LETTER TO THE EDITOR

Superconductivity in a pyrochlore-related oxide KOs$_2$O$_6$

S Yonezawa, Y Muraoka, Y Matsushita and Z Hiroi

Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

E-mail: yonezawa@issp.u-tokyo.ac.jp

Abstract
We report the discovery of a new superconductor KOs$_2$O$_6$. The compound
crystallizes in a defect pyrochlore structure, where Os atoms form a corner-
sharing tetrahedral network called the pyrochlore lattice. Resistivity and
magnetic susceptibility measurements on a polycrystalline sample provide
evidence of bulk superconductivity with $T_c = 9.6$ K.

Pyrochlore oxides constitute a large family of transition metal (TM) oxides such as
perovskites [1]. They have a general chemical formula A$_2$B$_2$O$_7$ or A$_2$B$_2$O$_6$O′, where A is
a larger cation and B is a smaller TM cation. The valence combination of the two metals is
often either A^{3+}/B^{4+} or A^{2+}/B^{5+}. The ideal pyrochlore structure possesses cubic symmetry
with space group $Fd\bar{3}m$ and there are eight molecules per unit cell. Four crystallographically
nonequivalent kinds of atom exist in the cell: A, B, O and O′ atoms occupy the 16d, 16c, 48f
and 8b site, respectively. The structure is composed of two types of cation–oxygen sublattice:
one is a corner-sharing tetrahedral network made of A atoms with an O′ atom in the centre
of each tetrahedron and the other is that of B atoms with each B atom coordinated by six O
atoms quasi-octahedrally. In the case that either atom A or B has a localized magnetic moment
which interacts antiferromagnetically with the nearest-neighbours, one expects geometrical
frustration which may suppress long-range magnetic order and lead to an unusual ground state
such as a spin liquid [2]. Although many pyrochlores crystallize in the ideal cubic structure, in
a few cases, deviations from cubic by way of tetragonal, rhombohedral and triclinic distortion
have been noted [1]. Moreover, the pyrochlore structure sometimes tolerates vacancies at the
A and O′ sites. Particularly, for A = Tl, Pb and Bi, A$_2$B$_2$O$_6$-type pyrochlores are obtained
with all O′ atoms missing. On the other hand, AB$_2$O$_6$-type defect pyrochlores are known for
large univalent A cations such as Rb$^+$ [3].

   Most pyrochlore oxides containing 5d TM elements such as Re, Os and Ir are bad
metals [1]. Recently, superconductivity was found in Cd$_2$Re$_2$O$_7$ (Re^{5+}:5d^2) at $T_c = 1$ K
for the first time in the family of pyrochlore oxides [4]. In contrast, a related pyrochlore oxide
Cd$_2$Os$_2$O$_7$ (Os^{5+}:5d^3) undergoes a metal–insulator (MI) transition at 225 K [5]. The major

(a)

(b)

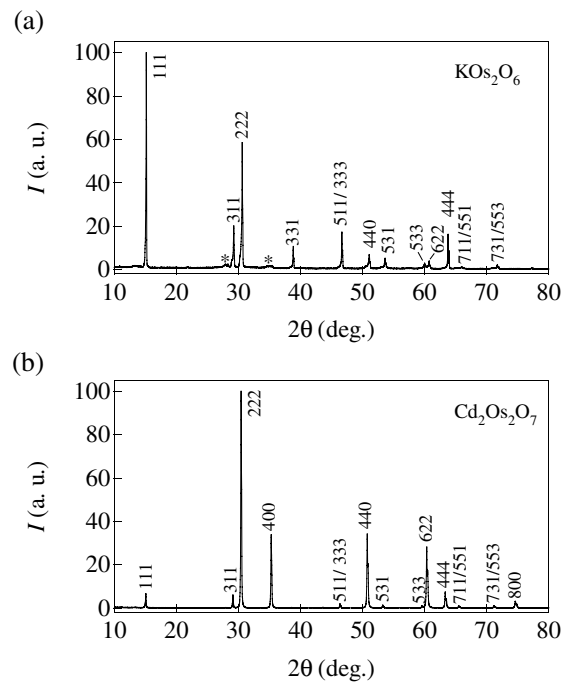**Figure 1.** Powder x-ray diffraction pattern of KOs_2O_6 (a) and $Cd_2Os_2O_7$ (b). The peak index is given, assuming a cubic unit cell with a lattice constant $a = 1.0099$ nm for KOs_2O_6 and $a = 1.0168$ nm for $Cd_2Os_2O_7$. Asterisks in (a) show extra peaks from OsO_2.

difference between them seems to be the number of d electrons on the B-site cations. These compounds illustrate the rich physics involved in the 5d TM pyrochlore oxides on the basis of electron correlations near the MI transition as well as frustration on the pyrochlore lattice. Thus, we have been trying to synthesize a new pyrochlore oxide containing 5d TM elements.

Osmium is a 5d TM element located below Fe and Ru in the periodic table. It adopts various valence states in oxides from Os^{4+} in OsO_2 to Os^{8+} in OsO_4. A summary of ternary osmium phases was given by Chamberland [6]. Three of the compounds crystallize in the pyrochlore structure; $Ca_2Os_2O_7$, $Cd_2Os_2O_7$ and $Pb_2Os_2O_7$. The Ca and Cd compounds exhibit an MI transition, while the Pb one is a Pauli paramagnetic metal. Recently, $Hg_2Os_2O_7$ was also prepared and reported to show metallic behaviour down to 4 K [7]. It is to be noted that no osmium compounds in the form of AB_2O_6 have been reported so far. Here, we report the discover of a new ternary phase KOs_2O_6 which shows superconductivity at about 10 K.

Polycrystalline samples were prepared from KO_2 and OsO_2 (Alfa Aesar). The two powders were mixed in an appropriate molar ratio ($KO_2:OsO_2 = 1:2$), ground and pressed into a pellet in a dry atmosphere. The pellet was heated in an evacuated silica tube at 873 K for 24 h. To control the oxygen partial pressure, Ag_2O was added in the silica tube: Ag_2O decomposes into silver and oxygen at about 430 K and thus generates an oxidizing atmosphere. The chemical composition of the product examined by energy dispersive x-ray analysis in a scanning electron microscope was K/Os $\sim 0.50(5)$. The oxygen content was not determined in this study.

Figure 1 shows a powder x-ray diffraction (XRD) pattern taken at room temperature. All the intense peaks can be indexed assuming a cubic unit cell with a lattice constant $a = 1.0099(1)$ nm. A few extra peaks from OsO_2 are also detected. Electron diffraction (ED) patterns taken in a transmission electron microscope could be indexed with the same
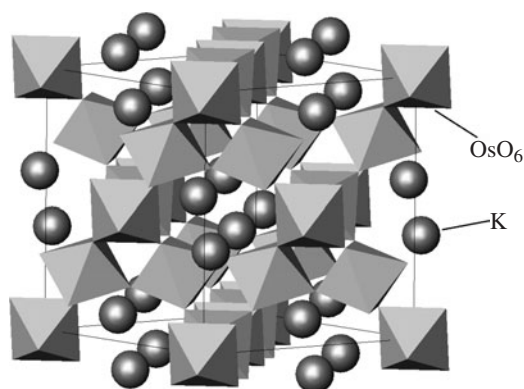
Figure 2. Probable crystal structure for KOs_2O_6. K, Os and O atoms occupy the 8b, 16c and 48f sites in the space group $Fd\bar{3}m$, respectively.

cubic cell. Extinctions observed both in XRD and ED experiments are compatible with the space group $Fd\bar{3}m$, the same as in the ideal pyrochlore structure. For comparison, the XRD pattern of $Cd_2Os_2O_7$ is shown in figure 1(b). It is apparent that some particular peaks become more intense in the present compound, such as the (111) peak located at $2\theta \sim 15°$, compared with $Cd_2Os_2O_7$. This is not due to the preferred orientation of powders, because relative intensity ratios such as $I(111)/I(222)$ change greatly. Such a large difference in the relative peak intensity suggests a substantial deviation in the occupation of metal ions.

It is known that AB_2O_6-type defect pyrochlores are formed in the case where the A cation is a large univalent metal such as Rb^+, K^+ or Tl^+ [3]. A typical example is found in $Tl^+(Nb^{5+}W^{6+})O_6$ [8], where the Tl atom is 'delocalized' from the ideal 16d site to occupy the 32e positions statistically. On the other hand, in the case of large Rb pyrochlores such as $RbTa_2(O_5F)$, it has been reported that the Rb atom occupies the 8b site [9]. In the case of A = K, the structure seems to be in-between the two compounds, as in $KTa_2(O_5F)$ [9]. It is to be noted that there have been no metallic compounds reported in this AB_2O_6 family.

Judging from the two facts that our potassium osmate has the composition K/Os = 0.5 and that it crystallizes in the cubic structure compatible with the space group $Fd\bar{3}m$, it is reasonable to assume that it belongs to the AB_2O_6 family. Our preliminary Rietvelt analysis on a powder XRD pattern indicates that the K atom occupies the 8b site as in $RbTa_2O_5F$.

Figure 2 depicts the most probable crystal structure for KOs_2O_6. Os atoms form the pyrochlore lattice just as in an ordinary pyrochlore oxide, while K atoms are located in cages made of OsO_6 octahedra. At the present moment, we cannot exclude the possibility that small deformation occurs in this compound, as in $Cd_2Re_2O_7$ [10] or other AB_2O_6 compounds [11]. Detailed structural study will be reported later.

Resistivity measurements were carried out down to 2 K by the standard four-probe method in a Quantum Design PPMS. Figure 3 shows a typical temperature dependence of resistivity. When a sample is cooled below 10 K, the resistivity shows an sharp drop due to superconductivity. The resistivity below the transition is nearly zero within our experimental resolution. The onset temperature is 9.9 K, and zero resistivity is attained below 9.0 K. The critical temperature T_c defined as the midpoint temperature of the transition is 9.5 K. When a magnetic field was applied, the transition curve shifted to lower temperatures systematically. The resistivity above the transition shows a peculiar temperature dependence which is far from that of a conventional metal. For further discussion, we need a single crystal instead of a polycrystalline pellet to clarify this point.

In addition to the observation of the zero-resistive transition, a large diamagnetic signal associated with the Meissner effect was observed below 9.6 K. Figure 4 shows the temperature
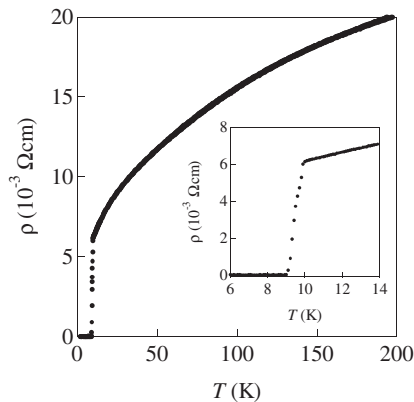
Figure 3. Temperature dependence of resistivity. The inset shows an enlargement around the superconducting transition.
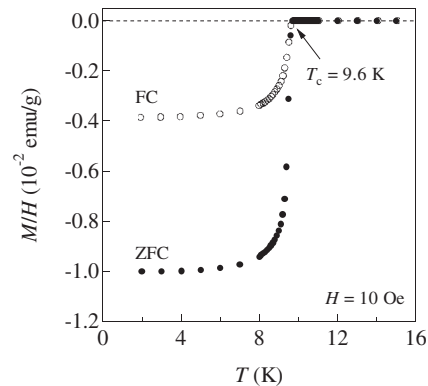
Figure 4. Temperature dependence of magnetic susceptibility measured on a powdered sample of KOs_2O_6 in an applied field of 10 Oe. ZFC and FC mean a zero-field cooling and a field cooling curve, respectively.

dependence of magnetic susceptibility measured on 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 about 80% that is large enough to constitute bulk superconductivity.

In conclusion, we found superconductivity with $T_c = 9.6$ K in the defect pyrochlore compound KOs_2O_6. The nature of superconductivity is not clear at present. However, our preliminary experiments indicate that the superconductivity is robust in high magnetic fields, possibly with an upper critical field larger than the Pauli limiting field. In addition, magnetic susceptibility shows a significant temperature dependence. Details will be reported elsewhere. We believe that an interesting physical process is involved in this compound on the basis of electron correlations near the MI transition as well as frustration on the pyrochlore lattice.

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