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# A novel isomorphous phase transition in $\beta$ -pyrochlore oxide $\text{KOs}_2\text{O}_6$ : a study using high resolution neutron powder diffraction

Kenzo Sasai<sup>1,3</sup>, Maiko Kofu<sup>1</sup>, Richard M Ibberson<sup>2,4</sup>,  
Kazuma Hirota<sup>3</sup>, Jun-ichi Yamaura<sup>1</sup>, Zenji Hiroi<sup>1</sup> and  
Osamu Yamamuro<sup>1</sup>

<sup>1</sup> Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

<sup>2</sup> ISIS Facility, STFC-Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

<sup>3</sup> Department of Earth and Space Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

E-mail: [yamamuro@issp.u-tokyo.ac.jp](mailto:yamamuro@issp.u-tokyo.ac.jp)

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## Abstract

We have carried out adiabatic calorimetric and neutron powder diffraction experiments on the  $\beta$ -pyrochlore oxide  $\text{KOs}_2\text{O}_6$ , which has a superconducting transition at  $T_c = 9.6$  K and another novel transition at  $T_p = 7.6$  K. A characteristic feature of this compound is that the K ions exhibit rattling vibrations in the cages formed by O atoms even at very low temperatures. The temperature and entropy of the  $T_p$  transition is in good agreement with previous data measured using a heat relaxation method, indicating that the present sample is of high purity and the transition entropy,  $0.296 \text{ J K}^{-1} \text{ mol}^{-1}$ , does not depend on the calorimetric method used. The neutron powder diffraction data show no peak splitting nor extra peaks over the temperature range between 2 and 295 K, suggesting that the  $T_p$  transition is a rather unusual isomorphous transition. Rietveld analysis revealed an anomalous expansion of the lattice and a deformation of the O atom cage below 7.6 K. In the low-temperature phase, the distribution of scattering density corresponding to the K ions becomes broader whilst maintaining its maximum at the cage center. Based on these findings, we suggest that the  $T_p$  transition is due to the expansion of the cage volume and cooperative condensation of the K ions into the ground state of the rattling motion.

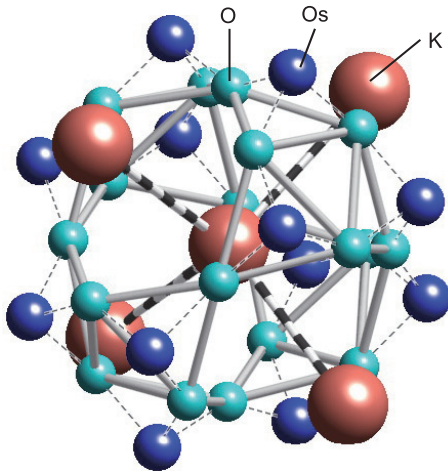
(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

When atoms, ions or molecules are confined in well-defined spaces larger than their diameters, they can exhibit anharmonic vibrations referred to as ‘rattling’. These rattling motions are typically only weakly correlated with surrounding atoms and so have characteristic frequencies independent from those of lattice vibrations. The rattling motions have been investigated in various clathrate and inclusion compounds since Palin

and Powell [1, 2] first recognized a clathrate structure of  $\beta$ -hydroquinone in 1947. More recently, rattling mode behavior has been of renewed interest to many solid state physicists due to the influence it can have on the electrical properties of materials. For example, in skutterudite and some Si- and Ge-based clathrate compounds, the rattling motions act as scatterers of heat transporting phonons which accounts for the thermoelectric properties of these materials [3, 4]. Some of these materials also exhibit superconductivity that is strongly influenced by the rattling vibrations [5]. Yonezawa *et al* [6] discovered that  $\beta$ -pyrochlore oxides,  $\text{AOs}_2\text{O}_6$  where  $A = \text{K}, \text{Rb}$  or  $\text{Cs}$ , exhibit superconducting transitions whose temperature strongly depends on the size of the A ions.

<sup>4</sup> Present address: Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA and The NIST Center for Neutron Research, NIST, 100 Bureau Drive, Gaithersburg, MD 20899, USA.



**Figure 1.** The cage structure of  $\text{KOs}_2\text{O}_6$ .

Figure 1 shows the structure of the rattling cage which consists of osmium cations and oxygen anions. An alkali metal cation, A, is located at the center of the cage with Td symmetry.

Hiroi *et al* [7] suggested that phonons responsible for the electron pairing mechanism are, in fact, rattling motions of the alkali cations. Recently, Raman [8], inelastic neutron [9, 10] and inelastic x-ray [11] scattering studies revealed the existence of such local vibrations in  $\beta$ -pyrochlore oxides. Among a series of  $\beta$ -pyrochlore oxides, only  $\text{KOs}_2\text{O}_6$  exhibits an additional phase transition, accompanied by a  $\lambda$ -type heat capacity anomaly at  $T_p = 7.6$  K, below its superconducting transition temperature  $T_c = 9.6$  K [12–14]. The origin of this novel transition is still unknown. *Ab initio* calculations on  $\text{AOs}_2\text{O}_6$  compounds [15] demonstrate that the effective potential for the K ion is anharmonic and has four shallow minima along each of four  $C_3$  axes, while those of Rb and Cs ions are more harmonic in nature with a minimum at the center of the cage. It has been speculated that the transition is due to localization of the K ions with a breaking of the Td symmetry. Recently Chang *et al* [16] were able to reproduce the heat capacity curves [7] below and above the  $T_p$  transition based on the calculated anharmonic potential [15]. A further possibility is that the transition is isomorphic and the Td symmetry is retained. In the latter case, it is an interesting and difficult problem to understand the nature of the order parameter of the transition. Recent single-crystal x-ray diffraction studies on  $\text{KOs}_2\text{O}_6$  compounds [17] reveal no symmetry breaking but observe small changes of peak intensities occurring below  $T_p$ , indicating the localization of K ions whilst maintaining the density maximum at the center of each cage. This result is partly supported by the recent theoretical works by Hattori *et al* [18].

Neutron diffraction is better suited than x-ray diffraction to investigate subtle structural changes of K and O ions in the presence of heavy Os ions. The scattering cross sections of K (1.96 barn) and O (4.23 barn) ions for neutrons are comparable to that of an Os (14.7 barn) ion, whereas x-ray diffraction data are dominated by scattering from Os. A further advantage of neutron diffraction is that neutrons are scattered by the atomic nucleus and, since the nucleus

is a point scatterer, the neutron scattering cross section can generally be considered to be independent of scattering angle or wavevector,  $\kappa = \sin\theta/\lambda = Q/4\pi$ . The access of high- $Q$  short  $d$ -spacing information is valuable in the precise determination of atomic displacement and in characterizing disordered atoms. Hence, neutron diffraction experiments with high resolution are desirable to give further structural insights on the nature of the  $T_p$  transition. Such measurements are sensitive to additional peaks and/or peak splitting appearing below  $T_p$ . However, if no symmetry breaking is observed, precise Rietveld analysis will help to elucidate the subtle structural change associated with the transition whilst retaining Td symmetry. Medium resolution neutron powder diffraction experiments have recently been done by Galati *et al* [19]. The authors observed no significant change below 7.6 K; however, this is explained by their use of powder samples which do not exhibit the  $T_p$  transition. The  $T_p$  transition has been observed only in single crystals and is sensitive to sample impurities. The impurities are most likely a result from sample exposure to moisture which is more readily absorbed with increased surface area of powder samples [7].

In this work, the heat capacity of  $\text{KOs}_2\text{O}_6$  crystals was first measured using an in-house-built adiabatic calorimeter in order to confirm both the transition temperatures and determine the quality of the sample. These measurements also served to determine the transition entropy by the more accurate adiabatic method compared with the heat relaxation method used in previous studies. High resolution neutron powder diffraction experiments were performed subsequently using HRPD at the ISIS facility, Rutherford Appleton Laboratory, UK.

## 2. Experimental details

$\text{KOs}_2\text{O}_6$  crystals were synthesized using a previously reported method [12, 17]. A sharp heat capacity peak due to the  $T_p$  transition is observed only for high quality single crystals [12–14] as stated above. Accordingly, crystals with clear surfaces and with a size of 50–200  $\mu\text{m}$  were selected using a microscope from 80 synthesized batches. The mass of the sample was 195.3 mg, corresponding to about 4000 single crystals, assuming cubes with an edge of 200  $\mu\text{m}$ . This size of crystal is too large for x-ray powder diffraction but acceptable for neutron powder diffraction since the penetration depth of neutrons is generally much greater than that of x-rays, and the typical beam size for neutron diffraction is much larger than for x-rays. Special care was taken during all sample handling procedures to prevent the samples absorbing moisture from the atmosphere.

Neutron diffraction experiments were performed using HRPD [20] at the ISIS facility, Rutherford Appleton Laboratory, UK. The resolution ( $\Delta d/d$ ) of this instrument is  $4 \times 10^{-4}$  and is effectively constant as a function of  $d$  spacing. The cone-like detector bank of HRPD was suitable for the present experiment using a relatively large size of crystals since neutron intensity averaged along a Debye–Scherrer ring can be recorded automatically. The sample was sealed using an indium gasket in a standard 5 mm diameter

vanadium can under He gas. A top-loading vanadium-tailed liquid- $^4\text{He}$  ‘orange’ cryostat was used for the low-temperature measurements. Data were recorded initially over the temperature range 2–50 K, using short run times in order to determine the temperature dependence of the cubic lattice constant  $a$ . The temperature step of each run was 1–2 K and the duration of each measurement was typically 1 h below 15 K and 30 min above 15 K. For detailed structural analysis, data were subsequently recorded at 1.5, 6, 9 and 15 K with run times of some 15 h. Background data at 4 K with no sample were also recorded. In this case the background scattering, for example vanadium Bragg peaks, is comparable with the sample intensity, given the small mass of the sample (195.3 mg) as described later.

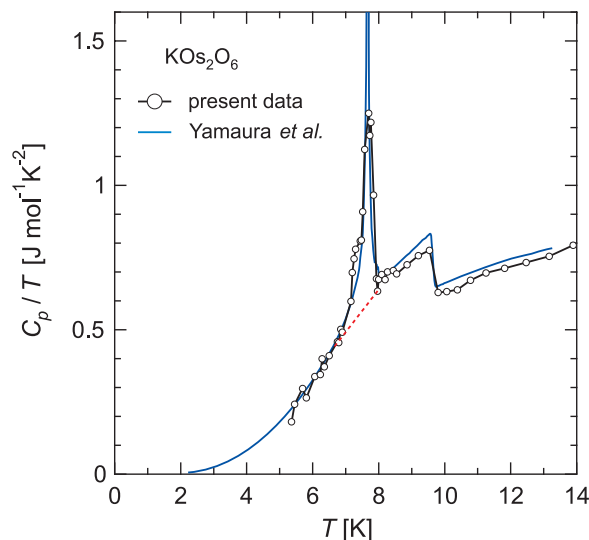
Heat capacity measurements were performed with an in-house-built calorimeter [21] in the temperature range 5–30 K. The sample of 195.3 mg, which is the same as used subsequently in the HRPD experiment, was loaded into the copper cell with an inner volume of 5.83 cm<sup>3</sup> and mass of 10.66 g. The ratio of the sample mass to the total mass was 1.8%, which is about 10 times smaller than for standard measurements. The accuracy of the present heat capacity measurement ( $\Delta C_p/C_p = 1\text{--}2\%$ ) is therefore much reduced as compared with typical measurements (approx. 0.1%) using this calorimeter.

### 3. Results

#### 3.1. Heat capacity

Figure 2 shows the heat capacity of  $\text{KOs}_2\text{O}_6$ . A  $\lambda$ -type transition and a second-order transition, which corresponds to the superconducting one, appeared at 7.6 K and 9.6 K, respectively. These heat capacity data are in good agreement with the data of Yamaura *et al* [17] also shown in figure 2. The shoulder of the peak may be due to a minor portion of the sample with reduced transition temperatures by impurities. Such a decrease in the transition temperature was observed in previous reports [7, 12–14]. The first-order component, latent heat, of the transition, recently found by Yamaura *et al* [17], was not observed because the temperature increment of each measurement, approx. 0.2 K, is larger than the first-order region of the transition, approx. 0.05 K. The present heat capacity data indicate that the present sample, comprising around some one thousand small crystals from 80 synthesis batches, is substantially the same as Yamaura’s sample of four single crystals, totaling 1 mg from a single batch.

By subtracting the baseline, as shown in figure 2, the total entropy change  $\Delta S$  due to the  $T_p$  transition was estimated to be 0.296 J K<sup>-1</sup> mol<sup>-1</sup> including the effect of the shoulder. This value is also similar to  $\Delta S$  (=0.280 J K<sup>-1</sup> mol<sup>-1</sup>) obtained by Yamaura *et al* [17]. It is significant that very similar values were obtained by the adiabatic and heat relaxation techniques because the heat relaxation method sometimes provides only an estimate of the transition entropy, especially in the case of a first-order transition. The transition entropy, 0.296 J K<sup>-1</sup> mol<sup>-1</sup>, which has considerable magnitude although smaller than  $R \ln 2$ , suggests that the  $T_p$



**Figure 2.** Heat capacities of  $\text{KOs}_2\text{O}_6$  crystals. Open circles denote the present data by adiabatic calorimetry and the gray line denotes the previous data [17] by the heat relaxation method. The dashed line gives the baseline for the  $T_p$  transition.

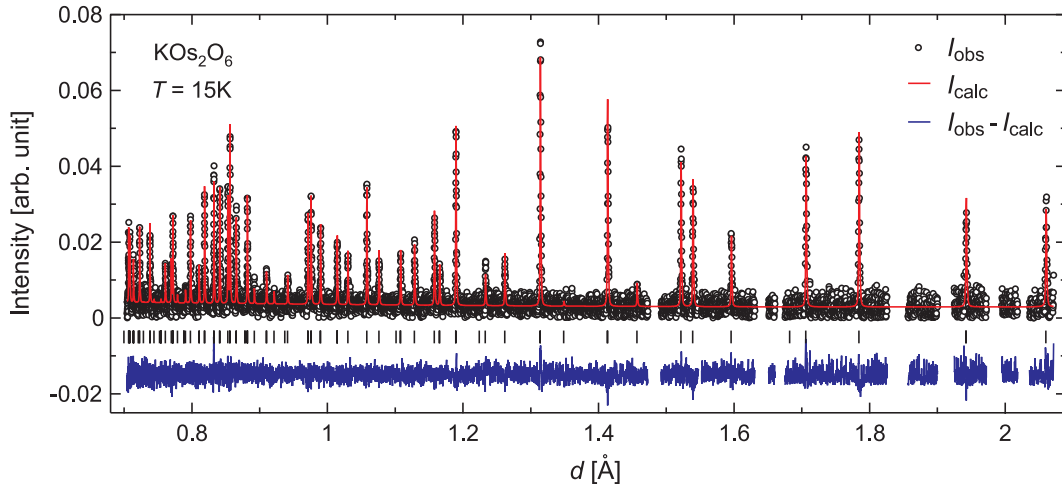
transition is not of a simple order–disorder type ( $\Delta S > R \ln 2$ ) nor of a simple displacive type ( $\Delta S \sim 0$ ).

#### 3.2. Neutron powder diffraction

Figure 3 shows the 15 K data and is representative of the powder diffraction patterns of  $\text{KOs}_2\text{O}_6$ . The background intensity due to sample environment equipment is subtracted. All of the diffraction peak positions were indexed well using space group  $Fd\bar{3}m$ .

Rietveld analyses against the diffraction data obtained at 1.5, 6, 9 and 15 K were performed using the GSAS program suite [22]. The data were refined over the time-of-flight range of 35–100 ms, corresponding to the  $d$ -spacing range of 0.7–2.1 Å. Space group  $Fd\bar{3}m$  was assumed, therefore the refinable structural parameters used for fitting were the lattice constant  $a$ , the fractional coordinate  $x_{\text{O}}$  of the O atom at the 48f site and the isotropic atomic displacement factors  $U_{\text{iso}}$  of the K, Os and O atoms. In addition to the structural parameters, three background terms, one absorption, one extinction and two sample-dependent peak profile parameters were refined. The final Rietveld fit is shown in figure 3 and structural parameters obtained at 15 K are given in table 1. Despite the large background of the data, caused by the small quantity of the sample, precise Rietveld analysis was viable, given the small number of refinable parameters owing to the high crystal symmetry and also because of limited peak overlap, again due to the high symmetry and also the high resolution of the diffractometer.

Figure 4 shows the profiles of the (931) peak at various temperatures, which are sensitive to the structural parameters of the K atom based on calculations of the structure factor of each atom. The integrated intensities of the peaks are also shown in the inset. Neither peak splitting nor peak broadening was observed below  $T_p$ . This observation was confirmed



**Figure 3.** Neutron powder diffraction pattern of  $\text{KOs}_2\text{O}_6$  at 15 K. The horizontal axis is converted from time-of-flight to  $d$  spacing. The open circle represents observed data, the gray line is a calculated pattern from the Rietveld analysis and the lower solid line is the difference between the observed and calculated intensities. The tick marks give the peak positions' calculated pattern from the Rietveld analysis. Excluded regions correspond to V and Cu Bragg peaks from sample environment equipment.

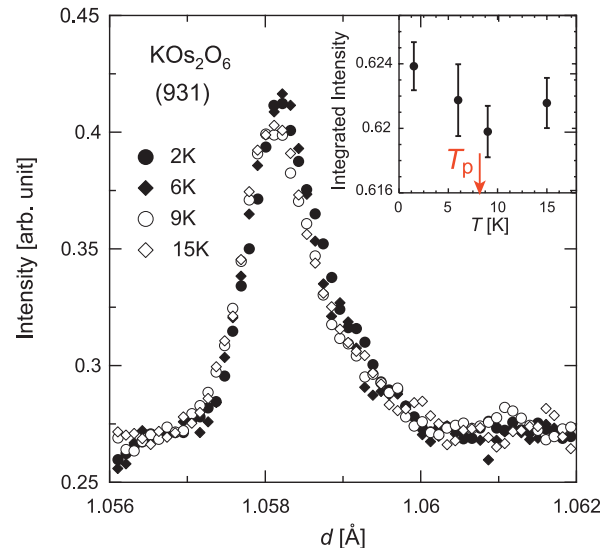
**Table 1.** Structural parameters of  $\text{KOs}_2\text{O}_6$  at 15 K.  
 $a = 10.09203(3)$ ,  $Fd\bar{3}m$ ,  $wR_p = 0.0212$ ,  $R_p = 0.0177$ ,  $S = 1.08$ .

Atom	Site	$x$	$y$	$z$	$U_{\text{iso}}$
K	8b	0.375	0.375	0.375	0.0143(11)
Os	16c	0.0	0.0	0.0	0.0017(6)
O	48f	0.318 18(13)	0.125	0.125	0.0056(6)

for other well-separated peaks with adequate intensity. The present result clearly shows that the symmetry of the  $\text{KOs}_2\text{O}_6$  crystal is not changed at the transition, indicating that the transition is isomorphic. This is consistent with the recent single-crystal x-ray diffraction data and  $^{39}\text{K}$  NMR data [17]. Another interesting aspect of figure 4 is that the peak intensity increases below  $T_p$ . This reflects a change in the atomic displacement parameter of the K atoms as described below.

Figure 5 shows the temperature dependence of the lattice constant  $a$  determined from the Rietveld analysis of the short run time data described in section 2. Surprisingly, the lattice constant increases significantly at  $T_p$ . The increase is 0.001 Å, corresponding to 0.01% of the lattice constant and 0.03% of the total cell volume. The volume change associated with a transition from a ‘more disordered’ high-temperature phase to a ‘more ordered’ low-temperature phase is usually negative. Therefore the volume expansion observed in the low-temperature phase is unique and can be a key to elucidate the mechanism of the phase transition.

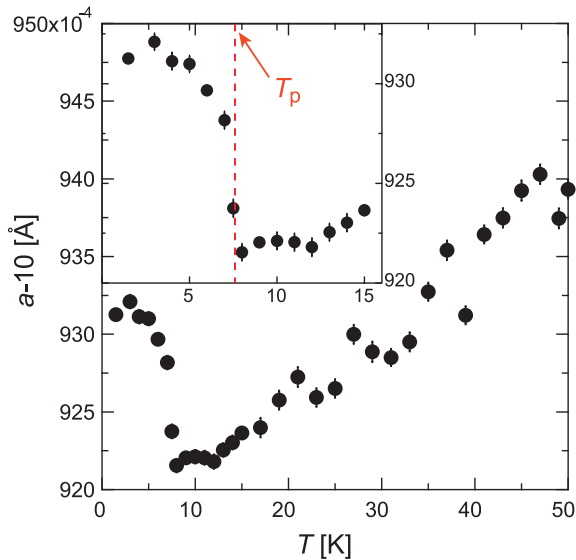
Figure 6 shows the temperature dependence of the fractional coordinate of the O atom  $x_O$ , which is the only fractional coordinate refined during profile fitting. On decreasing temperature,  $x_O$  decreases linearly, showing no significant change on passing through the phase transition temperature. However, it should be noted that this change in  $x_O$  is itself unusual since the structures of metal oxides and ionic crystals are usually rigid below 10 K. The observed decrease of  $x_O$  results in the change of the K–O atomic distance by +0.3% and the nearest-neighbor O–O atomic distance by –0.4%.



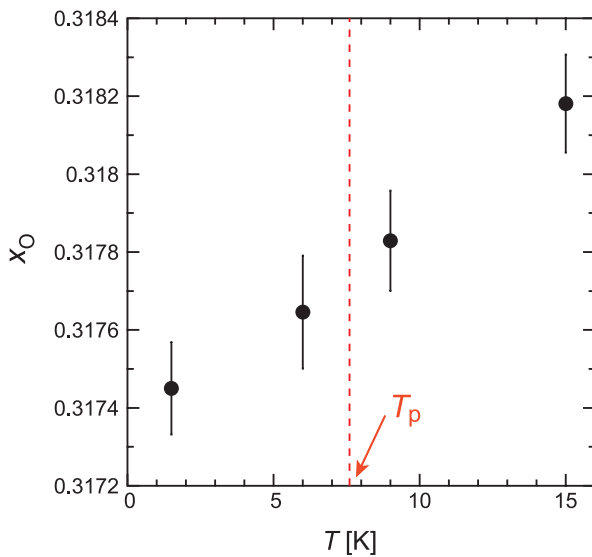
**Figure 4.** Peak profiles of the (931) reflection of  $\text{KOs}_2\text{O}_6$  at 1.5, 6, 9 and 15 K. Inset: the intensity of the peaks integrated in the  $d$ -spacing region between 1.0567 and 1.0608 Å.

Figure 7 shows the temperature dependence of the isotropic displacement parameters  $U_{\text{iso}}$  of the K, Os and O atoms. On decreasing temperature,  $U_{\text{iso}}$  (Os) and  $U_{\text{iso}}$  (O) show little variation while  $U_{\text{iso}}$  (K) abruptly increases across  $T_p$ . This increase of a  $U_{\text{iso}}$  value in the low-temperature phase is also quite unusual. This effect is consistent with the recent work by Yamaura *et al* [17]. In their difference Fourier analysis using the x-ray diffraction data on a  $\text{KOs}_2\text{O}_6$  single crystal, below  $T_p$  the distribution of scattering density of the K ion becomes broader, although the maximum density still resides at the center of the cage.

It is worth doing a further neutron diffraction experiment using a single crystal of  $\text{KOs}_2\text{O}_6$  to make more detailed structural analyses, e.g. using models with off-centered



**Figure 5.** Temperature dependence of the lattice constant  $a$ . The inset shows the enlarged figure around the  $T_p$  transition. Two sets of data from the short-time and long-time runs are plotted. The error bar corresponds to the estimated standard deviations obtained in the Rietveld analysis.

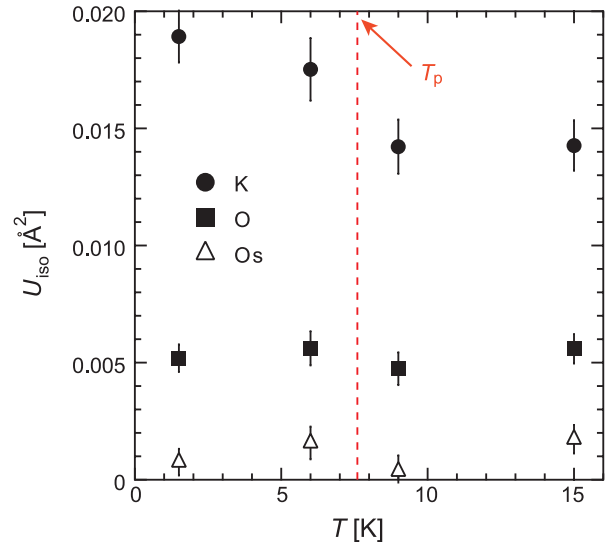


**Figure 6.** Temperature dependence of the fractional coordinate of oxygen  $x_O$ . The data from the long-time runs are shown. The error bars correspond to the estimated standard deviations obtained in the Rietveld analysis.

positions and/or anisotropic atomic displacement parameters of the K ions. A difference Fourier analysis and maximum entropy method will also provide more precise information on the distribution of the K ions in the cages.

#### 4. Discussion

The experimental observations for the  $T_p$  transition may be summarized as follows. Firstly, heat capacity measurements suggest that it is a clear  $\lambda$ -type transition with slight



**Figure 7.** Temperature dependence of the isotropic atomic displacement factors  $U_{iso}$ . The data from the long-time runs are plotted. The closed circles, open triangle and closed squares represent the quantities for K, Os and O atoms, respectively. The error bars correspond to the estimated standard deviations obtained in the Rietveld analysis.

latent heat [17]. Second, the transition entropy is about  $0.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , indicating that the transition is not a simple order–disorder transition. Diffraction data indicate that the symmetry of the crystal does not change at the transition, implying an unusual isomorphous transition. The transition is accompanied by an anomalous expansion of the lattice and increase of the isotropic atomic displacement parameter of the K ion on cooling. The position of the O atoms continues to change with temperature even below 10 K. The maximum scattering density of the K ion remains at the cage center even below  $T_p$ . Finally, there is evidence for some dynamic change of the K ion at  $T_p$  in the  $T_1$  measurement of  $^{39}\text{K}$ -NMR [17]. From all of this experimental evidence, it is most likely that the rattling motion of the K ion plays an important role in the transition.

$\text{KOs}_2\text{O}_6$  is not an obvious candidate for isomorphous phase transition behavior. Isomorphous transitions have been observed in lanthanide metals such as Ce and related rare earth compounds [23]. In these cases, the valence states of the rare earth metals are changed cooperatively with an accompanying volume expansion or contraction of the lattice. Therefore, the cell volume is an order parameter of the transition. This mechanism of the transition is supported by the fact that the transition is very sensitive to pressure. Another example of electronic isomorphous transitions is the Mott transition observed, for example, in Cr-doped  $\text{V}_2\text{O}_3$  [24]. There are some reports of isomorphous transitions without a change of electronic state.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  exhibits a higher-order phase transition with a symmetrical heat capacity anomaly at 218 K [25, 26]. X-ray [27] and neutron [27, 28] diffraction experiments revealed that the transition is due to the orientational ordering of  $\text{H}_2\text{O}$  molecules with keeping the space group  $P2_1/c$  and unit cell size. This isomorphous transition is reproduced well by a

statistical mechanics model called the dimer model [29]. In Ba- or K-doped Si clathrates, which have the rattling motions of Ba and K atoms as in the present study, isomorphic transitions with volume change appeared around 15 GPa in the rough x-ray powder diffraction experiments [30, 31]. The present case of  $\text{KOs}_2\text{O}_6$  is therefore the second observation of a structural isomorphic transition confirmed by precise diffraction experiments. However, this transition is rather similar to those of the lanthanide metals in the sense that they are cubic-to-cubic transitions and have characteristic volume changes at the transitions.

The following mechanism for this novel transition is suggested. With decreasing temperature, the cage of the O atoms surrounding the K ion tends to deform so that the cage is enlarged. At the transition temperature, the rattling K ions are condensed into a ground state to reduce kinetic energy in the enlarged space. The cage volume, the order parameter of the transition, significantly expands at the transition temperature to lower the potential energy of the K ions. The wavefunction of the rattling in the ground state of the low-temperature phase should be expanded relative to those of the excited states of the high-temperature phase since the cage volume of the low-temperature phase is larger than that of the high-temperature phase. In summary, the transition is the condensation from excited rattling states into a ground state with a more extended wavefunction and larger cage volume. The rattling state of the K ion may correspond to the valence state of the rare earth metal system described above [23].

Given this proposed phase transition mechanism, inelastic neutron spectroscopy using a high-energy resolution spectrometer is an important next experimental step. These measurements would be expected to show an increase in the intensity corresponding to the rattling mode peak below  $T_p$  since most of the K ions are in the ground state. There may also be a slight shift of the rattling frequency below  $T_p$ . To date there has been no inelastic neutron scattering data measured using high quality  $\text{KOs}_2\text{O}_6$  crystals; however, these experiments are now in the planning stage. A high pressure investigation of the  $T_p$  transition is also of interest. Based on the model presented here,  $T_p$  should decrease and finally disappear with the application of pressure as in the case of quantum critical systems [32, 33].

## 5. Conclusion

We have performed adiabatic calorimetric and neutron powder diffraction experiments on the  $\beta$ -pyrochlore oxide  $\text{KOs}_2\text{O}_6$  to investigate the mechanism of the novel transition at  $T_p = 7.6$  K. Adiabatic calorimetry confirmed that the present sample is of high quality and the transition entropy,  $0.296 \text{ J K}^{-1} \text{ mol}^{-1}$ , agreed with the previous data by the heat relaxation method. Neutron powder diffraction data showed neither peak splitting nor the appearance of extra peaks over the temperature range between 2 and 295 K, indicating that the  $T_p$  transition is isomorphic in nature. Rietveld analysis revealed an unusual expansion of the lattice and deformation of the oxygen atom cage associated with the  $T_p$  transition and onset of the low-temperature phase. In this phase, the scattering density distribution of the K ions becomes broader, though still with

a maximum value at the cage center. This suggests a model of the transition that is due to a condensation of the K atoms from their rattling state to a ground state with an expanded wavefunction residing in a larger cage volume.

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