The effect of strong electron-rattling phonon coupling on some superconducting properties

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Abstract: Using the Eliashberg theory of superconductivity we have examined several properties of a model in which electrons are coupled only to rattling phonon modes represented by a sharp peak in the electron-phonon coupling function. Our choice of parameters was guided by experiments on $\beta$-pyrochlore oxide superconductor KO$\text{S}_2$O$\text{S}_6$. We have calculated the temperature dependence of the superconducting gap edge, the quasiparticle decay rate, the NMR relaxation rate assuming that the coupling between the nuclear spins and the conduction electrons is via a contact hyperfine interaction which would be appropriate for the O-site in KO$\text{S}_2$O$\text{S}_6$, and the microwave conductivity. We examined the limit of very strong coupling by considering three values of the electron-phonon coupling parameter $\lambda = 2.38, 3, \text{and} 5$ and did not assume that the rattler frequency $\Omega_0$ is temperature dependent in the superconducting state. We obtained a very unusual temperature dependence of the superconducting gap edge $\Delta(T)$, very much like the one extracted from photoemission experiments on KO$\text{S}_2$O$\text{S}_6$.

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1. Introduction

The $\beta$-pyrochlore osmium oxide superconductors AO$\text{S}_2$O$\text{S}_6$ ($A=$Cs, Rb, K) have been extensively studied experimentally and theoretically since the discovery of superconductivity in these compounds in 2004 (for reviews see [1, 2]). The key structural feature of this class of compounds is that alkali ion A is located in an oversized cage composed of OsO$\text{S}_6$ octahedra and moves in a flat anharmonic potential well [3]. This motion results in almost localized anharmonic modes at low energies — so-called rattling modes. The rattling modes are responsible for many of the observed physical properties of $\beta$-pyrochlores, such as the nuclear magnetic resonance (NMR) relaxation rate $1/(T_1T)$ of potassium nucleus in KO$\text{S}_2$O$\text{S}_6$ which is dominated by coupling of the electric field gradient to the nuclear quadrupole moment [4, 5]. As the size of the alkali ion is reduced from Cs to K the potential in which the ion moves becomes flatter and wider [3] which results in an increased anharmonicity. At the same time the superconducting transition temperature $T_c$ increases from 3.25 K for $A=$Cs to 9.60 K for $A=$K leading to a conclusion that rattling modes play an important role in superconductivity of these compounds, in particular because the electronic structures of these compounds and the electronic density of states at the Fermi level are almost identical to each other (see [2], section 4.1, and the references therein).

The most direct evidence that the low frequency phonon modes play an important role in superconductivity of KO$\text{S}_2$O$\text{S}_6$ comes from the photoemission spectroscopy measurements by Shimojima et al. [6] of the electronic density of states (DOS) in superconducting state $N_e(\omega)$. The observed peak at 3.7 meV followed by a dip at 4.5 meV (see the inset in Fig. 1(a) in [6]) are directly related to a sharp peak in the electron-phonon coupling function $\alpha^2(\Omega)F(\Omega)$ at energy $\Omega_0$ equal to 3.7 meV minus the gap edge $\Delta(T) = 1.63$ meV at $T = 4.7$ K. For excitation energy $\omega \leq \Omega_0 + \Delta(T)$ the electron-phonon interaction is attractive and the real part of the gap function $\Delta_1(\omega) = \text{Re}\,\Delta(\omega)$ is positive and attains maximum near $\omega = \Omega_0 + \Delta(T)$ caused by resonant exchange of (virtual) phonons (see Fig. 34 in [7]). At the same time a quasiparticle added at energy $\omega$ near $\Omega_0 + \Delta(T)$ can decay down to the gap edge $\Delta(T)$ by emitting a real phonon of energy $\Omega_0$ leading to an increase of the quasiparticle damping rate which is given by the modulus of the imaginary part of the gap $\Delta_2(\omega) = 1\text{Im}\,\Delta(\omega)$. As a result, the electronic density of states in the superconducting state

$$\text{Re}\,\frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}} \approx 1 + \frac{\Delta_1^2(\omega)}{2\omega^2} - \frac{\Delta_2^2(\omega)}{2\omega^2},$$

shows a peak near $\Omega_0 + \Delta(T)$ followed by a dip (see Fig. 38 in [7]). The energy $\Omega_0 \approx 2.1$ meV of the rattling mode obtained from photoemission spectroscopy measurements in the superconducting state of KO$\text{S}_2$O$\text{S}_6$ [6] is very similar to the value of 2.3 meV obtained by Dahm and Ueda [5] in their fits of the NMR relaxation rate of the potassium nucleus in this compound.

Several experiments point independently to a very strong electron-phonon coupling in $\beta$-pyrochlores, in particular in the case of KO$\text{S}_2$O$\text{S}_6$. The ratio of the measured Sommerfeld coefficient $\gamma$ of the normal state electronic specific heat to the value found in band structure calculations $\gamma_{\text{band}} = \gamma/\gamma_{\text{band}} = 7.3$ [2]. Since enhancement of magnetic susceptibility in $\beta$-pyrochlores is nearly absent [2], a large electron mass enhancement implied by a large value $\gamma/\gamma_{\text{band}}$ is caused by the electron-phonon interaction, and in that case theory [8] gives $\gamma/\gamma_{\text{band}} = 1 + \lambda$, where

$$\lambda = 2\int_0^{\infty} d\Omega \frac{\alpha^2(\Omega)F(\Omega)}{\Omega}.$$
Thus, for KOs$_2$Os$_6$ $\lambda = 6.3$ which is the largest value for any known electron-phonon superconductor. This value is essentially identical with the one obtained from de Haas-van Alphen oscillation measurements and a band structure calculation [9] (see Fig. 3 in [9]). In [9] it was found that orbit-resolved mass enhancements are homogeneous with the $\lambda$-values concentrated in the range 5-8.

The photoemission spectroscopy measurements [6] obtained temperature dependent superconducting gap edge $\Delta(T)$ and found $2\Delta(0)/k_BT_c \geq 4.56$ which is indicative of a very strong electron-phonon coupling in KOs$_2$Os$_6$ [10, 11] (the weak-coupling BCS value is 3.53). The measured ratio of the jump $\Delta C$ in the specific heat at $T_c$ to the normal state electronic specific heat $\gamma T_c$ is $\Delta C/\gamma T_c = 2.87$ [12], which is much larger than the weak-coupling BCS value of 1.43 and indicates strong electron-phonon coupling [13]. Similarly, the measured ratio $\gamma T_c^2/H_0^2(0)$, where $H_0(0)$ is the thermodynamic critical field at zero temperature, is 0.128 [2] (the BCS value is 0.168), which is one among the smallest values for strong coupling superconductors [13] (Pb-Bi alloy shown in Fig.4 of reference [13] should be Pb$_{65}$Bi$_{35}$). The thermodynamic critical field deviation function $D(t) = H_c(t)/H_c(0) - (1-t^2)$, $t = T/T_c$, was measured in a limited temperature range [12] above 8.5 K [1] (see Fig. 12 in [1]) and the values were positive, slightly below those for Pb, suggesting strong electron-phonon coupling in KOs$_2$Os$_6$. In β-pyrochlores the alkali atom donates one electron to the cage making it metallic and the measurements of the NMR relaxation rate on O-sites [4] probed the spin dynamics of conduction electrons. These measurements on KOs$_2$Os$_6$ found that the Hebel-Slichter peak below $T_c$ is strongly suppressed which is consistent with very strong conduction electron-phonon coupling in this compound [14, 15].

In this work we consider a model system in which superconductivity arises exclusively from the conduction electron coupling to a rattling phonon modeled by a single sharp peak in $\alpha^2(\Omega)F(\Omega)$ at rattling frequency $\Omega_0$ [16]. We do not aim to reproduce the experimental results obtained for KOs$_2$Os$_6$, although our choice of parameters, such as $\Omega_0$ and $\lambda$, is motivated by what was obtained for this compound. One earlier study [17] examined the behavior of the gap function and density of states in the extreme strong coupling limit. Certainly the applicability of Eliashberg theory is questionable for the extreme strong coupling parameters explored in [17] and here. Nonetheless, we further and explore the temperature dependence of the gap edge $\Delta(T)$, and various dynamic and thermodynamic properties in such an extreme case. Before one tries to model KOs$_2$Os$_6$ by making a more realistic choice for $\alpha^2(\Omega)F(\Omega)$ which includes electron coupling to phonon modes other than the rattling one, it is important to delineate the effects of electron-rattler coupling.

2. Model and theoretical background

We model the $\alpha^2(\Omega)F(\Omega)$ of electrons coupled to the rattling phonon with a cut-off Lorentzian centered at energy $\Omega_0$ and having the half-width $\varepsilon$

$$\alpha^2(\Omega)F(\Omega) = \frac{g\varepsilon}{\pi} \left[ \frac{1}{(\Omega - \Omega_0)^2 + \varepsilon^2} - \frac{1}{\Omega_0^2 + \varepsilon^2} \right],$$

for $|\Omega - \Omega_0| \leq \Omega_c$ and zero otherwise. We assume that at superconducting temperatures $\Omega_0$ and $\varepsilon$ are temperature-independent. Motivated by experiments on KOs$_2$Os$_6$ we take $\Omega_0 = 2.2$ meV and choose $\varepsilon = 0.01$ meV and $\Omega_c = 2.1$ meV. The strength $g$ in (3) was chosen to obtain a particular value for $\lambda$ given by (2), and we considered $\lambda = 2.38, 3, and 5$.

First, Eliashberg equations on the imaginary axis [18, 19] were solved for the superconducting transition temperature $T_c$. At $T = T_c$ these equations can be cast into a Hermitian eigenvalue problem

$$\tilde{\phi}(n) = e(T) \sum_{|\omega_m| \leq \omega_c} \frac{\pi T}{\sqrt{|\omega_n|Z(n)|\omega_m|Z(m)}} \phi(m),$$

and $T_c$ is the highest temperature $T$ at which the largest eigenvalue $e(T)$ is equal to 1. In (4) $\omega_c$ is a cutoff on Matsubara frequencies $\omega_n = \pi T(2n - 1)$ and $\mu^*(c_{\omega_c})$ is the Coulomb pseudopotential for that cutoff. We took $\omega_c = 30$ meV ($\gg \Omega_0$) and $\mu^*(c_{\omega_c}) = 0.1$ for all values of $\lambda$. Furthermore, in (4)

$$\phi(n) = \phi(n)/\sqrt{|\omega_n|Z(n)},$$

where $\phi(n)$ is the pairing self-energy at $i\omega_n$, and

$$Z(n) = 1 + \int_{-\infty}^{+\infty} \frac{\lambda(\omega - \omega_m) \omega_m}{|\omega_m|^2} \frac{\omega_m}{\omega_n}$$

is the renormalization function at $i\omega_n$. In (4) and (5)

$$\lambda(\omega - \omega_m) = \int_{0}^{\infty} d\Omega \alpha^2(\Omega)F(\Omega)$$

is the electron-phonon kernel at temperature $T$.

Next, the gap function $\Delta(\omega)$ and the renormalization function $Z(\omega)$ are obtained by solving the Eliashberg equations at finite temperature on the real axis

$$\phi(\omega) = \int_{0}^{\omega} d\omega' \text{Re}[M(\omega')] \left[ f(-\omega')K^+(\omega, \omega') - f(\omega')K^+(\omega, -\omega') \mu^*(\omega_c) \tanh \frac{\omega'}{2T} + K^+(\omega, \omega') - K^+(\omega, -\omega') \right],$$

$$Z(\omega) = 1 - \frac{1}{\omega} \int_{0}^{+\infty} d\omega' \text{Re}[N(\omega')] \left[ f(-\omega') \times K^-(\omega, \omega') - f(\omega')K^-(\omega, -\omega') + K^-(\omega, \omega') - K^-(\omega, -\omega') \right],$$

where $\phi(\omega) = \Delta(\omega)Z(\omega)$ is the pairing self-energy,

$$M(\omega) = \frac{\Delta(\omega)}{\sqrt{\omega^2 - \Delta^2(\omega)}},$$

$$N(\omega) = \frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}},$$

and $f$ is the Fermi function. The electron-phonon coupling function $\alpha^2(\Omega)F(\Omega)$ enters via the zero temperature kernels.
and the thermal phonon kernels \( \tilde{K}^{\pm}(\omega, \omega') \) defined by

\[
[11] \quad K^{\pm}(\omega, \omega') = \int_{0}^{+\infty} d\Omega \alpha^{2}(\Omega) F(\Omega) \times \left[ \begin{array}{cc} 1 & 1 \\
\omega' + \omega + \Omega + i0^{+} & \omega' - \omega + \Omega - i0^{+} \end{array} \right],
\]

\[
[12] \quad \tilde{K}^{\pm}(\omega, \omega') = \int_{0}^{+\infty} d\Omega \alpha^{2}(\Omega) F(\Omega) e^{\Omega/2T - 1} \times \left[ \begin{array}{cc} 1 & 1 \\
\omega' + \omega + \Omega + i0^{+} & \omega' - \omega + \Omega - i0^{+} \end{array} \right].
\]

These equations can be solved through iterative methods. Alternatively, one can solve a hybrid set of equations, based on solutions already converged on the imaginary axis \([20]\). We have checked our results by using both methods.

From the solutions of the real-axis Eliashberg equations at a given temperature \( T \) below \( T_{c} \) one can compute the ratio of the NMR relaxation rate in the superconducting state \( R_{s} = 1/(T_{1}T) \) to its value in the normal state \( R_{n} \), assuming that the coupling between the nuclear spins and the conduction electrons is via a contact hyperfine interaction

\[
[13] \quad \frac{R_{s}}{R_{n}} = 2 \int_{0}^{+\infty} d\omega \left( -\frac{\partial f}{\partial \omega} \right) \times \left[ (\text{Re} N(\omega))^{2} + (\text{Re} M(\omega))^{2} \right]
\]

(for derivation see, for example, \([21]\)).

The frequency dependent conductivity is given by \([22]\)

\[
[14] \quad \sigma(\nu) = \frac{\omega_{p}^{2}}{8\pi\nu} \int_{0}^{+\infty} d\omega \frac{\sinh(\omega_{p}\sqrt{T})}{\omega_{p}^{2}} \times \frac{1}{\nu(T_{c}) - M(\omega + \nu)}
\]

\[
\times \left\{ 1 - N(\omega)N(\omega + \nu) - M(\omega)M(\omega + \nu) \right. \right. 
\]

\[
\left. \left. - \text{Im} \Delta(\omega + \nu) \right\} \right.
\]

\[
+ \int_{0}^{+\infty} d\omega \sinh(\omega_{p}\sqrt{T}) \times \frac{1}{\nu(T_{c}) - M(\omega + \nu)}
\]

\[
\times \left\{ 1 - N(\omega)N(\omega + \nu) - M(\omega)M(\omega + \nu) \right. \right. 
\]

\[
\left. \left. - \text{Im} \Delta(\omega + \nu) \right\} \right.
\]

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+ \int_{0}^{+\infty} d\omega \sinh(\omega_{p}\sqrt{T}) \times \frac{1}{\nu(T_{c}) - M(\omega + \nu)}
\]

\[
\times \left\{ 1 - N(\omega)N(\omega + \nu) - M(\omega)M(\omega + \nu) \right. \right. 
\]

\[
\left. \left. - \text{Im} \Delta(\omega + \nu) \right\} \right.
\]

where \( \omega_{p}^{2} \) is the square of the plasma frequency. The quasiparticle energy \( E(\omega) \) appearing in the denominators in (14) is defined by

\[
[15] \quad E(\omega) = Z(\omega) \sqrt{\omega^{2} - \Delta^{2}(\omega)}
\]

where \( Z(\omega) \) is the total renormalization function which includes the electron-phonon interaction and impurity scattering [22]. In (15) the branch of the square root with positive real part is taken.

3. Results and discussion

The computed critical temperatures for our model were \( T_{c} = 5.06 \text{ K}, 5.99 \text{ K} \) and 8.32 K for \( \lambda = 2.38 \) [12] (Fig. 25 in [12]), 3 and 5 [2, 9], respectively.

The gap edge at temperature \( T \), \( \Delta(T) \) was obtained from solution of

\[
[16] \quad \text{Re} \Delta(\omega = \Delta(T), T) = \Delta(T)
\]

when it existed and the the results are shown in Figs. (1-3). The computed values for the ratio \( 2\Delta(0)/k_{B}T_{c} \) were 5.32, 5.74 and 6.36 for \( \lambda = 2.38 \), 3 and 5, respectively, indicating very strong coupling regime in all three cases.

In Figs. (1-3) we also show the absolute value of the imaginary part of the gap at the gap edge which rigorously gives the quasiparticle decay rate \( \Gamma(T) = -\text{Im} \Delta(T) \) [23]. In all cases considered \( \Delta(T) \) deviates from the BCS temperature dependence [24]. Note that for very strong coupling and for temperatures very close to \( T_{c} \), the density of states becomes sufficiently smeared that a ‘gap’ as defined by (16) does not even exist [17]. The non-BCS temperature dependence of the gap shown in Figs. (1-3) and a large damping rate as given by the imaginary part of the gap function are quite unusual even for
Fig. 1. Temperature dependence of the gap edge $\Delta(T)$ and of the quasiparticle decay rate given by $-\text{Im} \Delta(T)$ for $\lambda = 2.38$. The solid line represents the BCS temperature dependence. The equation (16) did not have a solution for $T > 7.34$ K.

Fig. 2. Temperature dependence of the gap edge $\Delta(T)$ and of the quasiparticle decay rate given by $-\text{Im} \Delta(T)$ for $\lambda = 3$. The solid line represents the BCS temperature dependence.

Fig. 3. Temperature dependence of the gap edge $\Delta(T)$ and of the quasiparticle decay rate given by $-\text{Im} \Delta(T)$ for $\lambda = 5$. The solid line represents the BCS temperature dependence.

strongly coupled electron-phonon superconductors such as Pb where $\Delta(T)$ closely follows the BCS curve (see Fig. 44 in [7]). A very similar behavior to the one we find was observed in KOs$_2$O$_6$ ($T_c = 9.6$ K) using photoemission spectroscopy [6] (see Fig. 3 in [6]), and $2\Delta(0)/k_B T_c$ for this compound was estimated to be $\geq 4.56$. Note that in all three cases shown in Figs. (1-3) the temperature at which the most rapid drop in $\Delta(T)$ sets in coincides with the temperature at which the quasiparticle damping rate $\Gamma(T) = -\text{Im} \Delta(T)$ attains maximum $\Gamma_{\text{max}}(T)$. We found $\Gamma_{\text{max}}(T)/\Delta(T)$ equal to 11%, 30% and 59% for $\lambda = 2.38$, 3 and 5, respectively, and in the last two cases the quasiparticle picture most definitely breaks down [25]. In [6] $\Gamma_{\text{max}}(T)/\Delta(T)$ for KOs$_2$O$_6$ was found to be $\approx 100$ % and the fits to the measured density of states using the Dynes formula [26] were clearly invalid (for the validity of the Dynes formula it is necessary that $\Gamma(T)/\Delta(T) \ll 1$ [23]).

In Figs. (4-6) we show the NMR relaxation rate $R_s(T)$ and the microwave conductivity $\sigma_s(T)$, both normalized to their normal state values, together with $\Delta(T)/\Delta(0)$ as functions of reduced temperature $T/T_c$. $R_s(T)/R_n(T)$ and $\sigma_s(T)/\sigma_n(T)$ have very similar shapes for each value of $\lambda$. The coherence peaks in $R_s(T)/R_n(T)$ and $\sigma_s(T)/\sigma_n(T)$ at about 95% of $T_c$ are reduced with increasing $\lambda$ and disappear for $\lambda = 5$. We note again that the measurements of the NMR relaxation rate on O-sites in KOs$_2$O$_6$ [4] found that the Hebel-Slichter peak below $T_c$ is strongly suppressed, and our results in (4-6) suggest that for this compound $\lambda \geq 5$ in agreement with specific heat [2] and Fermi surface [9] measurements.
An increase in slope of $R_s(T)/R_n(T)$ and $\sigma_s(T)/\sigma_n(T)$ near the temperature where $\Delta(T)/\Delta(0)$ undergoes a sharp drop occurs in all cases, (4-6), and is most notable for $\lambda = 3$.

In conclusion, we have examined the temperature dependence of the superconducting gap edge, the quasiparticle decay rate, the NMR relaxation rate assuming that the coupling between the nuclear spins and the conduction electrons is via a contact hyperfine interaction, and the microwave conductivity for a model of electrons coupled only to the rattling phonon. We examined the limit of very strong coupling by considering three values of electron-phonon coupling parameter $\lambda = 2.38, 3,$ and $5$ and did not assume that the rattler frequency $\Omega_0$ is temperature dependent in the superconducting state. We obtained very unusual temperature dependence of the superconducting gap edge $\Delta(T)$, very much like the one extracted from photoemission experiments on KO$_2$O$_6$ [6].

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