Superconductivity in $\beta$-pyrochlore superconductor KOs$_2$O$_6$: treatment within strong-coupling Eliashberg theory

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We study the influence of the rattling phonons on superconductivity in $\beta$-pyrochlore KOs$_2$O$_6$ compound based on the strong-coupling Eliashberg approach. In particular, analyzing the specific heat data we find that the rattling phonon frequency changes discontinuously at the critical temperature of the first order phase transition. Solving the strong-coupling Eliashberg equations with temperature dependent $\alpha^2 F(\omega)$, we investigate the consequence of this first order phase transition for the anomalous temperature dependence of the superconducting gap. We discuss our results in context of the recent experimental data.

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The superconductivity in the family of the $\beta$-pyrochlore oxides KO$_2$O$_6$, RbO$_2$O$_6$, and CsO$_2$O$_6$ exhibits many exotic properties. Among them, KO$_2$O$_6$ with superconducting transition temperature $T_c = 9.6$K shows the most anomalous behavior. For example, the electrical resistivity demonstrates strong concave $T$ dependence down to $T_c$, in contrast to the normal $T^2$ behavior in Rb and Cs compounds. The specific heat measurements have found an existence of low frequency Einstein modes and that the $T$-linear coefficient of the specific heat $\gamma = 70 mJ/K^2 \cdot mol$, (see Refs. [8]), is strongly enhanced over the value obtained from band structure calculations. The band structure calculations have indicated that these anomalies may be due to highly anharmonic low frequency rattling motion of the alkali-ions inside an oversized cage formed by the Os and O ions. Furthermore, this is consistent with the x-ray observation of anomalously large atomic displacement for the $K^+$ ions, and the low frequency phonon structures seen in photoemission spectra. Moreover, recent NMR data[13] have indicated that the relaxation at the K sites is entirely caused by fluctuations of the electronic properties, and finally, from a point of view of studying further aspects of the strong coupling Eliashberg theory in presence of coupling between conduction electrons and rattling phonons. Previously, an attempt to consider the effect of the temperature-independent rattling phonons has been considered in Ref.[16] in application to CsO$_2$O$_6$.

In this Brief Report, we analyze the superconductivity in KO$_2$O$_6$ using the standard Eliashberg formalism supplemented by a quasiharmonic treatment of the rattling mode and its renormalization by the coupling with conduction electrons. We find that the phonon spectrum can be modeled by the two Lorentzians peaked at the Os and O sites, representing the lowest energy rattling phonons. An additional contribution arises from the Debye frequency at $\omega_D$. To explain the superconducting transition temperature in KO$_2$O$_6$, we have employed the mean-field analysis of the temperature dependence of the lowest Einstein mode proposed previously. We show that its energy should decrease with temperatures down to $T_p < T_c$ and then jump to a higher frequency indicating the first order structural phase transition. Solving the non-linear Eliashberg equations below $T_c$, with temperature dependent electron-phonon coupling function, $\alpha^2 F(\omega)$ we compare our results with various experiments.

On the real frequency axis the finite temperature Eliashberg equations for the superconducting gap $\Delta(\omega, T)$ and the renormalization function $Z(\omega, T)$ are

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given by\textsuperscript{12}:

\[
\Delta(\omega, T) = \frac{1}{Z(\omega, T)} \int_0^\infty d\omega' \text{Re} \left\{ \frac{\Delta(\omega', T)}{\sqrt{\omega'^2 - \Delta^2(\omega', T)}} \right\} \\
\times \left[ K_+(\omega, \omega', T) - \mu^* \tanh \left( \frac{\beta \omega'}{2} \right) \right], \quad (1)
\]

\[
\omega(1 - Z(\omega, T)) = \int_0^\infty d\omega' \text{Re} \left\{ \frac{\omega'}{\sqrt{\omega'^2 - \Delta^2(\omega', T)}} \right\} \\
\times K_-(\omega, \omega', T), \quad (2)
\]

where

\[
K_{\pm}(\omega, \omega', T) = \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{\pm f(-\omega') + n(\Omega)}{\omega' - \omega + \Omega} + \frac{f(\omega') + n(\Omega)}{-\omega' + \omega + \Omega} - \frac{f(\omega') + n(\Omega)}{-\omega' - \omega + \Omega}, \quad (3)
\]

and

\[
\alpha^2 F(\Omega) = \alpha_{E1}^2 F_{E1}(\Omega) + \alpha_{E2}^2 F_{E2}(\Omega) + \alpha_p^2 F_p(\Omega), \quad (4)
\]

is the generalized electron-phonon coupling function averaged over the Fermi surface. We assume that there are two contributions to the Eliashberg function. The second is arising from the usual dispersive acoustic phonons limited by the Debye energy \(T_D = 325\) K. The first contribution is due to local low energy rattling phonons whose energies we denote by \(\omega_{E1}\) and \(\omega_{E2}\). The latter requires a special consideration.

It has been shown recently that the low-energy phonons ascribed to the heavy rattling of the K ions confined in an oversized cage made of OsO\textsubscript{6} octahedra are responsible for the unusual scattering processes in K\textsubscript{9}Os\textsubscript{2}O\textsubscript{6}\textsuperscript{2}. In particular, it has been assumed that contrary to the RbOs\textsubscript{2}O\textsubscript{6} and CsOs\textsubscript{2}O\textsubscript{6} cases where a single Einstein mode due to rattling motion is enough, there exits two modes at \(h\omega_{E1} = 22\)K, and \(h\omega_{E2} = 61\)K in K\textsubscript{9}Os\textsubscript{2}O\textsubscript{6} corresponding to the first two excited energy levels of the corresponding anharmonic potential. Simultaneously, the mean-field description of the local alkali-ion anharmonic motion has been developed in Ref.\textsuperscript{14}. Starting from the standard anharmonic Hamiltonian

\[
H = \frac{p^2}{2m} + \frac{1}{2} ax^2 + \frac{1}{4} bx^4, \quad (5)
\]

where \(x, p, m\), and \(M\) are the spatial coordinate, momentum, and mass of the alkali ion, respectively and \(a, b\) are constants with \(b > 0\) one finds that according to \textit{ab initio} calculations\textsuperscript{2}, for K\textsubscript{9}Os\textsubscript{2}O\textsubscript{6}, the quadratic term becomes negative, \textit{i.e.} \(a < 0\), that results in a double well potential. We note that in reality the double wells are not in the plane\textsuperscript{9}. Treating the Hamiltonian\textsuperscript{15} in the self-consistent quasiharmonic approximation Dahm and Ueda have found that the oscillation of Potassium ions can be described by an effective harmonic oscillation with effective low-energy frequency that now depends on temperature\textsuperscript{14}. In particular, it decreases monotonically upon decreasing temperature\textsuperscript{14}. At low enough temperatures \((T \ll \omega_0)\), this frequency becomes nearly temperature independent. Obviously this model requires certain modification when applied to K\textsubscript{9}Os\textsubscript{2}O\textsubscript{6}. In particular, although this effective model works well at high temperatures, it fails to explain the occurrence of the first order phase transitions at temperature \(T_p < T_c\). The occurrence of the second Einstein frequency at higher energy.

Therefore, modeling the contribution of the rattling K ions to the Eliashberg function we adopt two Einstein like modes centered at \(\omega_{E1}\) and \(\omega_{E2}\). Furthermore, to take into account the upper lying energy levels of the shallow potential we use the self-consistent quasiharmonic approximation for the lowest mode, \(\omega_{E1}\) that results in its temperature dependence. Most importantly, before entering the temperature independent regime the effective rattling phonon frequency shows a discontinuous jump towards higher frequency that will result in the specific heat anomaly at \(T_p\). The increase of the \(\omega_{E1}\) at \(T_p\) is in accordance with recent experiments showing no structural changes below the phase transition\textsuperscript{9,13,20}. Indeed, below \(T_p\) the K ions seem to be stabilized in their equilibrium positions which corresponds to the increase of \(\omega_{E1}\).

To find the exact shift of the lowest frequency at \(T_p\), and also the approximate positions of the rattling mode frequencies we made a simulation of the specific heat data around \(T_p\) following the model proposed by Ref.\textsuperscript{8} with temperature dependent \(\omega_{E1}\). The contribution from the two frequencies representing the rattling modes is given by

\[
C = aC_{E1} + (1 - a)C_{E2} \quad (6)
\]

where \(a = 0.24\) and \(\omega_{E_i}\) with \(i = 1, 2\) are the corre-
In particular, the spectral function of the renormalizing its energy position and introducing an extra damping. In particular, the spectral function of the corresponding Einstein phonons. As mentioned above, for the sake of simplicity we assume that the higher mode is temperature independent and the lower one follows the mean-field temperature dependence that originates from integrating out the upper-lying energy levels with temperature. Generally, for the contribution of temperature dependent Einstein frequency one finds

$$C_E = 3R \left( \frac{\hbar \omega_E}{k_B T} \right)^2 \frac{\exp \left( \frac{\hbar \omega_E}{k_B T} \right)}{\exp \left( \frac{\hbar \omega_E}{k_B T} \right) - 1}^2 \left[ 1 - \frac{\partial \ln \omega_E}{\partial \ln T} \right]$$

where $R$ is the gas constant. The last term is absent for the upper temperature-independent frequency, $\omega_{E2}$. The results of the fit are shown in Fig. 1. The change of the specific heat at $T_p$ is reproduced by assuming the jump of the lower Einstein frequency from $\hbar \omega_{E1}=27.4K$ to $\hbar \omega_{E1}=30K$ at this temperature with $\omega_{E2}$ being constant. Above $T_p$ the lower frequency mode is temperature dependent and the overall behavior of $\omega_{E1}(T)$ is shown in Fig. 2. Note that the strong temperature dependence of the lowest rattling phonon mode frequency has been recently observed by the Raman scattering experiment.

In addition to the anharmonic temperature dependence of the rattling phonon mode which modifies the usual approximation for the Eliashberg function, the conduction electrons couple to the rattling phonons, further renormalizing its energy position and introducing an extra damping. In particular, the spectral function of the low-energy rattling phonon frequency is given by

$$\alpha^2 F_{E1}(\omega) = -\frac{\alpha^2(T)}{\pi} \text{Im} D(\omega) = \frac{\alpha^2(T)}{\pi} \frac{4 \omega_{E1}(T) \Gamma_0 \omega}{(\omega^2 - \omega_{E1}^2)^2 + 4 \Gamma_0^2 \omega^2},$$

where $\Gamma_0$ is a anharmonic phonon damping rate. The real part of the rattling phonon self-energy leads to a renormalized phonon frequency,

$$\omega^2_r(T) = \omega_{E1}^2(T) + 2 \omega_{E1}(T) \text{Re} \Pi(\omega).$$

Following previous estimation we have used $\text{Re} \Pi(\omega) = 1$ meV and $\Gamma_0 = 0.25$ meV. It is important to remember that the electron-phonon coupling parameter $\alpha^2(T) \sim c/\omega_{E1}(T)$ with $c=1.23\text{meV}^2$ is also temperature dependent. In Fig. 3 we show the Eliashberg function $\alpha^2 F(\omega)$ including all three contributions for $T=0.5K$ i.e. well below $T_p$. In contrast to the usual Eliashberg theory the $\alpha^2 F(\omega)$ spectrum and the coupling constant $\lambda = 2 \int_{-\infty}^{\infty} d\Omega \alpha^2 F(\Omega)/\Omega$ are now temperature dependent. Setting $\mu^* = 0.091$ and solving the Eqs. (1)-(3) in the linearized limit we find the superconducting transition temperature $T_c=9.6K$. In Fig. 4 we show the results of the solution of the Eliashberg equations for $T=0.5K$. One finds the typical behavior of a strong-coupling superconductor. In particular, $\text{Re} \Delta(\omega)$ shows three peaks at the energy of the rattling phonons and at $\omega_D$. For larger energies it becomes negative reflecting the effective repulsion for $\omega > \omega_D$. Due to presence of the low-energy rattling phonons one obtains a strong renormalization of the quasiparticle mass and we also find $2 \Delta_0/k_B T_c \approx 5.0$. The latter is in good agreement with experimentally observed value.
Although the detailed understanding both theoretically and experimentally is still required.

Our calculation shows that the superconducting properties of KO\textsubscript{2}O\textsubscript{6} should be sensitive to the external pressure. Due to proximity to the first-order phase transition the application of the pressure may result in a modification of the electron-phonon coupling strength. Such an unusual behavior has been indeed recently found experimentally\cite{Khasanov} although the detailed understanding both theoretically and experimentally is still required.

In summary, we have investigated the superconducting properties of β-pyrochlore KO\textsubscript{2}O\textsubscript{6} compound based on the strong-coupling Eliashberg approach. Analyzing the specific heat data we find that rattling phonon frequency changes discontinuously at the critical temperature of the first order phase transition. Solving the strong-coupling Eliashberg equations with temperature dependent $\alpha^2 F(\omega)$, we discuss the consequence of this first order phase transition for the anomalous temperature dependence of the superconducting gap. In particular, we have found that the superconducting gap as a function temperature is anomalous reflecting the temperature dependence of the Eliashberg function.

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\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{FIG4.png}
\caption{Calculated frequency dependence of the real part of the superconducting gap function $\Delta(\omega)$ for KO\textsubscript{2}O\textsubscript{6} compounds. The inset shows the renormalization function, $Z(\omega)$ at $T = 0.5$K. Note that we set the cutoff frequency to $8\omega_D$ and introduce a finite damping $\Gamma_0 = 0.25$ meV.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{FIG5.png}
\caption{Calculated temperature dependence of the superconducting gap $\Delta_0(T)$ as determined from Re$\Delta(T,\omega) = \omega$ for KO\textsubscript{2}O\textsubscript{6}. The black squares show the experimental data from Ref.\cite{Khasanov} as obtained from the fit of the experimental curve by the Dynes formula.}
\end{figure}

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It is important to remember that the effective frequency, \( \omega_0 \), is a thermodynamical average frequency and should not be mixed with the discrete, temperature independent energy levels of the original Hamiltonian.

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