

Superconducting to spin-glass state transformation in β -pyrochlore $K_xOs_2O_6$ C. C. Lee,¹ W. L. Lee,² J. -Y. Lin,³ C. C. Tsuei,⁴ J. G. Lin,¹ and F. C. Chou^{1,5,*}¹*Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan*²*Institute of Physics, Academia Sinica, Taipei 11529, Taiwan*³*Department of Physics, National Chiao Tung University, HsinChu 30076, Taiwan*⁴*IBM, Yorktown Heights, New York 10598, USA*⁵*National Synchrotron Radiation Research Center, HsinChu 30076, Taiwan*

(Received 8 November 2010; published 14 March 2011)

β -pyrochlore KOs_2O_6 , which shows superconductivity below ~ 9.7 K, has been converted into $K_xOs_2O_6$ ($x \lesssim \frac{2}{3} - \frac{1}{2}$) electrochemically to show spin-glass-like behavior below ~ 6.1 K. A room-temperature sample surface potential versus charge transfer scan indicates that there are at least two two-phase regions for x between 1 and 0.5. A rattling model of superconductivity for the title compound has been examined using electrochemical potassium de-intercalation. The significant reduction of superconducting volume fraction due to minor potassium reduction suggests the importance of defect and phase coherence in the rattling model. Magnetic susceptibility, resistivity, and specific heat measurement results have been compared between the superconducting and spin-glass-like samples.

DOI: [10.1103/PhysRevB.83.104503](https://doi.org/10.1103/PhysRevB.83.104503)

PACS number(s): 74.70.-b, 75.50.Lk, 74.25.Bt, 74.25.F-

I. INTRODUCTION

Frustration has been one of the most intriguing cooperative phenomena in magnetism. The geometrically frustrated system becomes one fascinating class of material with emergent novel physical properties by its complex nature, including the layered triangular and Kagome lattice in two dimensions, and the three-dimensional (3D) pyrochlore structure with a corner-sharing tetrahedral sublattice.^{1,2} The discovery of the first superconducting 3D pyrochlore transition metal oxides $Cd_2Re_2O_7$ with $T_c \sim 1$ K in 2001 was surprising.³ The following exploration of superconductivity in the pyrochlore family has raised T_c up to 9.7 K in AOs_2O_6 with $A = Cs, Rb,$ and K since then.⁴⁻⁶

The most general formula of 3D pyrochlore, $A_2B_2O_6O'$, is usually described in the cubic of $Fd\bar{3}m$ (No. 227) symmetry with A at $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), B at $16c$ (0, 0, 0), O at $48f$ ($x, \frac{1}{8}, \frac{1}{8}$), and O' at $8b$ ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$).¹ The 3D pyrochlore $A_2B_2O_6O'$ can be best described as the frustrating corner-shared tetrahedral as shown in Fig 1, where either one or both A and B sublattices can be magnetic. Different valence combinations including A^{+3}/B^{+3} , A^{+2}/B^{+4} , and A^{+1}/B^{+5} are possible, although the preferred site of the monovalent ion occupies the O' site ($8b$) instead of the A site ($16d$) as a result of a lower and stable electrostatic potential.⁷

The deficient-type pyrochlore with a monovalent ion occupying the $8b$ (O' site) instead of $16d$ (the regular A site) is called β -type pyrochlore, in contrast to the regular α -type $A_2B_2O_7$ but usually written as AB_2O_6 , which is the common structure of the title compound of KOs_2O_6 . KOs_2O_6 has a frustrating structure for the Os sublattice in corner-shared OsO_6 octahedra as shown in Fig. 1(a). Another aspect with which to describe the system for the K and O relationship is shown in Fig. 1(b), where K is caged by 18 oxygen ions while sitting in the K-tetrahedral center. As seen in Fig. 1(b), the empty $16d$ site, which is usually occupied by higher-valence A in regular α - $A_2B_2O_7$, is located near the midpoint, connecting two $Os_{12}O_{18}$ cages within the large pore center formed by six oxygens.

The origin of superconductivity found in $(K,Rb,Cs)Os_2O_6$ has been proposed by a rattling model and tested experimentally,⁸ where effective interaction between two electrons is proposed to be coming from the anharmonic potential generated by the rattling motion of the K^+ ions caged in $Os_{12}O_{18}$ clusters. Such rattling-induced superconductivity has been partially supported by study of photoemission as well.⁹ On the other hand, the strong dependence of unit cell size on T_c , i.e., the higher T_c from Cs to the K family with progressively larger ion size,⁴ seems to suggest that an even higher T_c is waiting to be found if Na substitution becomes possible. Although Na has been introduced into the system successfully through an ion exchange route from KOs_2O_6 ,¹⁰ the nonstoichiometric product $Na_{1.4}Os_2O_6 \cdot H_2O$ turns out to be nonsuperconducting down to 2 K. Structure refinement suggests that the Na ion does not occupy the original K site at $8b$ within the $Os_{12}O_{18}$ cage, but at the $32e$ site, which is in the neighborhood of the $16d$ site near the large O_6 pore center; i.e., $Na_{1.4}Os_2O_6 \cdot H_2O$ practically belongs to the regular α -type pyrochlore instead of the β -type pyrochlore such as KOs_2O_6 .

While Na substitution failed to produce the identical structure of KOs_2O_6 and to raise T_c as expected, we decided to use an alternative route on tuning K content to test the validity of the proposed rattling-induced superconductivity model further. Using the electrochemical chronoamperometry method, we have reduced the potassium content from the pristine KOs_2O_6 to $K_xOs_2O_6$ ($x \sim 0.5$) successfully. We find that the system can be transformed from a superconducting to a spin-glass state below $T_g \sim 6.1$ K after potassium is reduced to half of its original level. The resistivity and specific heat measurement results are also reported for a detailed comparative study.

II. EXPERIMENT

A polycrystalline sample of KOs_2O_6 was prepared from reagent-grade oxide powders of KO_2 and OsO_2 mixed with an appropriate molar ratio ($KO_2 : OsO_2 = 1 : 2$) in an argon-filled glove box and pressed into a pellet with mass ~ 0.167 g. The

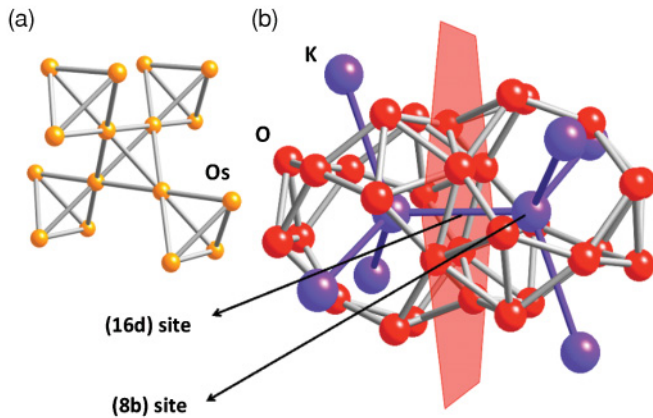


FIG. 1. (Color online) (a) The osmium ions form a 3D frustrated pyrochlore structure. (b) The potassium ions can be viewed as rattling in a cage formed with 18 oxygens, and the cages are connected through tunnels formed with six oxygens as indicated by a hexagonal mirror plane. Ideally K ions sit at the $8b$ site as shown in the center of O_{18} cage, and the center of the O_6 pore corresponds to the $16d$ site.

compressed pellet was wrapped with gold foil, sealed in an evacuated glass tube, and heated to 450°C for 72 hours. To control the oxygen partial pressure, a 0.06 g Ag_2O pellet was added to the sealed glass tube to create an oxygen partial pressure at about ~ 12 atm at 450°C . Potassium content of the as-prepared sample is near 1 per formula unit based on the electron probe microanalysis (EPMA) using a spray-on layer of polycrystalline powder, which is consistent with that reported from a sample prepared and analyzed using the identical method as previously.⁴

Additional potassium content tuning was accomplished through an electrochemical de-intercalation process. An electrochemical cell was set up using 1N NaClO_4 in propylene carbonate (PC) as electrolyte, an Ag/AgCl reference electrode, and platinum as counter-electrode. Due to the potential formation of the hydrated form,¹¹ the KOs_2O_6 sample working electrode was heated to 175°C for 8 hours before the electrochemical experiment, and a nonaqueous electrolyte was used. The working electrode was composed of polycrystalline KOs_2O_6 compressed in pellet form. An initial chronopotentiometry scan with current density of 1.5 A/g was used to trace the quasiequilibrium potential first. Final samples were prepared with the chronocoulometry technique, applying voltages from -0.05 to $1.25\text{ V}/\text{Ag}-\text{AgCl}$ until the induced charge transfer current level had reached a time-independent constant background. Potassium content can be reduced progressively from the original 1 to about ~ 0.5 by applying constant anodic potentials from -0.05 to 1.25 V relative to the Ag/AgCl reference electrode. Crystal structure were analyzed by Bruker D8 X-ray diffractometer. Magnetic properties were measured using a SQUID magnetometer (Quantum Design SQUID-VSM). Since powder samples were prepared using a close oxidation environment at a relatively low temperature of 450°C , all following resistivity and specific heat measurement was done on a cold compressed pellet under 6 GPa for 20 minutes to reach maximum density. Resistivity measurements were carried out by a resistance bridge at low current excitation using standard four-probe geometry. Since

the hydration is a reversible process, we made all physical property characterization on samples dried at 175°C for 8 hours beforehand.

III. RESULTS AND DISCUSSIONS

A. Electrochemical de-intercalation

Since K ions rattle within the large $\text{Os}_{12}\text{O}_{18}$ cage of $\sim 1\text{ \AA}$ anharmonically as suggested by the detectable phonons from the fine spectral structure of ARPES experiment,⁹ and the ion exchange has been shown to be possible between Na and K ions,¹⁰ plus the fact that Os ion has $5d$ electrons of rich valence variation from $+2$ to $+6$, we believe that it is highly possible that the reduction of K content can raise the average valence of Os from the current mixed valence of $\text{Os}^{+5.5}$ in KOs_2O_6 to the Os^{+6} state in Os_2O_6 as a result of the completely emptied cations that potentially occupy the $16d$ and $8b$ sites. To explore the existence of possible stable phases as a function of x in $\text{K}_x\text{Os}_2\text{O}_6$, we have employed an electrochemical de-intercalation process to control the K level, starting from the as-prepared KOs_2O_6 . Similar to the reduction of sodium level in Na_xCoO_2 ,¹² potassium de-intercalation becomes possible when ClO_4^- is adsorbed to the sample surface and react with the surface K, and the following K ion self-diffusion proceeds to reach a new equilibrium at a lower average total K level for the bulk, which should be allowed according to the relatively high electrical and ionic conductivity for the similar pyrochlore structure compounds at room temperature.¹³

A chronopotentiometry technique was applied to the system on an electrochemical cell constructed as $\text{KOs}_2\text{O}_6/1\text{N NaClO}_4$ in PC/Pt. Nonequilibrium surface potential (V_{cp}) versus total charge (Q) passing through a sample working electrode is shown in Fig. 2 under applied constant current

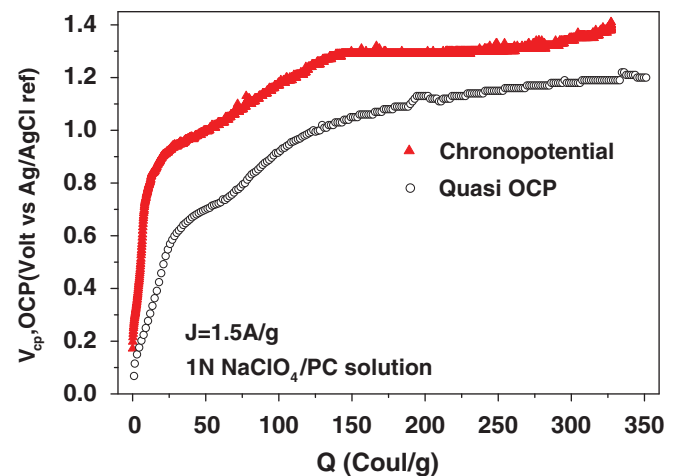


FIG. 2. (Color online) Surface potential and quasiequilibrium OCP versus charge transfer Q for a working electrode made of compressed KOs_2O_6 powder, where surface potential is obtained from a chronoampereometry scan of the constant current density of 1.5 A/g (red line), and the quasiequilibrium OCP (black line) is described in the text. Samples of different potassium content are prepared using applied voltages $V_{\text{ap}} = \text{OCP}$ to produce samples with specific x and verified by EPMA.

TABLE I. Summary of sample preparation and physical properties.

Applied voltage (V)	Lattice constant (Å)	Magnetic behavior	T_c/T_g	S.C. vol. fraction	x_{EPMA}
Pristine	10.072	S.C.	9.7 K	20.1%	1.00(4)
0.16	10.077	S.C.	9.7 K	17.4%	*
0.20	10.080	S.C.	9.7 K	3.9%	1.01(3)
0.24	10.079	S.C.	9.7 K	4.9%	*
0.50	10.079	S.C.	9.7 K	1.2%	0.97(2)
0.64	10.081	S.C.	9.7 K	5.8%	*
0.85	10.078	Spin glass	4.6 K	*	0.65(6)
1.05	10.078	Spin glass	6.1 K	*	*
1.16	10.078	Spin glass	3.3 K	*	0.48(6)

density of 1.5 A/g. The initial open circuit potential V_o of ~ 0.12 V has been raised to ~ 0.85 V after nearly one half of the K^+ ions had been reduced from the original, assuming 100% efficiency of charge transfer. Continued de-intercalation process reduced the potassium level further until a side reaction was observed after surface potential had reached beyond ~ 1.2 V. Based on the preliminary chronopotentiometry scan shown in Fig. 2, three plateau-shape regions corresponding to the two-phase character can be roughly identified, i.e., the first extremely narrow region near $V \sim 0.2$ -0.4, the middle plateau between 0.5 and 1.1, and the final plateau above ~ 1.3 V. A significantly higher charge transfer was observed for $V_{\text{cp}} \gtrsim 1.2$ V due to side reactions, as observed from the black deposit on the counter electrode Pt surface and volatile vapor bubbling at the cathode. Since the black deposit found on the Pt counter electrode disappeared after being exposed to the air, it is possible that the deposit was the highly toxic and volatile OsO_4 .

A separate quasiequilibrium open circuit potential (OCP) versus Q has been obtained from the same piece of KOs_2O_6 working electrode *in situ* using the chronopotentiometry scan after the current is off for 260 seconds. Since the background current cannot be estimated accurately before the $I(t)$ curve is fully saturated to the background level, and there may be other undetectable reactions (either anodic or cathodic) included in the total charge transfer, we cannot convert the obtained total charge transfer Q (Coul/g) into actual amount of K de-intercalated accurately, i.e., assuming one electron loss corresponds to one K^+ de-intercalated from the KOs_2O_6 surface. There are three plateau regions to be noted in the quasiequilibrated OCP versus Q diagram: one narrow plateau onset near ~ 0.15 V, the second onset near 0.55 V, and the final plateau onset near ~ 0.90 V, which must correspond to the side reaction as discussed above. There exist at least two distinguishable stable phases that are separated by the two-phase plateau regions: One is proximate to the pristine KOs_2O_6 phase, and the second has stoichiometry close to $\text{K}_{0.5}\text{Os}_2\text{O}_6$ as later verified by the EPMA chemical analysis. Following this quasiequilibrium OCP plot, samples of specific potassium content reported in this study have been prepared using corresponding $V_{\text{ap}} = \text{OCP}$, and final potassium contents were determined based on EPMA chemical analysis. Samples prepared using different V_{ap} are summarized in Table I.

B. X-ray diffraction

Figure 3(a) shows an X-ray diffraction (XRD) pattern for the as-grown KOs_2O_6 powder at room temperature. All diffraction peaks can be indexed by a $\text{Fd}\bar{3}m$ structure with lattice constant $a = 10.073(3)$ Å. A few extra peaks labeled with an asterisk correspond to the existence of an OsO_2 impurity phase, and it has been reported that the existence of KOsO_4 and OsO_2 impurity phases are unavoidable for the polycrystalline sample prepared using similar preparation conditions.^{4,11} However, we find that the KOsO_4 impurity can

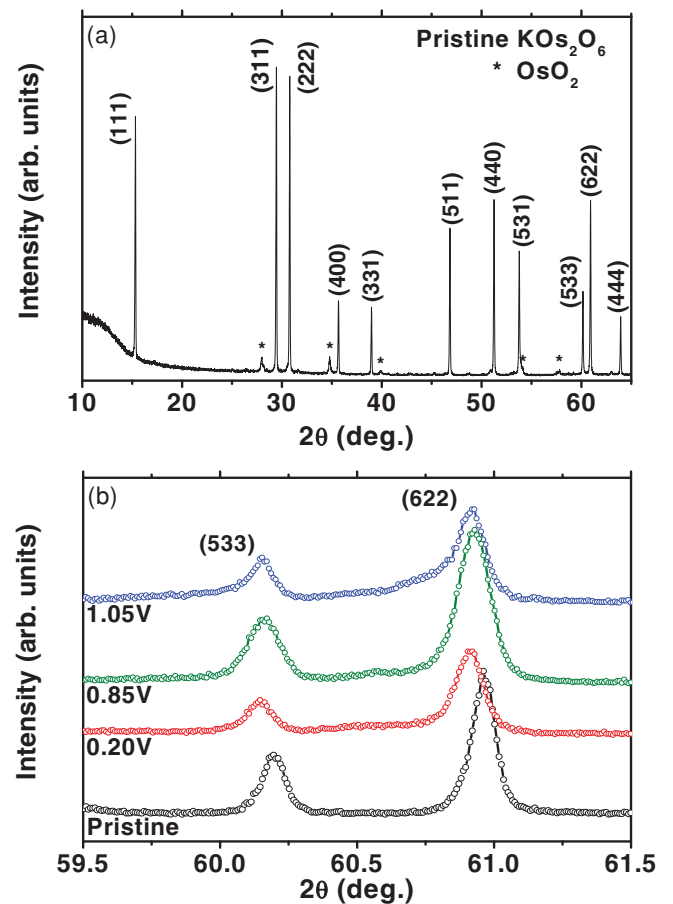


FIG. 3. (Color online) X-ray diffraction (XRD) patterns for (a) the as-grown KOs_2O_6 and (b) various de-intercalated $\text{K}_x\text{Os}_2\text{O}_6$ samples that show slightly shifted diffraction angles.

be washed off with PC solution effectively. Figure 3(b) illustrates the XRD patterns at high angles for the de-intercalated KOs_2O_6 treated with electrochemical de-intercalation at various applied voltages, which indicates the occurrence of a slightly enlarged cell size as a result of application using an even minimal overpotential as low as $V_{\text{ap}} \sim 0.15$ V. It is obvious that high angle diffraction peaks shift to lower after the electrochemical processing, and there are no observable extra diffractions peaks to suggest extra impurity phases generated otherwise.

The lattice parameters calculated from high angle diffraction peaks have been indexed with the $\text{Fd}\bar{3}m$ space group and summarized in Table I. We find that the lattice size has an insignificant ($\lesssim 0.01$ Å) jump from the pristine superconducting sample of KOs_2O_6 in general and levels off quickly to be nearly independent of V_{ap} after $V_{\text{ap}} \sim 0.2$ V and x . Such change occurs immediately after a small overpotential is applied with V_{ap} as low as ~ 0.2 V to induce K reduction, which is rather surprising since the corresponding potassium is reduced by less than 1% only, as indicated in Fig. 2. Water intercalation is a common phenomenon for KOs_2O_6 sample, which causes deterioration of superconductivity and is accompanied by a slight lattice size increase.¹¹ In fact, most reported lattice parameters of the pristine KOs_2O_6 were possibly overestimated as a result of potential water intercalation, whereas our data fall closest to the sample prepared and processed strictly in a dry box.¹¹ Since the hydration is a reversible process, we made all physical property characterization on samples dried at 175 °C for 8 hours beforehand. Contrary to what is expected from potassium reduction through de-intercalation by progressively higher V_{ap} , the lattice size increases while it is expected to decrease when more smaller Os^{6+} ions are generated. It is highly possible that average valence of Os higher than + 5.5 may not be preferred in the pyrochlore structure and induces oxygen defect formation, which is partly supported by the fact that most compounds of high average Os valence prefer a perovskite-type crystal structure, e.g., $\text{Ba}_2\text{CaOsO}_6$ and $\text{Ba}_3\text{LiOs}_2\text{O}_9$.^{14,15}

C. Magnetic susceptibility

Bulk superconductivity of $T_c \sim 9.7$ K has been verified for the pristine KOs_2O_6 sample as shown in Fig. 4 by its superconducting volume fraction of $\sim 20\%$ from the field-cooled data without demagnetization factor correction due to particle geometry. Interestingly, superconducting volume fraction is significantly reduced after a minor ($\sim 1\%$) potassium reduction using $V_{\text{ap}} \gtrsim 0.2$ V while T_c remains about the same, as shown in the inset of Fig. 4(a). Such drastic reduction is concomitant with the relatively sharp increase in lattice size within the same narrow range below $\lesssim 0.20$ V, also shown in Table I, beyond which there is no more lattice change and the superconducting volume fraction is reduced to the trace level before falling into the spin-glass region. In fact, a similar drastic change on the surface potential (OCP) has also been observed at the same time for low V_{ap} in the range ~ 0.16 – 0.26 V (first plateau) as shown in Fig. 2. It is clear that superconductivity exists within an extremely narrow window of stoichiometry KOs_2O_6 and is sensitive to the lattice size. From the point of chemical pressure in a

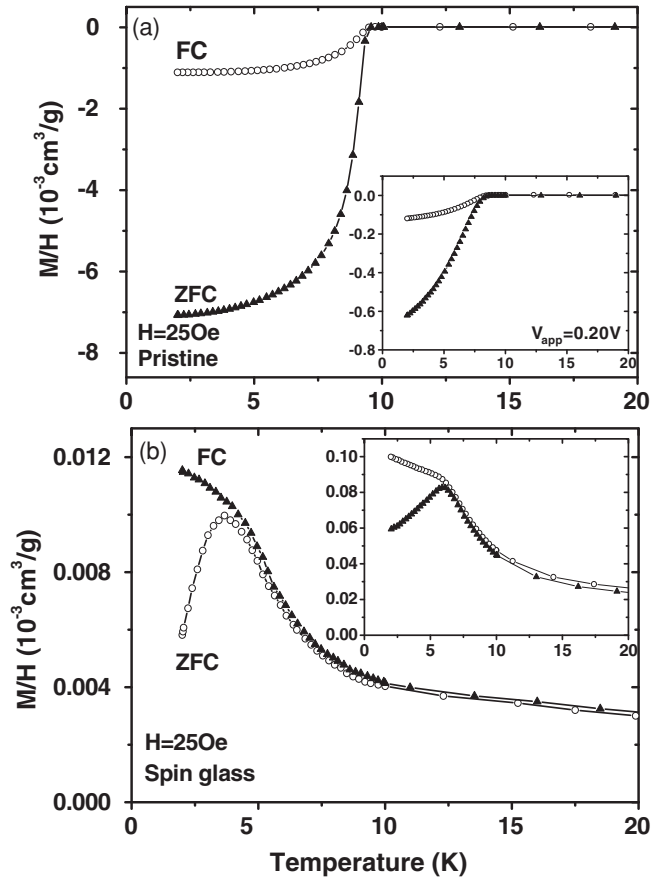


FIG. 4. Temperature dependence of dc average susceptibility for $\text{K}_x\text{Os}_2\text{O}_6$ measured under applied magnetic field of 25 Oe. (a) Superconducting sample of the pristine KOs_2O_6 , and the inset shows a sample with slightly reduced K using $V_{\text{ap}} = 0.20$ V; the latter has a similar T_c onset but with a much lower superconducting volume fraction. (b) Spin glass samples of $\text{K}_x\text{Os}_2\text{O}_6$ ($x \lesssim 2/3$) prepared using $V_{\text{ap}} + 1.16$ V ($T_g \sim 3.3$ K) and $V_{\text{ap}} + 1.05$ V (inset, $T_g \sim 6.1$ K), respectively.

single-band model of a conventional Bardeen, Cooper, and Schrieffer (BCS) picture, the easily enlarged cell size reduces density of state (DOS) effectively to kill superconductivity. If we follow the rattling model interpretation, the requirement of highly stoichiometric KOs_2O_6 implies the importance of phase coherence and intolerance of defects under the rattling model, which can be compared with the similar phenomenon of hydration-reduced superconductivity, especially when the water molecule occupies the $32e$ site, which is near potassium ($8b$ site) and reduces phonon frequency significantly.¹¹

After passing the two-phase region using $V_{\text{ap}} \gtrsim 0.85$ V as indicated by the rough plateau region in Fig. 2, a single-phase sample of $\text{K}_x\text{Os}_2\text{O}_6$ ($x \lesssim \frac{2}{3} - \frac{1}{2}$) has been found to show a spin-glass-like zero field cool/field cool (ZFC/FC) irreversible behavior below $T_g \sim 6.1$ K, as seen in Fig. 4(b). This is the first time observation has been made of a spin-glass-like phase in the β - $\text{K}_x\text{Os}_2\text{O}_6$ system. Consider that the possible random distribution of potassium ions after the reduction, the impact of potassium ion random distribution on its nearby Os spins, and the natural frustration requirement for Os spins in 3D pyrochlore structure provide the perfect necessary conditions

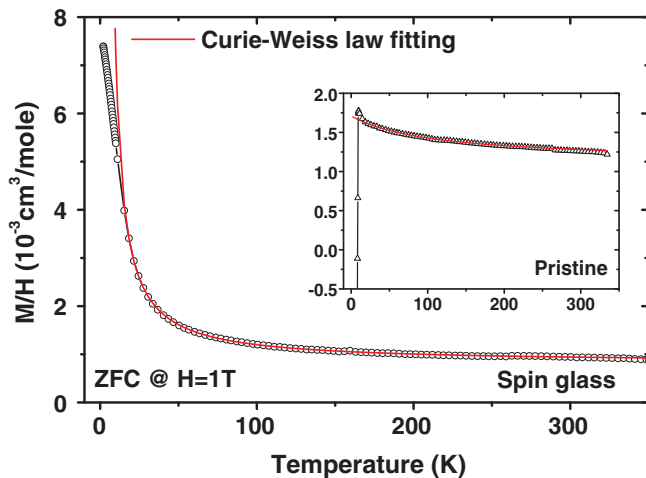


FIG. 5. (Color online) Normal state magnetic susceptibility of $K_x\text{Os}_2\text{O}_6$ as a function of temperature under applied field of 1 Tesla for the (a) pristine powder sample and (b) potassium de-intercalated sample using $V_{\text{ap}} = 1.05$ V. The corresponding low field data are shown in Fig. 4.

for a canonical spin-glass state with localized spins on Os.¹⁶ While it is difficult to secure reliable structure refinement on the low-temperature synthesized powder samples, it is reasonable to assume that the randomness could be coming from the increased occupancy of the $16d$ site (i.e., the preferred site of high-valence A in $\alpha\text{-A}_2\text{B}_2\text{O}_7$) when the original $8b$ site is becoming half empty. We find that as the potassium content is reduced progressively under higher V_{ap} , there is no significant change on the superconducting transition temperature T_c and spin-glass-like transition T_g , although there is a clear relative superconducting volume fraction change, which indicates that only two single phases coexist, and is in agreement with the middle V - Q plateau as shown in Fig. 2. In addition, the application of overpotential to the sample electrode could also induce possible potassium diffusion from the original $8b$ site to the $16d$ site similar to that of the regular α -pyrochlore, which can also partly explain the significant reduction of superconducting volume fraction when only less than $\sim 1\%$ potassium is reduced electrochemically as shown in Table I.

High field magnetic susceptibilities for both the pristine superconducting KOs_2O_6 and the nonsuperconducting de-intercalated $\text{K}_{0.5}\text{Os}_2\text{O}_6$ are shown in Fig. 5. Since the pristine sample is metallic above T_c , the application of the Curie-Weiss law to describe localized spins is not justified for an itinerant system; in fact, the relatively low and weak temperature dependence of $\chi(T)$ does suggest that the contribution seems to be mostly coming from itinerant Pauli paramagnetic spin contribution, assuming all other temperature-independent terms from core diamagnetic and Van Vleck paramagnetic contributions are canceled out. On the other hand, unlike the usually strongly magnetic $3d$ and $4d$ elements, the more spreading $5d$ orbitals make the electron correlations and spin-orbit interactions more complex and unexpected. For example, the semiconducting-metal transition near 225 K found in $\text{Cd}_2\text{Os}_2\text{O}_7$ pyrochlore has been explained in Slater mechanism of local band antiferromagnetic ordering.¹⁷

Enforcing a Curie-Weiss law fitting for $\chi(T)$ as $\chi_o + C/(T - \theta)$ to both the superconducting and spin-glass samples returns satisfactory fitted values of $C \sim 0.061$ and $0.035 \text{ cm}^3 \text{ K/mole}$ plus $\theta \sim -106 \text{ K}$ and -8 K , respectively. The Curie constants are significantly lower than that calculated from the theoretical value for a completely localized spin with average valence of $+5.5$ in a high-spin state.¹⁰ The effective moment for the spin-glass sample calculated from a fitted C value is $\sim 0.53 \mu_B$. For $\text{K}_{0.5}\text{Os}_2\text{O}_6$ in a completely localized ionic picture for an Os ion with octahedral oxygen ligands, the average Os valence is $+5.75$, i.e., $25\% \text{ Os}^{5+} + 75\% \text{ Os}^{6+}$. Comparing the fitted μ_{eff} with the theoretical μ_{eff} estimated from various possible low-spin (LS) and high-spin (HS) combinations, the most probable case is that both are in the LS state (i.e., $25\% \text{ Os}^{5+} = 1/2$ and $75\% \text{ Os}^{6+} = 0$) with a theoretical spin μ_{eff} only of $0.43 \mu_B$. The LS state assumption is in drastic contrast to most of the Os^{5+} compounds with double perovskite structure in a HS state, such as $\text{La}_2\text{NaOsO}_6$,¹⁸ and the triple perovskite $\text{Ba}_3\text{LiOs}_2\text{O}_9$ of mostly HS Os^{5+} ,¹⁴ while $5d$ orbitals are more spreading compared with the usually magnetic $3d/4d$ compounds, which makes the electron correlation and spin-orbit coupling more complex. The current spin only LS implication still could be misleading, and its impact on the spin-glass formation remains unclear. Further characterization using a larger single crystal of improved homogeneity is necessary.

The Weiss temperature θ for the pristine KOs_2O_6 is comparable to that found in $\text{Na}_{1.4}\text{Os}_2\text{O}_6 \cdot \text{H}_2\text{O}$,¹⁰ but θ is found to be significantly reduced for the spin-glass sample $\text{K}_{0.5}\text{Os}_2\text{O}_6$; i.e., the antiferromagnetic correlation among isolated spins is significantly reduced for the latter. The generation of a canonical spin-glass state requires satisfaction of both frustration and randomness conditions, which has led to the puzzling observation on the finding of a spin-glass state in pyrochlore $\text{Y}_2\text{Mo}_2\text{O}_7$ of unclear origin of randomness.¹⁹ Current observation of spin-glass-like behavior in $\text{K}_{0.5}\text{Os}_2\text{O}_6$ implies that the K^+ ions (or oxygen defects, if any) must distribute randomly, most probably between $16d$ and $8b$ sites, and lead to the randomness on top of the tetrahedrally coordinated frustrating Os spin substructure. Because of the limitation on sample quantity and powder inhomogeneity, detailed exploration of spin-glass properties using ac spin susceptibility measurement should be performed once a sizable single-crystal sample is available.

D. Resistivity

Resistivity data for both the pristine superconducting sample KOs_2O_6 and $\text{K}_{0.5}\text{Os}_2\text{O}_6$ with spin-glass-like behavior are shown in Fig. 6. The onset of superconductivity occurs at $T \sim 9.7 \text{ K}$ for KOs_2O_6 is confirmed, with ρ monotonically increases with temperature in a concave curvature. This behavior agrees with data previously obtained using a single-crystal sample,²⁰ where anharmonic potential resulting from the K^+ ion rattling plays an important role. However, we do notice that $\rho(200 \text{ K}) = 12.5 \text{ m}\Omega\text{-cm}$ is 50-fold higher than that in a single crystal. This suggests a significant contribution from the grain boundary scattering in our cold-compressed polycrystalline sample. Nevertheless, the electron-phonon scattering dominates at higher temperature, which gives residual resistiv-

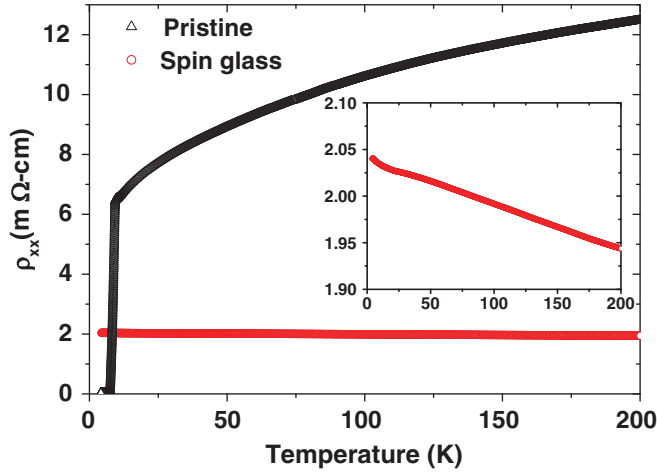


FIG. 6. (Color online) Resistivity versus temperature for the superconducting KOs_2O_6 and spin-glass-like $\text{K}_{0.5}\text{Os}_2\text{O}_6$ samples. The spin-glass sample has $T_g \sim 3.3$ K as shown in Fig. 4(b). The inset shows a detailed view for the $\text{K}_{0.5}\text{Os}_2\text{O}_6$ sample.

ity ratio (RRR) $+\rho(250\text{ K})/\rho(10\text{ K}) \sim 2$. On the other hand, $\rho(200\text{ K}) \sim 1.9\text{ m}\Omega\text{-cm}$ for a spin-glass-like $\text{K}_{0.5}\text{Os}_2\text{O}_6$ sample of $T_g \sim 3.3\text{ K}$ [see Fig. 4(b)] is sixfold smaller than that for the pristine superconducting KOs_2O_6 . It increases only by 5% as T drops to 4.2 K, as shown in the inset of Fig. 6. The significantly weaker T dependence in ρ for $\text{K}_{0.5}\text{Os}_2\text{O}_6$ stands in great contrast to that of the superconducting KOs_2O_6 sample. As pointed out by Nagao *et al.*,⁸ electron-phonon coupling is significantly enhanced by the rattling of alkali ions, which makes KOs_2O_6 a strong-coupling superconductor with the highest T_c in the pyrochlore family. We therefore attribute the strong suppression of T dependence of ρ for the spin-glass-like $\text{K}_{0.5}\text{Os}_2\text{O}_6$ is associated with the removal of rattlers (K^+ ion), which shuts off the electron-phonon coupling that leads to the superconductivity. However, with the complications from the grain boundary scattering and also the disordering from K^+ ion extraction, the weaker T dependence of ρ due to the absence of rattling phonons is further suggested by the specific heat measurements to be discussed next. Further investigation using a single-crystal sample is needed to clarify this issue.

E. Specific heat

Specific heat measurement results for both the pristine and the K^+ de-intercalated samples are shown in Fig. 7. KOs_2O_6 has a pronounced anomaly onset $\sim 9.7\text{ K}$ due to the superconducting phase transition. C/T extrapolates to zero at $T \sim 0$, which indicates a nearly 100% superconducting volume fraction in KOs_2O_6 . Hiroi *et al.* have reported the observation of an additional first-order phase transition near 7.5 K, which can be observed only in a single crystal but never in powder samples.^{21,22} The origin of this additional phase transition below T_c has been suggested to be due to the multipolar transition driven by the octupolar oscillation component.²³ While a current specific heat measurement is based on a powder sample of greater inhomogeneity compared with a single crystal, it is not surprising that one should fail

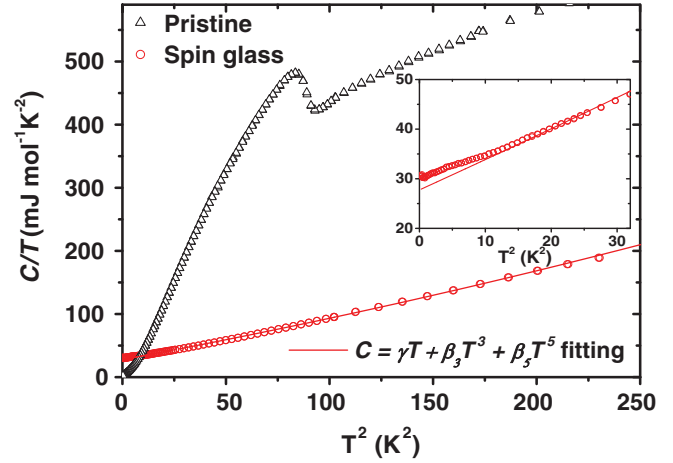


FIG. 7. (Color online) Specific heat measurement results of pristine superconducting KOs_2O_6 and $\text{K}_{0.5}\text{Os}_2\text{O}_6$. This particular batch of reduced potassium has a spin-glass-like transition of $\sim 3.3\text{ K}$ as revealed by the ZFC/FC hysteresis onset in magnetic susceptibility as shown in Fig. 4(b).

to observe such multipolar isomorphous structural transition of first order in nature.

$\text{K}_{0.5}\text{Os}_2\text{O}_6$ carries no sign of superconductivity and behaves like a normal metal. Furthermore, while the magnetization measurements reveal a spin-glass like signature near $\sim 3.3\text{ K}$ [see Fig. 4(b)], there is no apparent associated specific heat peak in this case. The lack of a $C(T)$ peak is exactly one of the features for spin-glass phase transition,¹⁶ owing to the much released entropy above T_g . To further illustrate the spin-glass signature of $C(T)$ in $\text{K}_{0.5}\text{Os}_2\text{O}_6$, $C(T)$ is fit by $C = \gamma T + \beta_3 T^3 + \beta_5 T^5$ above $T^2 > 10\text{ K}^2$, where γT and $\beta_3 T^3 + \beta_5 T^5$ correspond to the electronic and phonon contributions. The fitted results are $\gamma = 27.8\text{ mJ/mol K}^2$, $\beta_3 = 0.607\text{ mJ/mol K}^4$, and $\beta_5 = 0.00049\text{ mJ/mol K}^6$. As seen in the inset of Fig. 7, there exists a small but clear extra contribution beyond the electronic and phonon contributions, which could well be attributed to the spin-glass phase. This spin-glass contribution makes $C(T)$ deviate from the $C = \gamma T + \beta_3 T^3 + \beta_5 T^5$ at $T^2 \lesssim 10\text{ K}^2$, in accord with the observed magnetic susceptibility cusp with onset near 3.3 K.

The phonon contribution to $C(T)$ in $\text{K}_{0.5}\text{Os}_2\text{O}_6$ is another intriguing subject. In both superconducting samples of CsOs_2O_6 and RbOs_2O_6 , phonon contributions were described with dominant $\beta_5 T^5$ term and $\beta_3 \sim 0$.⁸ This anomalous phonon contribution has been argued to be due to the anharmonicity that led to the alkali ion rattling. The investigation of the phonon term for KOs_2O_6 has been claimed to be hindered by its superconductivity with higher T_c . Nevertheless, based on our results shown in Fig. 7, both the magnitude and temperature dependence of $C(T)$ for KOs_2O_6 above T_c are very different from those of $\text{K}_{0.5}\text{Os}_2\text{O}_6$, while the rattling phonon contribution is believed to be similar to that of CsOs_2O_6 and RbOs_2O_6 . The Debye temperature derived from β_3 is $\sim 300\text{ K}$ for $\text{K}_{0.5}\text{Os}_2\text{O}_6$, in contrast to the nearly zero contribution for the reported superconducting samples of $(\text{Cs,Rb})\text{Os}_2\text{O}_6$.⁸ The revival of the lattice contribution of the Debye phonons clearly suggests the absence of rattling in $\text{K}_{0.5}\text{Os}_2\text{O}_6$. Consequently, the rattling-induced superconductivity is not realized

in $\text{K}_{0.5}\text{Os}_2\text{O}_6$ owing to this drastic change of the electron-phonon interaction, which is consistent with the $\rho(T)$ data as shown in Fig. 6. In $\text{K}_{0.5}\text{Os}_2\text{O}_6$, $\gamma = 27.8$ mJ/mol K^2 is much smaller than $\gamma = 70$ mJ/mol K^2 of KOs_2O_6 . It is not clear whether this smaller γ is due to the lower K^+ level or the change in band structure owing to the absence of the rattling electron-phonon interaction.

IV. CONCLUSIONS

In summary, spin-glass-like behavior below ~ 6.1 K is observed when the potassium level is reduced below $\sim \frac{2}{3} - \frac{1}{2}$ from its original level of one through an electrochemical de-intercalation process. The existence of a spin-glass state has been supported by the thermal hysteresis below T_g in dc spin susceptibility and the deviation from the fitting of specific heat in $C(T) = \gamma T + \beta_3 T^3 + \beta_5 T^5$ beyond electronic and phonon contributions below T_g . The randomness and frustration requirement for the existence of spin-glass state could be justified by the randomly distributed K^+ vacancies and the frustrating tetrahedral coordinated Os substructure. An

homogeneous and sizable single-crystal sample is desirable for further investigation on the origin of this newly found spin-glass phase and its deeper connection to the superconducting state.

Based on the rattling model interpretation of superconductivity, the crossover from the superconducting to spin-glass state must be related to the strong suppression of electron-phonon coupling responsible for the occurrence of superconductivity, which has been supported by both the transport and thermodynamic property measurement results. While no clear phase diagram has been mapped using the existing powder samples, the proximity of superconducting and spin-glass states has been once more demonstrated to be similar to that found in the high T_c and iron pnictide superconducting systems.

ACKNOWLEDGMENT

FCC acknowledges the support from National Science Council of Taiwan under project number NSC-98-2119-M-002-021.

*fcchou@ntu.edu.tw

- ¹J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, *Rev. Mod. Phys.* **82**, 53 (2010).
- ²A. P. Ramirez, *Annu. Rev. Mater. Sci.* **24**, 435 (1994).
- ³M. Hanawa, Y. Muraoka, T. Tayama, T. Sakakibara, J. Yamaura, and Z. Hiroi, *Phys. Rev. Lett.* **87**, 187001 (2001).
- ⁴S. Yonezawa, Y. Muraoka, and Z. Hiroi, *J. Phys. Soc. Jpn.* **73**, 1655 (2004).
- ⁵S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, *J. Phys. Soc. Jpn.* **73**, 819 (2004).
- ⁶S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, *J. Phys. Condens. Matter* **16**, L9 (2004).
- ⁷J. Pannetier, *J. Phys. Chem. Solids* **34**, 583 (1973).
- ⁸Y. Nagao, J. I. Yamaura, H. Ogosu, Y. Okamoto, and Z. Hiroi, *J. Phys. Soc. Jpn.* **78**, 064702 (2009).
- ⁹T. Shimojima *et al.*, *Phys. Rev. Lett.* **99**, 117003 (2007)
- ¹⁰Y. G. Shi, A. A. Belik, M. Tachibana, M. Tanaka, Y. Katsuya, K. Kobayashi, K. Yamaura, and E. T. Muromachi, *J. Solid Stat. Chem.* **182**, 881 (2009).
- ¹¹R. Galati, C. Simon, C. S. Knee, P. F. Henry, B. D. Rainford, and M. T. Weller *Chem. Mater.* **20**, 1652 (2008).
- ¹²G. J. Shu, A. Prodi, S. Y. Chu, Y. S. Lee, H. S. Sheu, and F. C. Chou, *Phys. Rev. B* **76**, 184115 (2007).

- ¹³A. W. Sleight, J. E. Gulley, and T. Berzins, *Solid State Chemistry of Energy Conversion and Storage*, in: Advances in Chemistry Series, No. 163, Amer. Chem. Soc. (Washington, D. C., 1971), Chap. 11, p. 195,
- ¹⁴K. E. Stitzer, A. E. Abed, M. D. Smith, M. J. Davis, S. J. Kim, J. Darrie, and H. C. Z. Loye, *Inorg. Chem.* **42**, 947 (2003).
- ¹⁵K. Yamamura, M. Wakeshima, and Y. Hinatsu, *J. Solid Stat. Chem.* **179**, 605 (2006).
- ¹⁶J. A. Mydosh, *Spin Glass: An Experimental Introduction* (Taylor & Francis, New York, 1993).
- ¹⁷D. 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**, 195104 (2001).
- ¹⁸W. R. Gemmill, M. D. Smith, R. Prozorov, and H.-C. zur Loye, *Inorg. Chem.* **44**, 2639 (2005).
- ¹⁹J. E. Greedan, M. Sato, and Xu Yan, *Solid State Commun.* **59**, 895 (1986).
- ²⁰T. Dahm and K. Ueda, *Phys. Rev. Lett.* **99**, 187003 (2007).
- ²¹J. I. Yamaura, M. Takigawa, O. Yamamuro, and Z. Hiroi, *J. Phys. Soc. Jpn.* **79**, 043601 (2010).
- ²²Z. Hiroi, S. Yonezawa, and J. I. Yamaura, *J. Phys. Condens. Matter* **10**, 145283 (2007).
- ²³K. Hattori and H. Tsunetsugu, e-print arXiv:1101.0647v1.