Pressure effect on the superconductivity of \( \beta \)-pyrochlore oxides

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Abstract. We report the results of the specific heat measurements for \( \beta \)-pyrochlore oxide superconductor \( \text{RbOs}_2\text{O}_6 \) with superconducting transition temperature \( T_c \approx 6.3 \) K in magnetic field and under pressure. We find that \( T_c \) rises up to 9.3 K by applying the pressure concomitant with an increase of the initial slope of the upper critical field \( H_{c2} \) and a jump of the specific heat at \( T_c \). From the analysis of our data, the effective mass of conduction electrons and the electron-phonon coupling appear to increase under the pressure.

1. Introduction

Conventional superconductivity in simple metals and metal alloys is well described by the BCS theory based on attractive force between electrons through the exchange of phonons. Recently, much attention has been directed toward clarifying the issue that superconducting properties in some cage compounds are not simply explained by the conventional BCS theory \cite{1, 2}.

\( \beta \)-pyrochlore oxide superconductors \( \text{AOs}_2\text{O}_6 \) (\( \text{A} = \text{K}, \text{Rb}, \text{and Cs} \)) are one of the cage compounds in which anomalous phonons are observed as an anharmonic oscillation of an \( \text{A} \) ion, called “rattling” motion, located inside a large atomic cage \cite{3}. Intriguingly, the rattling motion participates the superconducting properties \cite{2, 4}. For instance, the superconducting transition temperature \( T_c \) of \( \text{AOs}_2\text{O}_6 \) rises from 3.3 K for \( \text{CsOs}_2\text{O}_6 \) to 9.6 K for \( \text{KOs}_2\text{O}_6 \) with increasing the magnitude of the rattling motion and the electron-phonon coupling \cite{5}, while the density of state decreases from \( \text{CsOs}_2\text{O}_6 \) to \( \text{KOs}_2\text{O}_6 \) \cite{6}. Apparently, this trend is opposite to what is expected from the weak-coupling BCS theory.

In this paper, we report the high-pressure specific heat measurements on a single-crystalline \( \text{RbOs}_2\text{O}_6 \) under the magnetic field in order to further explore the role of the rattling motion on the superconductivity. The pressure is one of a powerful tool for this purpose because it directly affects on the rattling motion by modifying the crystal structure. We discuss implications for the pressure variation of \( T_c \) in terms of the rattling motion.

2. Experimental

High-quality single crystals of \( \text{RbOs}_2\text{O}_6 \) were synthesized by a solid-state reaction at \( 470 - 520 \) °C for 24 hours, as reported previously \cite{2}. As-grown sample was cut into a size of \( \sim 0.20 \times 0.20 \times 0.05 \) mm\(^3\) for the measurements. The specific heat measurements on two different samples
were performed by an ac-calorimetry method, which is a good measure to evaluate a relative change in a specific heat. In ac-calorimetry, a thermal response of a sample $T_{ac}$ with respect to an input ac-heat $P_0$ provides information of the specific heat $C$: $T_{ac} = \frac{P_0}{\kappa + \omega C}$ [7], where $\omega$ and $\kappa$ are a frequency of the input ac-heat and a thermal conductivity between the sample and bath, respectively. Moreover, we can estimate the specific heat by measuring a phase difference $\phi$ between the thermal response and the input ac-heat in addition to $T_{ac}$: $C = \frac{P_0}{\omega T_{ac}} \sin \phi$ [8]. In our measurements, the ac-heating power was produced by a laser modulated at the frequency $\omega \sim 3 - 6$ kHz by an acousto-optic elements. $T_{ac}$ was determined by a measured voltage $V_{ac}$ of a thermocouple Au/AuFe (0.07 %) and its thermoelectric power $S$: $T_{ac} = V_{ac}/S$. Pressure was generated by using a diamond anvil cell filled up by argon as a pressure medium, providing high hydrostatic pressure environment. The applied pressure was determined by a ruby fluorescence around 4.2 K. The measurements were performed in the temperature down to 2 K, under the pressure up to 9 GPa, and in magnetic fields up to 7 T.

3. Results and discussion
First, we show the temperature variation of the specific heat divided by temperature $C/T$ for RbOs$_2$O$_6$ under the several pressures in Figure 1. The data are shifted upward for clarity. At ambient pressure, the specific heat exhibits a clear anomaly associated with the superconducting transition at $T_c \sim 6.3$ K. By applying the pressure, $T_c$ monotonically increases up to $\sim 9$ K. In addition to the superconducting anomaly, a shoulder like anomaly appears around 7.2 K at 5.8 GPa, as denoted by the upward arrows. Interestingly, this anomaly becomes sharp with increasing the pressure, concomitant with a sudden disappearance of the superconducting anomaly at 6.0 GPa. It has been found that this second anomaly is also attributed to the superconducting transition from the electrical resistivity measurements [9]. With further increasing the pressure, an additional anomaly appears at $\sim 3$ K above 7.1 GPa as denoted by a dashed arrow, indicating the presence of a high-pressure phase. The nature of this high-pressure phase is unclear.

From the high-pressure specific heat measurements, we construct a thermodynamic temperature vs. pressure phase diagram of RbOs$_2$O$_6$ as shown in Fig. 3(a). We found the following remarkable features in the phase diagram: (1) $T_c$ increases up to 9.3 K with increasing the pressure, while a slope of $dT_c/dP$ levels off above 3 GPa. (2) The superconducting phase (SC1) unexpectedly vanishes and a secondary superconducting phase (SC2) appears at the critical pressure $P^* \sim 6.0$ GPa. (3) In addition to the SC2, another high-pressure phase emerges above 7.1 GPa.

In order to clarify the superconducting properties of the SC1, we performed the high-

![Figure 1](image-url)

**Figure 1.** Temperature dependence of the specific heat divided by temperature $C/T$ for RbOs$_2$O$_6$ under the several pressures. The downward and upward arrows denote the superconducting transition temperature of the two different superconducting phase, respectively. The dashed arrows represent the transition temperature of the high-pressure phase. The data are shifted upward for clarity.
pressure specific heat measurements in the magnetic fields. Figure 2 (a) shows the temperature dependence of the specific heat divided by temperature $C/T$ under the pressure of 1.6 GPa in the several magnetic fields. The data are shifted upward for clarity. As it can be seen, the superconducting anomalies become smaller and shift to lower temperatures. We plot the temperature dependence of the upper critical field $H_{c2}(T)$ under the various pressures in Fig. 2 (b). Here, $T_c$ is determined by the entropy conserving construction. At ambient pressure, $H_{c2}(T)$ shows a linear increase at low fields, but has a concave-upward curvature at high fields [2]. It should be noted that an initial slope of $H_{c2}(T)$ at $T_c$ ($-dH_{c2}/dT|_{T=T_c}$) monotonically increases with the pressure from 0.9 T/K at ambient pressure to 2.5(2) T/K at 5.2 GPa. Moreover, with increasing the pressure, the initial slope at 5.2 GPa is close to the one for KOs$_2$O$_6$ at ambient pressure. From the initial slope, we estimate the effective mass $m^*$ of the conduction electrons through a relation $-dH_{c2}/dT|_{T=T_c} \propto m^*T_c$ as shown in Fig. 3(b). Interestingly, $m^*$ monotonously increases with the pressure in the SC1 phase.

To further elucidate the superconducting properties of the SC1 and a role of the rattling motion, we examine the electron-phonon coupling from a jump of the specific heat $\Delta C/\gamma T_c$ at $T_c$. Although the qualitative estimate of $\Delta C/\gamma T_c$ is not straightforward by the ac-calorimetry method, we evaluate the relative change of $\Delta C/\gamma T_c$ against the pressure as follows. First, we multiply constant values to each $C(T)$ curve, so as to fall on an identical curve above $T_c$. Then, we obtain the relative change of the specific heat $\Delta C$. Next, we substitute $m^*$ to $\Delta C/\gamma T_c$, which is determined above, instead of the Sommerfeld coefficient $\gamma$ because of the proportionality between $m^*$ and $\gamma$. Figure 3 (c) displays the pressure dependence of $\Delta C/m^*T_c$ in the SC1. It is clearly seen that $\Delta C/m^*T_c$ shows a steep increase up to 3 GPa and a weak pressure dependence above 3 GPa. Notice that the pressure variation of $\Delta C/m^*T_c$ resembles that of $T_c$, suggesting that $T_c$ is governed by the electron-phonon coupling under the pressure. Here, a question is raised the issue of what is a leading source providing the enhancement of the electron-phonon coupling. One possible answer is the rattling motion of the Rb ions, which might become stronger by the applied pressure. This is because one can expect the stronger electron-phonon coupling due to the enhanced rattling motion from the analogy to the variation of $T_c$ in the series of $\text{AO}_{2}\text{O}_6$. 

![Figure 2](image-url)

**Figure 2.** (a) Temperature dependence of the specific heat divided by temperature $C/T$ for RbOs$_2$O$_6$ under the pressure of 1.6 GPa in the various magnetic fields. The allows indicate $T_c$. The data are shifted upward for clarity. (b) Upper critical field $H_{c2}(T)$ as a function of temperature at various pressures. The present results are shown by the solid circles. The open circles and triangles denote $H_{c2}(T)$ for RbOs$_2$O$_6$ [2] and KOs$_2$O$_6$ [10] at ambient pressure, respectively.

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Figure 3. (a) Temperature vs. pressure phase diagram of RbOs$_2$O$_6$. Solid and open squares denote the superconducting transition temperature. Cross symbols show the transition temperature of the high-pressure phase. Pressure variation of (b) the normalized effective mass $m^*$ of the conducting electrons and (c) the jump of the specific heat $\Delta C/m^*T_c$ for RbOs$_2$O$_6$. Both data are normalized at 0.4 GPa. The solid line is a guide to the eye.

In summary, we constructed the thermodynamic temperature vs. pressure phase diagram for RbOs$_2$O$_6$ from the high-pressure specific heat measurements. We found the three different phases under the pressure; the former two are attributed to the superconducting phases. In the lower pressure superconducting phase, the effective mass of the conduction electrons and the electron-phonon coupling appear to increase by applying the pressure. These findings point to an intriguing possibility of a pressure-induced enhancement of the rattling motion of the Rb ions.

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