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New β-Pyrochlore Oxide Superconductor $CsOs_2O_6$

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The discovery of the new β-pyrochlore oxide superconductor $CsOs_2O_6$ with $T_c = 3.3$ K is reported. It is the third superconductor in the family of β-pyrochlore oxides, following KOs_2O_6 with $T_c = 9.6$ K and $RbOs_2O_6$ with $T_c = 6.3$ K. The T_c of this series decreases with increasing ionic radius of alkaline metal ions, imposing a negative chemical pressure upon the Os pyrochlore lattice.

KEYWORDS: superconductivity, β-pyrochlore oxide, pyrochlore lattice
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Pyrochlore oxides constitute a large family of transition metal (TM) oxides such as perovskites.[1] They have the general chemical formula $A_2B_2O_7$ or $A_2B_2O_6O'$, where A is a larger cation and B is a smaller TM cation. The first superconductor in the family of pyrochlore oxides was discovered in $Cd_2Re_2O_7$ at $T_c = 1.0$ K.[2–4] Recently, we found another type of pyrochlore oxides with the general formula AB_2O_6, called the β-pyrochlore oxide,[5] where A is a large monovalent alkaline metal cation. Two osmates, $RbOs_2O_6$ and KOs_2O_6, have been prepared in this family, which exhibit superconductivity at higher T_c's of 6.3 K and 9.6 K, respectively.[5–7] They crystallize in a modified pyrochlore structure, where Os atoms form a corner-sharing tetrahedral network called the pyrochlore lattice, as in $A_2B_2O_7$-type pyrochlore oxides, which is now called α-pyrochlore,[7] while alkaline metal atoms occupy the 8*b* site which is the O′ site in α-pyrochlore. Here, we report on the discovery of another new β-pyrochlore oxide superconductor $CsOs_2O_6$.

A polycrystalline sample was prepared from Cs_2CO_3 and Os. The two powders were mixed in an appropriate molar ratio ($Cs_2CO_3 : Os = 1 : 4$), ground and pressed into a pellet. The pellet was heated in an evacuated silica tube at 673 K for 24 h. To control the oxygen partial pressure, a certain amount of AgO was added separately from the pellet in the silica tube: AgO decomposes into silver and oxygen above 370 K, and thus generates an oxidizing atmosphere. Moreover, CaO was also added in the tube to remove CO_2 produced by the reaction of Cs_2CO_3 and Os : CaO reacts with CO_2 to form $CaCO_3$. The chemical composition of the product examined by energy-dispersive X-ray (EDX) analysis in a scanning electron microscope was $Cs : Os \sim 1 : 2$.

Figure 1 shows a powder X-ray diffraction (XRD) pattern obtained at room temperature. All the intense peaks can be indexed by assuming a cubic unit cell with the lattice constant $a = 1.0149$ nm. A few extra peaks from Os are detected. Moreover, a trace of an unknown impurity phase is also included in the product. Extinctions observed in the XRD pattern are consistent with the space group of $Fd\bar{3}m$, and the intensity profile is similar to those of other β-pyrochlore oxides. The lattice constant is larger than those of $RbOs_2O_6$ ($a = 1.0114$ nm) and KOs_2O_6 ($a = 1.0101$ nm), as expected from the difference in the ionic radius of alkaline metal ions.

Resistivity measurements were carried out down to 2 K by the standard four-probe method in a Quantum Design Physical Property Measurement System (PPMS). Figure 2 shows the temperature dependence of resistivity measured in a polycrystalline sample. It exhibits a good metallic behavior below room temperature. A clear T^2 dependence is observed below 45 K. As shown in the inset in Fig. 2, the resistivity shows a sharp drop below 3.4 K due to superconductivity. The zero resistivity is attained below 3.2 K. The critical temperature T_c, defined as the midpoint temperature of the transition, is 3.3 K.

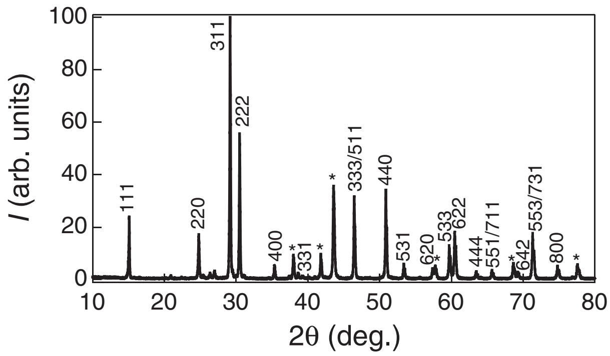

Fig. 1. Powder X-ray diffraction pattern of $CsOs_2O_6$. The peak index is given by assuming a cubic unit cell with the lattice constant $a = 1.0149$ nm. Asterisks mark extra peaks from Os.

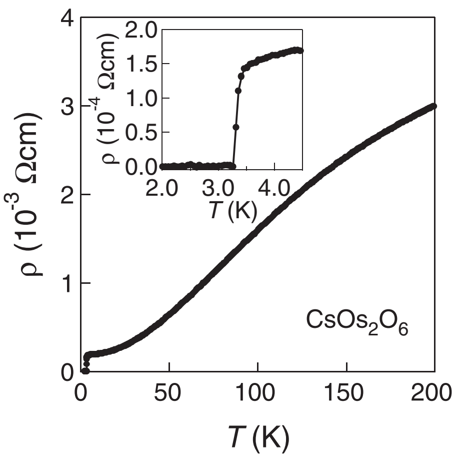

Fig. 2. Temperature dependence of resistivity measured in a polycrystalline sample. The inset shows enlargements around the superconducting transition.

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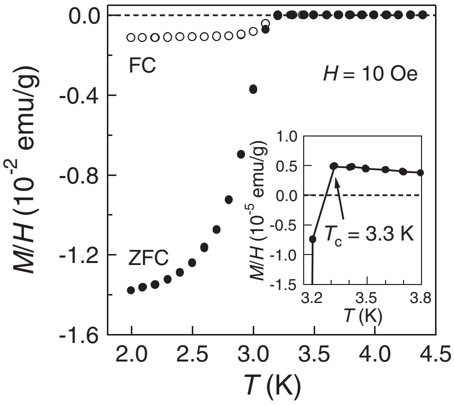

Fig. 3. Temperature dependence of magnetic susceptibility measured in a powdered sample of $CsOs_2O_6$ in an applied field of 10 Oe. ZFC and FC indicate zero-field cooling and field cooling curves, respectively.

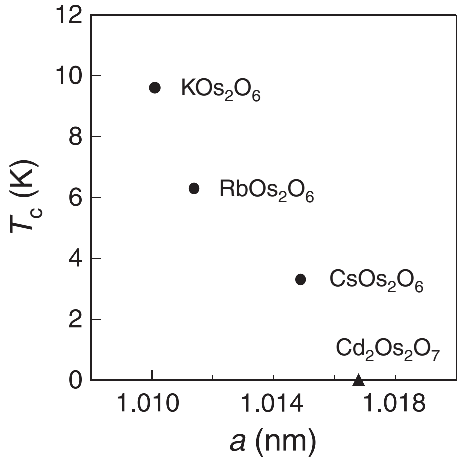

Fig. 4. Relationship between the lattice constant a and critical temperature T_c for three β-pyrochlore oxide superconductors: $CsOs_2O_6$, $RbOs_2O_6$ and KOs_2O_6. $Cd_2Os_2O_7$ is an α-pyrochlore osmates, which is a nonsuperconductor.

In addition to the observation of the zero-resistivity transition, a large diamagnetic signal associated with the Meissner effect was observed below 3.3 K. Figure 3 shows the temperature dependence of magnetic susceptibility measured in a powdered sample in a Quantum Design MPMS. The measurements were carried out in a magnetic field of 10 Oe on heating after zero-field cooling and then on cooling in a field. A superconducting volume fraction estimated at 2 K from the zero-field cooling experiment is nearly 100%, indicating bulk superconductivity.

Now we have three β-pyrochlore oxide superconductors: $CsOs_2O_6$, $RbOs_2O_6$ and KOs_2O_6. With these alkaline metals the T_c changes to 3.3 K, 6.3 K and 9.6 K, respectively. It is plausible to assume that this change is due to the size effect of alkaline metal ions, because the bands near the Fermi level consist of Os 5d orbitals with a minor contribution from O 2p orbitals in the case of $Cd_2Os_2O_7$[8] and probably in KOs_2O_6 also.[9] Certainly, the lattice constant is almost proportional to the ionic radius of A ions. The relationship between the T_c and lattice constant is shown in Fig. 4. The T_c decreases with increasing a under a negative chemical pressure. This is in contrast to the case of conventional BCS superconductivity in a single-band model, where the T_c may increase under a negative pressure, because the density of state (DOS) increases. The reverse tendency found in AB_2O_6 may partly reflect the complex band structure with many sharp peaks in the DOS. However, it can be also related to the mechanism of superconductivity, which would be clarified by systematically studying these compounds. It is expected from the figure that a positive pressure would increase the T_c. High-pressure experiments are now in progress.

In conclusion, we found superconductivity with $T_c =$ 3.3 K in the new β-pyrochlore oxide $CsOs_2O_6$. Although the nature of this superconductivity is not known at the moment, we believe that an interesting aspect of physics is involved in the superconductivity of $CsOs_2O_6$, as in KOs_2O_6 and $RbOs_2O_6$.[7]

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