 = (\hbar/e^2 l)(3\pi^2)^{1/3} n^{-2/3}$, where l is the mean free path of carriers and n is carrier density. Thus, the observed enhancement of ρ_0 near P_c means that either l or n is reduced there. The mean free path at low temperature may be determined by the concentration of impurities or defects and thus should not be affected by pressure. It is known, however, that the mean free path is reduced largely, and thus the residual resistivity increases due to a quantum fluctuation such as a valence fluctuation [17,18]. Although in the present case a valence fluctuation associated with Os ions in a 5.5 valent state is to be considered, this may not be so important because the bandwidth of Os $5d$—O $2p$ hybridized bands is large, ~3 eV, from the band structure calculations [19–21]. The possibility of carrier density varying with pressure must be examined in the future experiment.

A key issue for understanding the observed pressure dependences of T_c and other parameters must be the evolution of the Fermi surface as a function of lattice constant or pressure. At ambient pressure a strong tendency to nesting has been found in the band structure calculations [19–21]. Moreover, the tendency seems to be enhanced from Cs to K [21]. It would be intriguing to test how this feature changes by applying pressure.

In summary, we have obtained interesting and characteristic behavior in the pressure dependence of T_c and other parameters in the β-pyrochlore oxides $A\mathrm{Os_2O_6}$ by measuring resistivity under high pressure up to 10 GPa. Generally, T_c shows a domelike change as a function of pressure. The variations of the coefficient A of the T^2 term in resistivity and the residual resistivity ρ_0 are also anomalous and synchronized with the change in T_c.

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[1] S. Yonezawa *et al.*, J. Phys. Condens. Matter **16**, L9 (2004).
[2] S. Yonezawa *et al.*, J. Phys. Soc. Jpn. **73**, 819 (2004).
[3] S. Yonezawa, Y. Muraoka, and Z. Hiroi, J. Phys. Soc. Jpn. **73**, 1655 (2004).
[4] Z. Hiroi, S. Yonezawa, and Y. Muraoka, J. Phys. Soc. Jpn. **73**, 1651 (2004).
[5] A. Koda *et al.*, J. Phys. Soc. Jpn. **74**, 1678 (2005).
[6] R. Kadono *et al.*, J. Phys. Soc. Jpn. **71**, 709 (2002).
[7] K. Arai *et al.* (to be published); cond-mat/0411460.
[8] R. Khasanov *et al.*, Phys. Rev. Lett. **93**, 157004 (2004).
[9] M. Brühwiler *et al.*, Phys. Rev. B **70**, 020503(R) (2004).
[10] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **74**, 1255 (2005).
[11] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **74**, 1682 (2005).
[12] T. Muramatsu *et al.*, J. Phys. Soc. Jpn. **73**, 2912 (2004).
[13] D. Jaccard *et al.*, Physica B (Amsterdam) **259–161**, 1 (1999).
[14] A. W. Sleight *et al.*, Solid State Commun. **14**, 357 (1974).
[15] N. Mori *et al.*, Jpn. J. Appl. Phys. Ser. **8**, 128 (1993).
[16] J. Yamaura (private communication).
[17] K. Miyake, O. Narikiyo, and Y. Onishi, Physica B (Amsterdam) **259–261**, 676 (1999).
[18] Y. Onishi and K. Miyake, J. Phys. Soc. Jpn. **69**, 3955 (2000).
[19] R. Saniz *et al.*, Phys. Rev. B **70**, 100505(R) (2004).
[20] J. Kunes, T. Jeong, and W. E. Pickett, Phys. Rev. B **70**, 174510 (2004).
[21] H. Harima (to be published).