Raman scattering on KOs$_2$O$_6$

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Abstract. KOs$_2$O$_6$ with a $\beta$-pyrochlore structure undergoes a superconducting transition at $T_C = 9.6$ K, which is highest transition temperature among a series of compounds, AO$_x$Os$_2$O$_6$ ($A$=K, Rb, and Cs). To investigate structures and anharmonicity of vibrations of K, Raman scattering spectra were measured from 4 K to room temperature. A result at room temperature showed that the observed spectra were completely consistent to a structure with a space group Fd$\bar{3}$m among previously reported two structures. A vibration of K, $T_{2g}$ mode with 70 cm$^{-1}$, exhibits large anharmonicity, and the similar large anharmonicity has been also found for oxygen $E_g$ and $T_{2g}$ modes around 250 cm$^{-1}$. Therefore, not only K vibrations but also the oxygen vibrations are important to discuss the superconductivity and/or another transition at 7.5 K.

1. Introduction

AO$_x$Os$_2$O$_6$ ($A$=K, Rb, and Cs) are superconducting compounds with transition temperatures ($T_C$), 9.6 K, 6.3 K, and 3.3 K, respectively[1–5]. They have a $\beta$-pyrochlore structure, which is similar to conventional pyrochlore structure. Although only Cd$_3$Re$_2$O$_7$[6–8] shows superconductivity below 1.0 K among pyrochlore compounds, the $\beta$-pyrochlore compounds have relatively high $T_C$. A characteristic feature of the $\beta$-pyrochlore structure is that an A ion is weakly bounded in a very large space. In fact, large fluctuation of the A ions and anomalous lattice specific heat have been reported[4, 9–12]. From these observations, it is considered that the large amplitude of A ion vibrations relates to their high transition temperatures.

Vibrations of weakly bounded atoms show large anharmonic effects because of their large vibrational amplitude. In this case, their energies increase with increasing temperature, because of fourth-order potentials. This anharmonic effect has been recently reported[13–15] for compounds with a large cage and a small guest atom. Large amplitude of vibrations is important for a phonon to affect electric properties through electron-lattice interaction in addition to large interaction coefficients. It is interesting to clarify what phonons have large vibration and show large anharmonic effects.

KO$_x$Os$_2$O$_6$ has another transition at $T_p = 7.5$ K[4, 12, 16]. Since the transition is almost independent of magnetic field, it is considered as a structural transition. However, its microscopic detail remains unclear. On the other hand, two different structures have been reported by x-ray diffraction at room temperature as the space group of Fd$\bar{3}$m[9] or F$\bar{4}$3m[10]. Then, other method is necessary to determine the structure at room temperature. Raman scattering experiments are very sensitive to structural deformations and, especially, are useful to distinguish between similar structures with different symmetry.
Table 1. Irreducible representations of lattice vibrations of the Fd$\bar{3}$m and F$\bar{4}$3m structures for each atom with a wavevector $q = 0$. The Raman active representations are underlined.

| space group | atom | representations                              |
|-------------|------|----------------------------------------------|
| Fd$\bar{3}$m | K    | $T_{1u} \oplus T_{2g}$                       |
|             | Os   | $A_{2u} \oplus E_{u} \oplus 2T_{1u} \oplus T_{2u}$ |
|             | O    | $A_{1g} \oplus A_{2u} \oplus E_{g} \oplus E_{u} \oplus 2T_{1g} \oplus 3T_{1u} \oplus 3T_{2g} \oplus 2T_{2u}$ |
| F$\bar{4}$3m | K    | $2T_{2}$                                     |
|             | Os   | $A_{1} \oplus E \oplus T_{1} \oplus 2T_{2}$  |
|             | K    | $2A_{1} \oplus 2E \oplus 4T_{1} \oplus 6T_{2}$ |

Raman spectra of KO$_2$O$_6$ have been measured from 4 K to room temperature to clarify the anharmonicity of lattice vibrations and its structures at room and low temperatures.

2. Experimental procedure

Single crystals of KO$_2$O$_6$ were synthesized as reported previously[1, 9]. Raman spectra were measured on as-grown surfaces and the crystal axes were determined from polarization dependences of Raman spectra. Polarization of incident and scattered light are described as ($yz$), where the left vector and the right vector in the parentheses are directions of electric field of incident light and scattered light, respectively. Propagation directions of incident light and scattered light are omitted because back scattering configuration was used.

Raman spectra were measured by a triple-monochromator (JASCO NR-1800) and a liquid-N$_2$ cooled CCD detector (Princeton Instruments Inc. LN/CCD-1100PB). For excitation light, 514.5nm line of an Ar$^+$ laser (Modu-Laser STELLAR-PRO-L) was used with a monochromator to select the wavelength. A power of the incident light was 10 mW before a sample surface.

3. Result and discussion

Two structures with the space group Fd$\bar{3}$m[9] or F$\bar{4}$3m[10] have been reported at room temperature. A difference between two structures is a size of empty regular octahedra which were surrounded by four OsO$_6$ octahedra. The F$\bar{4}$3m structure is slightly distorted from the Fd$\bar{3}$m structure and has no inversion. As a result, the F$\bar{4}$3m structure has more Raman active phonons than the case of Fd$\bar{3}$m. Therefore, Raman spectra can determine the structure at room temperature.

The irreducible representations of lattice vibrations with a wavevector $q = 0$ for each atom are shown in Table 1 for both structures. The Fd$\bar{3}$m structure has 6 Raman active phonons with $A_{1g} \oplus E_{g} \oplus 4T_{2g}$ and 5 infrared active phonons with $5T_{1u}$. For the F$\bar{4}$3m structure, $3A_{1} \oplus 3E \oplus 9T_{2}$ become Raman active and 9$T_{2}$ modes in them are also infrared active. A soft mode from the Fd$\bar{3}$m structure to the F$\bar{4}$3m structure is $A_{2u}$ in the Fd$\bar{3}$m structure. The $A_{2u}$ representation in Fd$\bar{3}$m becomes Raman active $A_{1}$ representation in F$\bar{4}$3m. Therefore, if the structure at room temperature is the F$\bar{4}$3m, the soft mode can be observed at a low energy as a $A_{1}$ representation of the space group F$\bar{4}$3m.

Observed spectra on a [110] surface are shown in Fig. 1, where the irreducible representations of observed peaks are also presented. The representations of the peaks were determined by their polarization properties. The vectors in the figure are $s = (0.5 \ -0.5 \ 0.71)$, $t = (0.5 \ -0.5 \ -0.71)$, $u = (1 \ -1 \ 0)$, and $z = (0 \ 0 \ 1)$. As seen in the result, observed spectra are completely consistent to the Fd$\bar{3}$m structure, i.e., the representations of the observed six peaks are $A_{1g} \oplus E_{g} \oplus 4T_{2g}$. 

The $A_1$ soft mode which is expected in the $F\bar{4}3m$ structure was not observed above $25$ cm$^{-1}$. Moreover, any other additional modes were not found, in spite of the relatively large reported structural distortion. Therefore, we conclude that the structure at room temperature is the $Fd\bar{3}m$ structure or that structural distortion from the $Fd\bar{3}m$ structure is very small. This conclusion is also suggested by recent detailed analysis of structure using X-ray and electron diffraction measurements\[17\]. As the number of $T_{2g}$ modes are four, they are numbered from the lower energy as $T_{2g}(1)$, $T_{2g}(2)$, $T_{2g}(3)$, and $T_{2g}(4)$. The lowest energy $T_{2g}(1)$ mode is considered as a vibration of potassium ions, and the other modes are oxygen vibrations.

Measurements below room temperature were performed on a [111] surface. Although there are two transition, $T_C$ and $T_p$, no obvious difference among the spectra was found around these temperatures. Since the change at $T_p$ is very small in the results of X-ray diffraction\[9\], more accurate measurements will be necessary to detect the change, e.g., measurements below $25$ cm$^{-1}$ and higher resolution measurements.

Raman spectra with parallel polarization on a [111] surface at several temperatures are shown in Fig. 2, where the energies of the $T_{2g}(1)$, $T_{2g}(2)$, and $E_g$ modes are depicted by circles and triangles. As clearly seen, the energies of these three modes increase with increasing temperature. The anomalous result indicates that these modes are affected by large anharmonic interactions. About the other modes, the energy of the $A_{1g}$ mode is almost temperature independent and that of the $T_{2g}(4)$ mode decreases at high temperatures. The $T_{2g}(3)$ mode was not clearly observed because of its weak intensity. In the cage compounds where Raman spectra has been measured\[13–15\], only vibrations of guest ions in a cage show large anharmonicity. However, in KO$\text{S}_2$O$_6$ not only K vibration ($T_{2g}(1)$) but also oxygen vibrations show anharmonic temperature dependence. Energy differences between room temperature and 4 K are $8.9$ cm$^{-1}$, $4.0$ cm$^{-1}$, and $7.0$ cm$^{-1}$ for $T_{2g}(1)$, $T_{2g}(2)$, and $E_g$, respectively. It is worth to note that the difference is quite large compared with other cage compounds\[13–15\].

Line widths of $A_{1g}$, $E_g$, $T_{2g}(1)$, and $T_{2g}(2)$ modes decrease linearly at low temperatures. This temperature dependence will be generated by scattering processes produced by low-energy phonons and electric excitations. Since the line widths have similar gradient, these modes are similarly influenced by thermally excited fluctuations. Therefore, differences of the widths at 4 K suggest the differences of magnitude of electron-lattice interactions. Thus, the K mode ($T_{2g}(1)$) has not so large electron-lattice interaction in comparison with oxygen modes.

The line width of $T_{2g}(4)$ is very large, but almost temperature independent. This result indicates that the lifetime of $T_{2g}(4)$ is determined mainly by strong electron-lattice interactions. Among the Raman active modes, the $T_{2g}(4)$ mode is the only mode where bond lengths between
Os and oxygen are significantly modified. It is natural that the mode has large electron-lattice interactions, because electronic states near Fermi-surfaces are constructed by d-electrons of Os and p-electrons of oxygen[12, 18, 19].

4. Conclusions
Raman spectra of KOs$_2$O$_6$ were measured from 4 K to room temperature. Although two structures with space groups Fd$ar{3}$m and F$ar{4}3$m has been suggested at room temperature, present results showed that the structure at room temperature is the Fd$ar{3}$m structure, and all Raman active phonons in the Fd$ar{3}$m structure were assigned. No remarkable change of the spectra has been found at the superconducting transition temperature, 9.6 K, and at the first-order transition temperature, 7.5 K. Since the change at 7.5 K is very small according to the results of X-ray diffraction[9], measurements below 25 cm$^{-1}$ and higher resolution measurements are necessary.

As expected from anomalously large atomic displacement parameter of potassium, the T$_{2g}$(1) mode, which is a vibration of potassium, showed large anharmonicity so that the energy at 4 K decreased by 8.9 cm$^{-1}$ from that at room temperature. This change in energy is very large in comparison with other cage compounds[13–15]. In addition, energies of the T$_{2g}$(2) and E$_g$ modes, which are vibrations of oxygen, showed as large change as that of the T$_{2g}$(1) mode. This result indicates that vibrations of oxygen also have large amplitude and large anharmonicity. Therefore, not only K vibrations but also the oxygen vibrations are important to discuss the superconductivity and/or another transition at 7.5 K.

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