Ultrasonic measurement of $\beta$-type pyrochlore oxide KOs$_2$O$_6$

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Abstract.

We have measured the temperature dependence of the elastic constants of KOs$_2$O$_6$ single crystal. The longitudinal elastic constant $\frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$ and the transverse one $\frac{1}{3}(C_{11} - C_{12} + C_{44})$, which are obtained by the corresponding sound velocities propagating along $<111>$ direction, show a remarkable elastic softening toward low temperatures. No elastic anomaly was observed at the superconducting transition temperature. On the other hand, an anomaly was found at $T_p = 7.5$ K. These results suggest that the irreducible representation of $T_2$ in $T_d$ point group play an important role for the phase transition at $T_p$.

1. Introduction

Physical properties related to anharmonic vibration of atom in cage have been investigated intensively for many systems. Filled skutterudites and Clathlates show various interesting properties such as heavy electron mass, metal-insulator transition, peculiar magnetism and unconventional superconductivity. It has been believed that large anharmonic vibration, which is named rattling, is responsible for such interesting properties. Recently, $\beta$-type pyrochlore oxide AOs$_2$O$_6$ ($A = \text{Cs, Rb and K}$) has attracted much attention from view point of the correlation of superconductivity and rattling. They show superconductivity at 3.3 K, 6.3 K and 9.6 K for $A = \text{Cs [1], Rb [2, 3, 4] and K [5]}$, respectively.

In particular, KOs$_2$O$_6$ shows the highest superconducting transition temperature $T_c$ among these compounds. Hiroi et al. reported that its superconducting property is of BCS-type s-wave strong coupling [6]. An additional anomaly was found at $T_p = 7.5$ K in the superconducting phase [7]. $T_p$ is not affected by the magnetic field, then it has been discussed whether the rattling is responsible for the transition at $T_p$ as well as $T_c$, because K ion in KOs$_2$O$_6$ is surrounded by a cage formed by K and O ions. Electronic structure and potential was calculated by Kuneš et al [8]. They showed the existence of the off-center potential having four minima sitting along neighboring K $<111>$ directions. The rattling phenomena concerning various physical properties have been investigated experimentally and theoretically for NMR and resistivity [9, 10].

We will report the elastic properties of KOs$_2$O$_6$ single crystals as a function of temperature. We found a large elastic softening at low temperatures. We will discuss the origin of the elastic anomalies, particularly the relation to $T_p$ from the view of rattling, charge fluctuation and lattice instability.
2. Experimental

KOs$_2$O$_6$ single crystals used for the ultrasonic experiments were grown by annealing a mixture of KOsO$_4$ and OsO$_2$ at 748 K [6]. Typical size of the sample is $0.75 \times 0.5 \times 0.2$ mm$^3$. The crystal structure of KOsO$_4$ is cubic with the space group of $Fd\bar{3}m$ [11]. Then, independent elastic constants are $C_{11}$, $C_{12}$ and $C_{44}$. Due to a small size of the sample, we used the facet of (111) surface to glue the ultrasonic transducers. For the propagation of the sound along the $<111>$ direction, the elastic constants $C_L = \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$ and $C_T = \frac{1}{4}(C_{11} - C_{12} + C_{44})$ can be obtained from the corresponding longitudinal and transverse sound velocities by using the relation of $C = \rho v^2$, where $\rho$ and $v$ are the density and the sound velocity of the sample, respectively. We have polished the (111) surfaces to remove defects or vacancies, which are produced during the crystal growth, to get better ultrasonic signals.

Ultrasonic measurements have been performed with the pulse echo apparatus by a phase comparison method. The samples used in the experiments are so thin, that we adopted the measurement techniques with a sapphire buffer rod to delay sound wave signals as well as usual method without a buffer.

We have adopted two types of piezoelectric transducers. LiNbO$_3$ 36$^\circ$ Y-cut transducer was used for generating and detecting longitudinal sound, and LiNbO$_3$ X-cut and quartz AC-cut transducers for transverse sound. It is because LiNbO$_3$ transducer has so high piezoelectric constant, that it may generate longitudinal wave as well as transverse one even when we use the transverse transducers. On the other hand, quartz transducers emits pure transverse wave, although their piezo-electric efficiency is lower and they are hard to get good ultrasonic signals. We did not obtain the absolute value of the sound velocity, due to a small size of the sample.

3. Results

Figure 1 shows the temperature dependence of the longitudinal elastic constant $C_L$ below 100 K, and the transverse one $C_T$ below 28 K. The $C_L$ and $C_T$ increase gradually with decreasing temperature. No elastic anomaly was found at the superconducting transition temperature at 9.6 K. However, they show a remarkable elastic softening toward low temperatures, and an anomaly was found at $T_p = 7.5$ K. In the both $C_L$ and $C_T$ measurements, the buffer rod and LiNbO$_3$ transducer were used. Amount of the anomaly in the elastic constants is 0.7 % and 2.2 % for $C_L$ and $C_T$, respectively. We have also measured $C_T$ by using quartz transducer. We have got almost the same temperature dependence of the transverse sound velocity for the both transducers. The amount is similar to that by LiNbO$_3$, although the amount of the anomaly

![Figure 1. (a) Temperature dependence of the longitudinal elastic constant $C_L$ below 100 K. The inset shows the low temperature data without magnetic field and in 3T by (red) open circles and (green) diamonds (♦), respectively.](image-url)
depends on various experimental conditions such as the usage of the buffer, strictly speaking.

The inset of Fig. 1 shows the temperature dependence of $C_L$ below 15 K in the magnetic field of 3 T and without field. No difference is found between them, including the details around $T_c$ and $T_p$. The anomaly at $T_p$ is not influenced by the magnetic field. It may suggest that $T_p$ is related to a structural instability and not due to electronic origin.

4. Discussion and concluding remarks

We would like to discuss the origin of the low temperature elastic softening. No elastic anomaly at $T_c$ suggests that the Grüneisen parameter for $T_c$ is small. On the other hand, the Grüneisen parameter for $T_p$ is considerably large. Where does the low temperature elastic softening come from? Longitudinal elastic constant $C_L$ consists of $C_{44}$ and bulk modulus $C_B = \frac{1}{3}(C_{11} + 2C_{12})$, and transverse $C_T$ contains $C_{44}$ and $C_E = \frac{1}{2}(C_{11} - C_{12})$. When the elastic softening appears only in $C_L$ and not in $C_T$, the origin of the softening should be attributed to $C_B$. On the other hand, the $C_E$ should be responsible when $C_T$ shows an anomaly solely. In our experiment, it would be clear that the elastic mode responsible for the softening is $C_{44}$, because both $C_L$ and $C_T$ show elastic anomalies.

We tried to fit the experimental data by Jahn-Teller formula of $C = C_0 \frac{T-T_c}{T-T_Q}$, where $T_c$ and $T_Q$ are a critical temperature and a quadrupolar temperature, respectively \[12\]. The observed anomalies can be fitted well by this formula, as shown by solid curves in Fig. 2(a) and (b) for $C_L$ and $C_T$, respectively. The parameters for the longitudinal elastic constant were evaluated as follows: $C_0 = 1.0001$, $T_c = 7.302$ K and $T_Q = 7.300$ K for $C_L$, and $C_0 = 1.0006$, $T_c = 7.570$ K and $T_Q = 7.560$ K for $C_T$. This Jahn-Teller formula is brought from a bilinear coupling between the order parameter and the strain. Therefore, the low temperature elastic softening comes from the fluctuation of the order parameter, which has the same symmetry as the strain.

Potassium (K) ion in the cage occupies $T_d$ site symmetry. Recently, Hattori and Tsunetsugu proposed a mechanism of the transition at $T_d$ by focusing a particularity of $T_d$ symmetry \[13\]. Since the point group $T_d$ has no inversion symmetry, the irreducible representation of total symmetry $A_1$ has a base function of $xyz$ symmetry. This type of the symmetry belongs to $A_{2u}$ representation in $O_h$ point group, and would be a possible candidate of the order parameter that measures the degree of the off-center potential. However, the observed elastic anomaly cannot

![Figure 2](image-url)
be explained by the order parameter fluctuation of $A_1$, because it does not contain the elastic strain for $C_{44}$ as a base function.

It should be remarked that $T_d$ is particularly interesting. The polar vector with the symmetry of $\{x, y, z\}$, which is the basis of $T_{1u}$ for $O_h$, and the elastic strain with the symmetry of $\{yz, zx, xy\}$ for $C_{44}$ belong to the same irreducible representation (Table 1). According to the potential calculation of $\beta$-type pyrochlore oxide by Kunčes and Pikett, KOs$_2$O$_6$ has a shallow off-centered potential among this family. The excited multiplet, that is thought to be triplet, is lifted at 8K from the ground state singlet [14].

Such singlet-triplet system with small energy separation would bring about the elastic softening, which is mainly due to the excited state. This paper cannot deny a participation of $C_B$ and $C_E$ in the elastic softening. However, our experiment shows clearly $C_{44}$ to play a relevant role. It will be a key to the solution of $T_p$ transition, particularly the relation to the rattling phenomena.

Table 1. Irreducible representations, their base functions and corresponding elastic constants of point group $T_d$ and $O_h$.

| $T_d$   | $O_h$   | Base functions | Elastic constant |
|--------|--------|----------------|------------------|
| $A_1$  | $A_{1g}$, $A_{2u}$ | $r^2$, $x^4 + y^4 + z^4 - \frac{3}{2} r^4$, $xyz$ | $C_B = \frac{1}{9} (C_{11} + 2C_{12})$ |
| $A_2$  | $A_{2g}$, $A_{1u}$ | $x^4 (x^2 - y^2) + y^4 (z^2 - x^2) + z^4 (x^2 - y^2)$, $(A_{2g}) \times x y z$ | |
| $E$    | $E_g$, $E_u$ | $\{u, v\}, \{x y z v, -x y z u\}$ | $C_E = \frac{1}{2} (C_{11} - C_{12})$ |
| $T_1$  | $T_{1g}$, $T_{2u}$ | $\{y z \alpha, z x \beta, y x \gamma\}$, $\{x \alpha, y \beta, z \gamma\}$ | $C_{44}$ |
| $T_2$  | $T_{2g}$, $T_{1u}$ | $\{y z, x z, x y\}$, $\{x, y, z\}$ | |

$u \equiv 2z^2 - x^2 - y^2$, $v \equiv \sqrt{3} (x^2 - y^2)$
$\alpha \equiv y^2 - z^2$, $\beta \equiv z^2 - x^2$, $\gamma \equiv x^2 - y^2$

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