Raman scattering investigation of $\beta$-pyrochlore osmium oxides, $\text{AOS}_2\text{O}_6$ (A=K, Rb, and Cs)

T. Hasegawa$^1$, Y. Takasu$^2$, N. Ogita$^1$, J. Yamaura$^3$, Y. Nagao$^3$, Z. Hiroi$^3$, M. Udagawa$^1$

$^1$Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima, 739-8521, Japan
$^2$St. Marianna University School of Medicine, Kawasaki, 216-8511, Japan
$^3$Institute for Solid State Physics, The University of Tokyo, Kashiwa, 277-8581, Japan
E-mail: has@hiroshima-u.ac.jp

Abstract. Raman scattering spectra of RbOs$_2$O$_6$ and CsOs$_2$O$_6$ have been measured from 4 K to 300 K. Among six Raman active modes, we focus on $T_{2g}$ mode of alkaline atoms and $E_g$ mode of oxygen. Width of the $T_{2g}$ mode becomes quite large in KOs$_2$O$_6$. This is caused by very lower-frequency fluctuation and a candidate of the fluctuation is $T_{1u}$ mode, which is another vibration of alkaline atoms. Large frequency changes of the $E_g$ mode are found in KOs$_2$O$_6$ and RbOs$_2$O$_6$ in the temperature dependence. The large changes relate to low-frequency oxygen modes, which will be $E_u$ mode. Therefore, the frequency of the $T_{1u}$ mode becomes very small in KOs$_2$O$_6$, and the frequency of the $E_u$ mode becomes small in KOs$_2$O$_6$ and RbOs$_2$O$_6$. Since only KOs$_2$O$_6$ is considered as a strong-coupling superconductor, the $T_{1u}$ mode will play a very important role in superconductivity.

1. Introduction

$\beta$-pyrochlore compounds, $\text{AOS}_2\text{O}_6$ (A=K, Rb, and Cs), are superconductors with transition temperature ($T_c$), 9.6 K, 6.3 K, and 3.3 K, respectively[1–6]. Structure of the $\beta$-pyrochlore compounds is similar to that of $\alpha$-pyrochlore compounds, e.g. Cd$_2$Re$_2$O$_7$. Alkaline A atom of AOs$_2$O$_6$ corresponds to the Cd$_2$O unit in Cd$_2$Re$_2$O$_7$, thus, A atom are placed in a large space surrounded by Os-O network structure. Since the A atoms interacts weakly with the cage network, atomic displacement of the A atoms becomes large[6–9]. From the fact that a compound with smaller A atom shows higher $T_c$, it is expected that the large amplitude vibration of the A atom plays an important role in the superconducting state.

Raman scattering is one of the most useful tools to investigate lattice vibrations. We have reported the results of Raman scattering measurement of KO$_2$O$_6$[10, 11]. In KO$_2$O$_6$, frequency of K vibration with $T_{2g}$ representation increases with increasing temperature because of the large anharmonic effect due to the large amplitude. In addition, frequency of O vibration with $E_g$ representation also increases with increasing temperature. The frequency change of the O vibration is, surprisingly, large compared with that of the K vibration. The result has concluded that low-frequency O vibrations affect on the $E_g$ mode through the anharmonic interactions. As a candidate of the lower frequency vibration, we can point out the $E_{uu}$ mode, of which displacement is similar to that of the $E_g$ mode around K atoms.
In this paper, we present the results of Raman scattering measurements of RbOs₂O₆ and CsOs₂O₆ in the temperature region between 4 K and 300 K. From temperature dependence of frequency and linewidth, anharmonic effects of Raman active phonons are discussed for the T₂g mode of alkaline atoms and the Eg mode of oxygen.

2. Experimental procedure
Single crystals of RbOs₂O₆ and CsOs₂O₆ were synthesized as reported previously[2–4, 7]. Raman spectra were measured on (100) surfaces. Polarization geometry is described by the symbol of (yz), where y and z in the parentheses denote the polarization directions of incident light and scattered light, respectively. Propagation directions of incident light and scattered light are omitted, because back scattering geometry was used.

Raman spectra were measured by a triple-monochromator (JASCO NR-1800) with a liquid-N₂ cooled CCD detector (Pricneton Instruments Inc. LN/CCD-1100PB). The energy interval was about 0.7 cm⁻¹ for the spectra measured by the subtractive mode of the triple-monochromator. However, the linewidths of the T₂g mode of the alkaline atom is very narrow. The frequency and linewidth of the T₂g mode were measured by the additive mode with the energy interval of about 0.2 cm⁻¹. Frequency of all observed spectra was calibrated by the measurement of natural emission lines from He-Ne laser. For excitation light, 514.5nm line of an Ar⁺ laser was used with a pre-monochromator to remove natural emission lines from the laser. A power of the incident light was 10 mW before a sample surface.

3. Result and discussion
For β-pyrochlore compounds, it has been reported[3, 4, 7] that the structure belongs to Fd3m space group. On the other hand, another structure with a space group F43m has also proposed for KOs₂O₆[12] and RbOs₂O₆[13]. These two structure can be clearly distinguished by Raman scattering measurements and KOs₂O₆ has been already determined by Raman scattering as Fd3m structure[10, 11]. We examine the structure of RbOs₂O₆ and CsOs₂O₆.

According to the result of KOs₂O₆[10, 11], irreducible representations of Raman active phonons are A₁g⊕E₉g⊕4T₂g for Fd3m structure and 3A₁g⊕3E₉g⊕9T₂g for F43m structure. Figure 1 shows Raman spectra of (x, x) and (x, y) for RbOs₂O₆ and CsOs₂O₆ at room temperature. The figure also shows irreducible representations corresponding to Fd3m group for observed peaks. In the assignment, the additional (x + y, x + y) and (x + y, x – y) spectra on (100) surfaces hase been used. The observed peaks clearly correspond to the same number of the
representations as expected for Fd\text{"}3m. Moreover, since the spectra are quite similar to those of KO\textsubscript{2}O\textsubscript{6}, we conclude that the structure of RbOs\textsubscript{2}O\textsubscript{6} and CsOs\textsubscript{2}O\textsubscript{6} at room temperature is also Fd\text{"}3m. This conclusion agrees with the reported results for KO\textsubscript{2}O\textsubscript{6} and RbOs\textsubscript{2}O\textsubscript{6} obtained by Raman scattering measurements\cite{14}. We confirm that the structure does not change from 4 K to room temperature, because the spectra do not show any additional peaks even at 4 K.

As seen in Fig. 1, spectral shapes of E\textsubscript{g} mode and T\textsubscript{2g}(4) mode are asymmetric. Asymmetric line shape is the evidence of electron-phonon interaction. The asymmetric line shape is explained by Fano type interference effect between phonon and electronic excitation and is given by

\[ I(\omega) = I_0 \frac{(1 + \varepsilon(\omega)q)^2}{1 + \varepsilon(\omega)^2}. \]  \hspace{1cm} (1)

In this formulation, \( q \) is proportional to electron-phonon interaction coefficient, \( I_0 \) a scattering strength, and \( \varepsilon(\omega) = (\omega - \omega_0)/\Gamma \), where \( \omega_0 \) and \( \Gamma \) are frequency and linewidth of lattice vibration, respectively. To obtain the energies and linewidths of observed peaks, the fitting with this formula is used for all observed modes in addition to the E\textsubscript{g} and T\textsubscript{2g}(4) modes. Since the line shape of the other four modes is almost symmetric, we obtain very small \( \vert q \vert \) for these modes, as the results, the fitted spectra cannot be distinguished from the Lorenzian line shape expressed by \( I_0/(1 + \varepsilon(\omega)^2) \). At room temperature, the E\textsubscript{g} and T\textsubscript{2g}(4) modes have large \( q \) values, about -0.20. We have found that the \( q \) value of the E\textsubscript{g} mode depends on temperature, while that of the T\textsubscript{2g}(4) is almost constant. Although this temperature dependence of \( q \) of the E\textsubscript{g} mode is quite anomalous result, the detail will be reported elsewhere.

Obtained parameters, \( \omega_0 \) and \( \Gamma \), for T\textsubscript{2g}(1) and E\textsubscript{g} modes are shown in Fig. 2. The T\textsubscript{2g}(1) mode is a Rb or Cs vibration and the E\textsubscript{g} mode is an O vibration, which has large electron-lattice interactions and large anharmonic interactions with lower-frequency vibrations of oxygen\cite{11}. Including the result of KO\textsubscript{2}O\textsubscript{6}\cite{11}, we can discuss the A atom dependence for the anharmonic effect on frequency and linewidth. The frequency changes of T\textsubscript{2g}(1) between 4 K and 300 K become large from Cs to K. This changes relate to the strength of the fourth-order anharmonic term on the A atom vibrations and the present tendency is due to the change of the amplitude of the A atom vibration.

Figure 2. Temperature dependence of frequency (left) and full-width half maximum (right) of T\textsubscript{2g}(1) and E\textsubscript{g} modes for RbOs\textsubscript{2}O\textsubscript{6} and CsOs\textsubscript{2}O\textsubscript{6}.
The line width of $T_{2g}(1)$ mode is anomalously large in KOs$_2$O$_6$, about 8 cm$^{-1}$ at 4 K. In addition, the width change due to temperature change is very large for $T_{2g}(1)$ in KOs$_2$O$_6$, about 8 cm$^{-1}$, but small in RbOs$_2$O$_6$ and CsOs$_2$O$_6$, about 2 cm$^{-1}$. These dependences can be explained by an assumption of the existence of the lower-frequency lattice fluctuation in KOs$_2$O$_6$. Very low-frequency vibration is already observed in specific heat experiments for KOs$_2$O$_6$[8]. Therefore, $T_{1u}$ mode of A atom is a considerable possibility for this fluctuation. The $T_{1u}$ mode is a vibration of A atoms, where all of A atoms move along the same direction. Thus, the energy of $T_{1u}$ is lower than that of $T_{2g}(1)$, where a half of A atoms move opposite against to the rest.

The frequency change of the $E_u$ mode is large in KOs$_2$O$_6$ and RbOs$_2$O$_6$, about 10 cm$^{-1}$ and small in CsOs$_2$O$_6$, about 5 cm$^{-1}$. The same tendency is observed in the frequency change of the $T_{2g}(2)$ mode and the widths at 4 K of many oxygen modes. This result means that amplitude of low-frequency oxygen vibrations, which will be the $E_u$ mode, becomes large in KOs$_2$O$_6$ and RbOs$_2$O$_6$. In other words, the frequency of the $E_u$ mode will become low in KOs$_2$O$_6$ and RbOs$_2$O$_6$.

4. Conclusion
Raman spectra of RbOs$_2$O$_6$ and CsOs$_2$O$_6$ are measured from 4 K to 300 K. The structures of both compounds are Fd3m structure, which is the same as that of KOs$_2$O$_6$. Temperature dependence of frequency and linewidth of the $T_{2g}$ and $E_g$ modes are interpreted by means of low-frequency vibrations and anharmonic effects. The width of the A atom vibration $T_{2g}(1)$ mode becomes quite large in KOs$_2$O$_6$. This is caused by very low-frequency fluctuation and a candidate of the fluctuation is the $T_{1u}$ mode, which is another A atom vibration. The frequency change of the $E_g$ mode is large in KOs$_2$O$_6$ and RbOs$_2$O$_6$. This will relate to the low-frequency $E_u$ mode. Therefore, the frequency of the $T_{1u}$ mode becomes very small in KOs$_2$O$_6$, and the frequency of the $E_u$ mode becomes small in KOs$_2$O$_6$ and RbOs$_2$O$_6$. Since only KOs$_2$O$_6$ is considered as a strong-coupling superconductor, the $T_{1u}$ mode will play a very important role in superconductivity.

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