# Interplay of Superconductivity and Rattling Phenomena in $\beta$-Pyrochlore $KOs_2O_6$ Studied by Photoemission Spectroscopy

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The electronic structure near the Fermi level ($E_F$) of the $\beta$-pyrochlore superconductor $KOs_2O_6$ is studied using laser-excited ultrahigh-resolution photoemission spectroscopy. The superconducting gap clearly opens across the superconducting transition ($T_c = 9.6$ K), with the strong electron-phonon coupling value of $2\Delta(0)/k_BT_c \gtrsim 4.56$. A fitting analysis identifies clear anomalies at $T_p = 7.5$ K in the temperature dependencies of the superconducting gap size and the quasiparticle relaxation lifetime. These anomalies and the fine spectral structures arising from phonons suggest that the existence of the rattling behavior of K ions significantly affects the superconductivity in $KOs_2O_6$.

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Since the discovery of the first pyrochlore superconductor $Cd_2Re_2O_7$ ($T_c \sim 1$ K) [1], there has been growing interest in the superconductivity on the pyrochlore lattices which display inherent geometrical frustrations. Recently, a new series of $\beta$-pyrochlore superconductors $AOs_2O_6$ ($A$ = K, Rb, Cs) was discovered by Yonezawa *et al.* [2–4], with relatively high transition temperatures ($T_c$) of 9.6, 6.3, and 3.3 K, respectively. Experimental studies have distinguished $KOs_2O_6$ from other pyrochlore superconductors which are understood within the weak-coupling Bardeen-Cooper-Schrieffer (BCS) theory [5–8]. Although the electronic structure of the valence band is almost common to all $\beta$-pyrochlore superconductors [9], $KOs_2O_6$ shows the outstanding physical properties, such as the highest $T_c$, high $H_{c2}$, strong electron-phonon ($e$-ph) coupling, strong mass enhancement, etc. [10–13]. According to the specific heat measurements [11], $KOs_2O_6$ shows $\Delta C/T_c\gamma \sim 2.87$ ( > 1.43) which is classified as a strong-coupling superconductor while $RbOs_2O_6$ and $CsOs_2O_6$ are reported to be in the weak-coupling regime [14]. Experimental results on the superconducting (SC) pairing mechanism of $KOs_2O_6$ are still controversial. NMR measurements reported the absence of the coherent peak together with the power law behavior of $(T_1T)^{-1}$ below $T_c$, indicative of nodes existing in the SC gap function [15]. Penetration depth studies using $\mu$SR suggested an anisotropic $s$-wave or two-gap superconductivity [16]. On the contrary, a recent thermal conductivity measurement shows the evidence for the isotropic s-wave symmetry [17]. Regarding $RbOs_2O_6$, on the other hand, NMR [8,15] and $\mu$SR [7] measurements consistently concluded that the SC gap has the isotropic $s$-wave symmetry. The normal-state resistivity of $KOs_2O_6$ also shows an unusually slow decrease from higher temperature ($T$) down to $T_c$ with a convex upward $T$-dependence [4]. In contrast, $RbOs_2O_6$ and $CsOs_2O_6$ show $T^2$ law in resistivity up to 30 and 45 K [2,3], respectively, indicative of normal Fermi-liquid behavior. A number of differences as mentioned above has been discussed in terms of the rattling phenomena. A $K^+$ ion inside an $Os_{12}O_{18}$ cage moves ~1 Å around its ideal site anharmonically because of the much smaller ion radius compared to the cage size, and this is called rattling [18]. The specific heat measurements actually reported the anomaly at $T_p = 7.5$ K (below $T_c$) only for $KOs_2O_6$, which is considered to be a first order transition related to the rattling [19]. A theoretical study suggests that the independent rattling motion freezes at $T_p$, accompanied by the ordering of K ions [20]. The estimated rattling in $RbOs_2O_6$ and $CsOs_2O_6$ are much less than that in $KOs_2O_6$ due to their longer A ion radii, thus suggesting the peculiarity of $KOs_2O_6$. Such rattling may significantly influence the low energy electronic excitations in $KOs_2O_6$ via the coupling between the conduction electrons and the large fluctuation of the electric potential caused by the huge ion motions. The relation between the rattling phenomenon and superconductivity in $KOs_2O_6$, however, has not been well clarified so far.

In this Letter, we report the results of the photoemission spectroscopy (PES) on $KOs_2O_6$. Recent development of the PES technique especially in the energy resolution and the cooling ability enables us to study the mechanism of the "low-$T_c$" superconductors [21]. For $KOs_2O_6$, we observed the evolution of the SC gap together with phonon-derived spectral features. In the $T$-dependence of the SC gap and quasiparticle relaxation (QPR) lifetime, we found a clear anomaly at $T_p$. From our results, we discuss the SC

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gap symmetry, QP properties, and the possible relation between the superconductivity and the rattling phenomenon in $KOs_2O_6$.

Laser-PES measurements were performed on a spectrometer built using a GAMMADATA-SCIENTA R4000WAL electron analyzer and an ultraviolet laser ($h\nu = 6.994$ eV) as a photon source [22]. The energy resolution was set to 500–850 $\mu$eV. $E_F$ was determined by measuring the gold film evaporated near the sample within the accuracy of $\pm 0.1$ meV. Single crystals of $KOs_2O_6$ were mounted on a copper plate using a silver paste in a dry $N_2$ atmosphere in order to avoid the water adsorption. Because of the special care in handling the samples, we could observe the same PES spectra regardless of whether the samples were fractured in vacuum or not. It may be owing to the bulk sensitivity of the low energy PES [23]. All the PES shown in this Letter has been performed on the surface without any treatment in vacuum. Reproducibility of the data was confirmed by $T$-cycled measurements using several different crystals. All the PES spectra reported here did not show angle-resolved effects indicating that the spectra correspond to the angle-integrated electronic structure.

The electronic structure near $E_F$ is shown in Fig. 1(a). The SC peak and gap are clearly observed at 4.7 K. In order to determine the SC gap size, we used the Dynes function to fit the SC state spectra. The Dynes function introduces a phenomelogical broadening effect into the BCS gap function, which is known to well reproduce a SC gap spectrum with isotropic $s$-wave symmetry [24]. The Dynes function is defined by $D(E, \Delta, \Gamma) = \mathrm{Re}[(E - i\Gamma)/\{(E - i\Gamma)^2 - \Delta^2\}^{1/2}]$, where $\Delta$ is SC gap size and $\Gamma$ phenomenological broadening parameter, reciprocal to QPR lifetime. The QPR lifetime is mainly considered to be determined by the QPR processes of recombination of two quasiparticles into the superfluid condensate with phonon emission and inelastic scattering with phonons [24,25]. For the fitting function, we used the Dynes function which is multiplied by Fermi Dirac function, then convoluted with a Gaussian function including the experimental energy resolution. The spectrum at 4.7 K shows a fairly sharp QP peak and a very low intensity near $E_F$, which are quite well reproduced using this $s$-wave fitting function with $\Delta = 1.63$ meV and $\Gamma = 0.003$ meV, shown by the red solid curve in Fig. 1(a). This indicates that the SC gap of $KOs_2O_6$ has the isotropic $s$-wave symmetry. In addition to the SC peak, tiny but important fine structures are observed in the binding energy region of 3–5 meV and at 10 meV. The inset in Fig. 1(a) shows the former structure in an enlarged energy scale. The red broken curve represents the fitting function. The peak at 3.7 meV and the dip at 4.5 meV, which are indicated as $P$ and $D$ with arrows, are emphasized as a deviation from the BCS density of states (DOS). This feature is clearly observed only below $T_c$ and seems very similar to what is expected by the strong-coupling theory: the emergence of a peak followed by a dip at the energy of $\sim\Delta_{SC} + \omega_{ph}$, where $\Delta_{SC}$ is the SC gap size and $\omega_{ph}$ is the energy of the phonon mode pairing the electrons [26,27]. Similar features appearing in the SC state are also reported in a typical strong-coupling superconductor Pb $[2\Delta(0)/k_B T_c = 4.9]$ [21], which is a reflection of the peak structures in the phonon DOS. In the strong-coupling theory, DOS for SC states measured by PES or tunneling measurements is given by the energy($\omega$)-dependent complex gap function $\Delta(\omega)$. It describes the role of the phonon degrees of freedom which is neglected in BCS theory (i.e.,

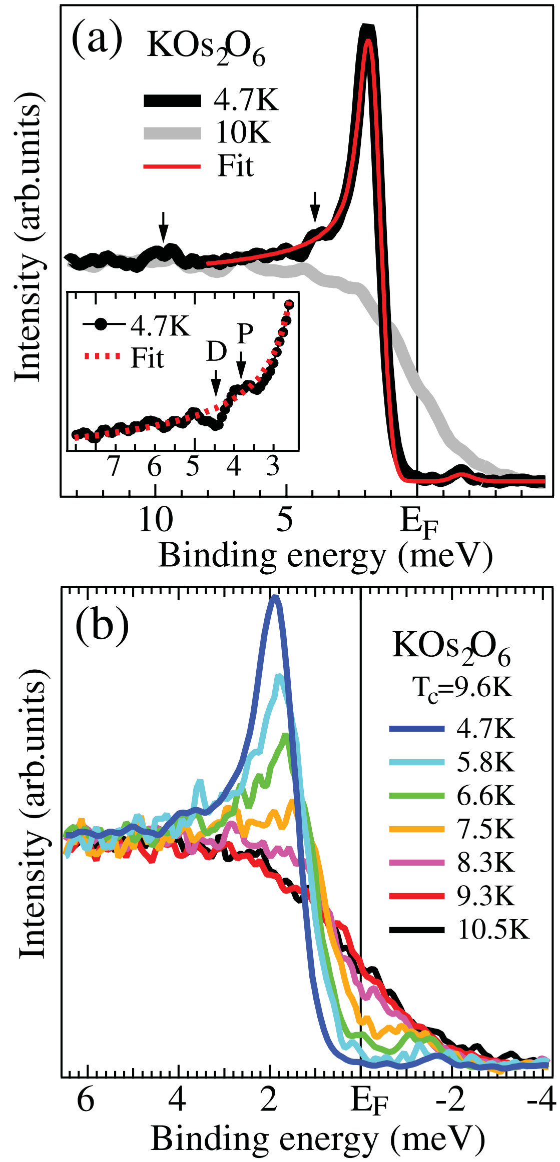


FIG. 1 (color). (a) Superconducting gap and fine electronic structures near $E_F$ are shown in an enlarged energy scale. The red solid curve represents the $s$-wave fitting function with $\Delta = 1.63$ and $\Gamma = 0.003$ meV. Black arrows indicate peaks centered around 3.7 and 10 meV. Inset shows the fine structures in an enlarged energy scale. The red broken curve represents the fitting function. The peak at 3.7 meV and the dip at 4.5 meV are indicated as $P$ and $D$ with arrows, respectively. (b) Temperature dependence of PES spectra observed in $KOs_2O_6$.

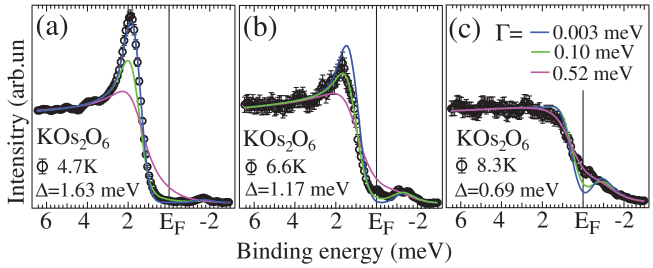


FIG. 2 (color). PES spectra and the fitting curves for $KOs_2O_6$ superconducting state. Black circles are spectra at (a) 4.7, (b) 6.6, and (c) 8.3 K. Error bars on the photoemission spectra are superimposed taking into account the total accumulated intensity of each spectrum. The blue, green, and pink curves represent the *s*-wave fitting functions with $\Gamma = 0.003$, 0.10, and 0.52 meV, which are the values for the best fitting at respective temperatures.

weak-coupling limit). In this case, the SC gap of $KOs_2O_6$ at 4.7 K is 1.63 meV, which gives the corresponding phonon DOS peak energy at around $\omega_{ph} = 3.7–1.63 \cong 2.1$ meV. According to the specific heat measurement on the normal-state $KOs_2O_6$, there are some anomalous components besides the usual $T^3$ (Debye-type) phonon term. It was ascribed to the existence of localized phonon modes whose Einstein temperatures are estimated to be $\Theta_{E1} = 22$ K (1.9 meV) and $\Theta_{E2} = 61$ K (5.2 meV) [11]. The former one, especially prominent in $KOs_2O_6$, indicates the energy scale of the rattling motions by K ions, which shows a good agreement with the phonon energy estimated from our PES measurement. Our result thus indicates the strong-coupling nature of SC in $KOs_2O_6$, and its possible relation to the rattling phonon at ~1.9 meV. For more quantitative analysis, a precise measurement of the phonon dispersion and/or DOS is highly required.

Next, we focus on the $T$-dependence of SC and QP properties below $T_c$. Figure 1(b) shows the $T$-dependence of the PES spectra in the range of 4.7–10.5 K. We can see the evolution of the SC peak and gap with lowering $T$. For the estimation of $\Delta(T)$ and $\Gamma(T)$, all the spectra measured in the SC state were fitted using aforementioned isotropic *s*-wave fitting function. Examples are shown in Figs. 2(a)–2(c). Black circles in Figs. 2(a)–2(c) are the PES data at 4.7, 6.6, and 8.3 K. The blue, green, and pink curves represent the fitting functions with $\Gamma = 0.003$, 0.10, and 0.52 meV, which are the values that gave the best fitting for 4.7, 6.6, and 8.3 K, respectively. $T$-dependencies of $\Delta(T)$ and $\Gamma(T)$, which were obtained from the fitting results, are shown as sample #1 in Figs. 3(a) and 3(b), respectively. We also show the results from two different samples (sample #2, #3), which were fractured *in situ*. The remarkable feature in the $T$-dependence of $\Delta(T)$ is the deviation from the BCS curve. The SC gap evolution seems to be suppressed between $T_c$ and $T_p$, and recovers rapidly below $T_p$. We can recognize the anomaly of $\Delta(T)$ also from the raw spectra in Fig. 1(b), as the drastic shift of the leading edge below 7.5 K. Since it is difficult to estimate the $\Delta(0)$

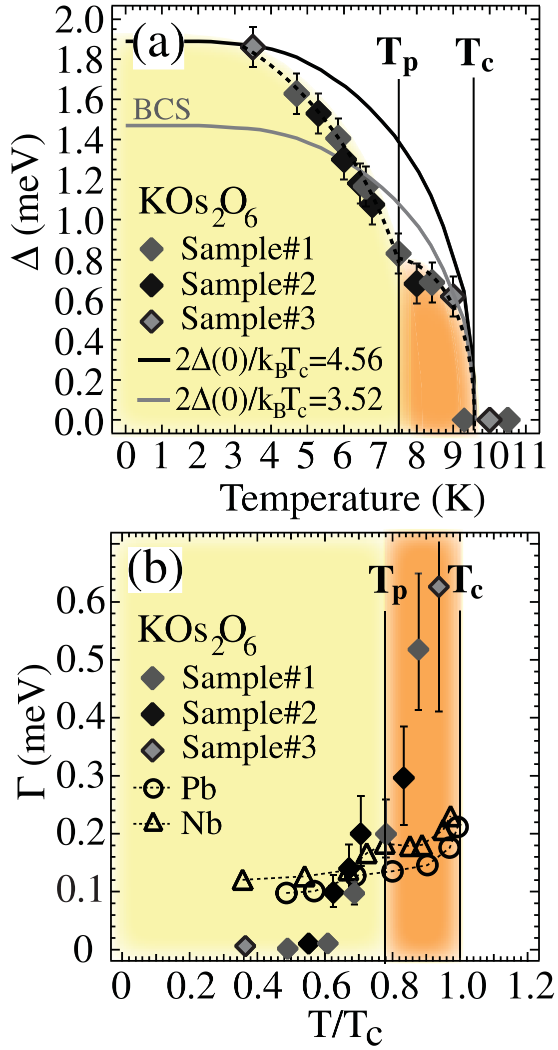


FIG. 3 (color). (a) Temperature dependence of $\Gamma(T)$ for $KOs_2O_6$. The black broken curves are the guides for eyes. The gray and black solid curves represent the BCS curves with $2\Delta(0)/k_BT_c = 3.52$ (theoretical value for weak-coupling limit) and $2\Delta(0)k_BT_c = 4.56$, respectively. The value of $2\Delta(0)k_BT_c = 4.56$ was estimated by fixing $T_c$ and the $\Delta(3.5\text{ K})$, which should indicate the lower limit of the reduced gap. The error bar of the temperature is within $\pm0.25$ K, corresponding to the marker size. (b) $T$-dependence of $\Gamma(T)$ for $KOs_2O_6$. $\Gamma(T)$ for Nb and Pb are also plotted for comparison.

due to the deviation of $\Delta(T)$ from the BCS curve, we estimated the lower limit of $\Delta(0)$ from the BCS function by simply connecting $T_c = 9.6$ K and $\Delta(3.5\text{ K}) = 1.86$ meV [see the solid black curve in Fig. 3(a)]. It gives $2\Delta(0)/k_BT_c \geq 4.56$ ($T_c = 9.6$ K), indicative of the strong-coupling superconductivity in $KOs_2O_6$. For comparison, we also plot the typical BCS curve in weak-coupling limit with $2\Delta(0)/k_BT_c = 3.52$ (solid gray curve), which apparently shows smaller gap sizes at low $T$. The specific heat measurements for $KOs_2O_6$ also reported $\Delta C/T_c\gamma \sim 2.87$ indicating the strong-coupling behavior [11]. This is consistent with the aforementioned result showing the peak-dip structure at $\omega \sim \Delta_{SC} + \omega_{ph}$ emerging below $T_c$, which are characteristic of the strong $e$-ph coupling. Regarding the anomaly of $\Delta(T)$, on the other hand, one possible scenario is that there are two different SC phases for below and above $T_p$ [colored by yellow and orange in Fig. 3(a)]. The $T$-dependence of $H_{c2}$ shows the discontinuity across $T_p$ [28], indicative of the separated SC phases with different SC parameters, while superconductivity in both phases is basically formed by the same phonon—mediated mechanism. However, if we assume that $\Delta$ formed at $T_p < T < T_c$ follows the BCS curve, the corresponding $2\Delta(0)/k_BT_c$ becomes 2.7, much lower than the weak-coupling limit value of 3.52. It is thus more likely that a SC gap suppression occurs at $T_p \leq T < T_c$. Nevertheless, it is clear that the transition at $T_p$ significantly affects the SC properties in $KOs_2O_6$.

Such anomaly at $T_p$ is also observed in $\Gamma(T)$, the $T$-dependence of the QPR lifetime, as shown in Fig. 3(b). $\Gamma(T)$ versus $T/T_c$ for several phonon-mediated superconductors, Pb [$T_c = 7.19$ K, strong-coupling, $2\Delta(0)/k_BT_c = 4.9$] and Nb [$T_c = 9.26$ K, weak-coupling, $2\Delta(0)/k_BT_c = 3.8$] are also plotted, which were similarly measured by the laser-PES. $\Gamma(T)$ for Pb and Nb are very close to each other regardless of the SC coupling strength and almost constant at low $T$ with slight increase toward $T_c$. Similar tendency was also reported for $Pb_{0.9}Bi_{0.1}$ thin film by the tunneling measurement, discussed in terms of the increasing recombination process on approaching $T_c$ [24]. In a strong contrast, $\Gamma(T)$ for $KOs_2O_6$ shows an unusually drastic increase at around $T_p$. One can also recognize this rapid increase of $\Gamma(T)$ from the PES spectra in Figs. 1(b) and 2(a)–2(c). The PES spectrum at $T > T_p$ shows an extraordinarily broadened spectrum compared to the very sharp SC peaks observed at lower $T$. Actually, as shown in Figs. 2(a)–2(c), the $T$-dependence of $\Gamma(T)$ is far beyond the fitting error. The $\Gamma(T)$ value needs to be changed more than 2 orders of magnitude for reasonably fitting the PES spectra at 4.7 and 8.3 K. The rapid increase of $\Gamma(T)$ at around $T_p$, which makes a great difference from other superconductors, suggests that the rattling behavior unique to $KOs_2O_6$ strongly affects the QP scattering at $T_p < T < T_c$. A similar effect is also discussed for the normal-state resistivity realized under the magnetic field. It shows an unusually slow $T$-dependence for $T > T_p$, which eventually turns into $T^2$ behavior below $T_p$ [28]. It is indicative of the electron scattering mechanism changing across $T_p$, from an anomalous scattering state at $T > T_p$ to a Fermi-liquid ($e$-$e$ scattering) state at $T < T_p$. A thermal conductivity measurement also suggested that QP transport is dominated by $e$-ph scattering at $T_p < T < T_c$, while by $e$-$e$ scattering at $T < T_p$ [17]. Our result seems to be consistent with these pictures. At the same time, it must be possibly causing the suppression of the SC gap evolution at $T_p < T < T_c$. It is most likely that the rattling transition at $T_p$ changes the QP scattering mechanism, also giving rise to the unusual dip at around $T_p$ in the SC gap evolution.

In conclusion, we have studied the electronic structure of $KOs_2O_6$ near $E_F$ using a laser-PES. The PES spectrum at 4.7 K shows a very sharp QP peak and is well reproduced using the Dynes function describing an isotropic $s$-wave SC gap with $\Delta = 1.63$ meV. In addition, we observed the fine peak-dip structure which can be explained by the manifestation of the Einstein mode originated in the rattling motion of K ions. This result, together with the reduced gap of $2\Delta(0)/k_BT_c \geq 4.56$, indicates that the SC in $KOs_2O_6$ has the strong-coupling nature possibly related to the rattling phenomenon. The $T$- dependencies of $\Delta(T)$ and $\Gamma(T)$ are quite unusual, indicating the dip in the SC gap evolution and the drastic increase of the QPR lifetime just around $T_p$, the rattling transition temperature. It is most likely that the huge rattling motion unique to $KOs_2O_6$ strongly scatters the QP while suppressing the SC gap evolution at $T > T_p$, thus giving an explanation for the number of unusual SC properties in this system.

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