Manifestations of fine features of the density of states in the transport properties of KO$_2$O$_6$

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We performed high pressure transport measurements on high quality single crystals of KO$_2$O$_6$, a β-pyrochlore superconductor. While the resistivity at high temperatures might approach saturation, there is no sign of saturation at low temperatures, down to the superconducting phase. The anomalous resistivity is accompanied by a non-metallic behavior in the thermoelectric power (TEP) up to temperatures of at least 700 K, which also exhibits a broad hump with a maximum at 60 K. The pressure influences mostly the low energy electronic excitations. A simple band model based on enhanced density of states (DOS) in a narrow window around the Fermi energy ($E_F$) explains the main features of this unconventional behavior in the transport coefficients, and its evolution under pressure.

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Recent discovery$^{1,4}$ of superconductivity at $T_c$ of 9.6 K in pyrochlore-structured KO$_2$O$_6$ has strengthened the viewpoint that magnetic frustration may have considerable role in promoting superconductivity.$^5$ Pyrochlore structure is known to impose frustration on magnetic ordering in several systems with localized spins, although the role of frustration in electronically itinerant pyrochlore systems is presently unclear. KO$_2$O$_6$ has the highest superconducting transition temperature among the pyrochlore-structured compounds, and is therefore of particular interest. However, there are indications that geometrical frustration may not be the most important factor for the physics of this compound. OsO$_6$ octahedrons, positioned at the nodes of a pyrochlore lattice, form large cages where potassium atoms move in an anharmonic potential.$^6$ This “rattling motion” of the K ions appears to have significant influence on the physical properties in this material. The electronically identical Rb and Cs compounds have much lower $T_c$’s$^{7,8}$ and simultaneously, this rattling motion is significantly less pronounced. Another remarkable property of KO$_2$O$_6$ is the large value of the Sommerfeld constant found in the specific heat measurements.$^9$ The Sommerfeld coefficient implies a density of states (DOS) at the Fermi energy ($E_F$) an order of magnitude higher than the one predicted by the band structure calculations.$^{10,11}$ In this paper we argue that the high DOS at the Fermi level dominates the shape of the electronic transport properties in the normal state over a wide range of temperatures and pressures.

Interestingly, frustration, the rattling of the K ions and the high DOS at $E_F$ in a broad sense relate KO$_2$O$_6$ to the high temperature superconducting cuprates. There, the magnetic frustration is related to missing spins introduced by doping, often at the expense of the non-stoichiometric crystal structure. The strongly anharmonic phonon modes are also often encountered in the cuprates and are sometimes regarded as important for superconductivity.$^{12}$ Lastly, the band structure calculations and photoemission measurements suggest a van Hove enhancement in the DOS in the vicinity of $E_F$.$^{13}$ Similarly to the copper oxide superconductors, the normal state properties of KO$_2$O$_6$ may prove more intriguing than those of the superconducting phase.

Application of pressure on KO$_2$O$_6$ may tune the coupling constants of the electron-electron and electron-phonon interaction, change the size of the rattling cage, or widen the bands. We have measured the high pressure behavior of the transport coefficients, resistivity $\rho(T)$ and the thermoelectric power (TEP) $S(T)$ on high quality single crystals of KO$_2$O$_6$. Previously reported high pressure resistivity measurements were done on polycrystalline samples,$^{13}$ which made it difficult to separate the intrinsic behavior from the grain-size effects. Focusing on the anomalous normal state rather than on the superconducting phase, we also investigated the transport properties on a much finer pressure scale than previously reported.$^{14}$ Additionally, we have measured the ambient pressure transport coefficients up to high temperatures, reaching 700 K. The TEP data indicates a behavior unusual for ordinary metals stretching up to at least 700 K, which links to the unconventional resistivity $\rho(T)$.

We argue that this may be understood as a result of high electronic DOS, confined to a rather narrow energy window around $E_F$. Such a DOS enhancement, which is indicated by the large Sommerfeld coefficient, is probably related to the rattling mode, as our high pressure results suggest.

The growth of single crystals of KO$_2$O$_6$ is described in the work of G. Schuck et al.$^{15}$ Resistivity was measured by a standard four-point method on a crystal of approximate dimensions $0.2 \times 0.2 \times 0.2$ mm$^3$. For the TEP measurement, which is insensitive to the grain size, we used a single-crystal conglomerate approximately 1 mm long. The sample was attached onto a ceramic surface, which was heated by a small metallic heater. The temperature gradient was determined by a differential thermocouple and the contribution of the golden metallic heater. The temperature gradient was determined by a differential thermocouple and the contribution of the golden leads to the TEP was subtracted. The measurements were carried out in a clamped piston pressure cell, with an InSb pressure gauge determining the pressure in situ. The applied pressure was hydrostatic, and the maximum pressure reached was 2.3 GPa.

The ambient pressure resistivity and TEP measured in the temperature range from 4.2 to 700 K are shown in Figure 1.
The quality of the crystals is reflected in a comparatively high residual resistivity ratio (RRR) of 15. Since there is no saturation in resistivity at low temperatures, under residual resistivity, we refer here to the value of the resistivity right above the superconducting transition. At temperatures above 200 K, $\rho(T)$ grows, exhibiting neither a strong increase which we would have in case of scattering on phonons, nor a saturation, which was seen, for instance, in the pyrochlore superconductor Cd$_2$Re$_2$O$_7$. A plausible reason for the absence of saturation immediately above 200 K is the still large mean free path. It was estimated to be of the order of ten lattice constants from the characteristic value of the Fermi velocity $v_F$ and the DOS obtained in band structure calculation. At low temperatures, there is a strong downward curvature in resistivity below 200 K. However, contrary to what was reported previously, no concave behavior, such as $\rho_0 + AT^2$, is observed in resistivity at low temperatures, even down to the superconducting transition temperature $T_c$.

The pressure evolution of the resistivity is shown in Figure 2. These are the first reported high pressure measurements on single crystals of KO$_2$O$_6$. At high temperatures the resistivity is not considerably influenced by the pressure. However, important changes start to happen in the low temperature part. The low temperature resistivity at the highest pressure of 2.3 GPa increases by 300% (inset of Figure 2), which is reflected in the drop of RRR from its ambient pressure value of 15 to a modest 3.5. Such an increase in the residual resistivity $\rho_0$ is anomalous. It asserts that pressure affects mostly the low energy electronic excitations.

The temperature dependence of the TEP up to 700 K is shown in Figure 1. In the whole temperature range the TEP is negative. The most prominent feature is a strong peak around 60 K. As temperature is increased further, the TEP drops precipitously. With the application of pressure, the absolute value of TEP is reduced, as shown in Figure 2. The largest changes happen around the maximum, although the position of the maximum does not shift. Again, the high temperature part of TEP is much less affected.

There are several reasons to eliminate the interpretation of the maximum in the TEP as a consequence of a conventional phonon drag. Even at temperatures as high as 700 K the TEP does not recover normal metallic behavior, marked by a linear temperature dependence. The temperature dependence of resistivity below 60 K shows no usual signs of the scattering of electrons on acoustic phonons, as it is convex in the whole temperature range. In addition, that part of resistivity strongly depends on pressure, but in the opposite sense to what is expected if the velocity of the acoustic phonons increases with pressure. Finally, the maximum value of the TEP decreases with pressure, contrary to what one would expect if the coupling to acoustic phonons increased under pressure, as the rise in resistivity may suggest. The conventional phonon drag being eliminated, the observed TEP may be only described as an anomalous electronic contribution. The resistivity and the TEP measurements together signal the unconventional transport in KO$_2$O$_6$.

The presented data accentuate the importance of the low energy electron dynamics in KO$_2$O$_6$. In what follows we will illustrate that the basic physics of the transport in the normal state of KO$_2$O$_6$ may be understood within a simple fermionic model with a marked DOS enhancement in the narrow window of energies. This enhancement is indicated by the Sommerfeld coefficient $\gamma$ of 75 – 110 mJ/(K$^2$mol) determined from the specific heat measurements. The Sommerfeld coefficient appears to be an order of magnitude higher than suggested by band structure calculations. The increase of the specific heat in applied magnetic field in the superconducting state demonstrates that the effect is electronic. The additional contribution to the electronic DOS is likely to be important in a narrow energy window of about 1 eV around the $E_F$, as the...
usual band transport formulae:

\[
\sigma = \int dE g(E) \sigma(E) \left( -\frac{\partial f_0(E,T)}{\partial E} \right)
\]

\[
S = -\frac{e}{T \sigma} \int dE g(E) \sigma(E)(E - \mu)
\]

(1)

where \( g(E) \) stands for the DOS and has values \( g_n \) and \( g_w \), for the narrow enhanced part and the wings respectively, and \( f_0(E,T) \) refers to the Fermi function. The model is simplified to the extent that no implicit temperature dependencies of the parameters are assumed. In such an approach, the only source of the temperature dependence of the transport quantities comes from the "softening" of the shape of \( f_0 \) as the temperature rises. The widening of the Fermi distribution then implies significant shift of the chemical potential as well as the progressive activation of different types of electronic states in the transport.

Our parametrization of \( \rho(T) \) and \( S(T) \) gives the following values for the ratios: \( \sigma_w/\sigma_n = 2.8 \), and \( g_n/g_w = 20 \). The half-width of the narrow portion of the DOS is \( W_n = 60 K \). The band filling at zero temperature is slightly below the center of the narrow portion of DOS, \( \mu_0 = -6.6 K \). The off-center shift is needed to explain the finite TEP. At a finite temperature, the chemical potential is calculated from the requirement that the number of particles stays thermally independent. This set of parameters, as shown in Figure 4 reproduces the temperature dependence of both the resistivity and TEP over a wide temperature range, in good accordance with experimental data. The value of \( g_n/g_w \) is of the order of what has been calculated from the specific heat measurements. The temperature of the pronounced maximum in \( S(T) \) corresponds to the value of \( W_n \).

The considerations of the microscopic sources of the values
of $g_n$, $g_w$, $\sigma_n$, and $\sigma_w$ are beyond the scope of this paper. However, even at the present level we learn much about the nature of the electronic states. Firstly, it is somewhat surprising that the model does not require any separate temperature dependencies for the parameters $\sigma_n$ and $\sigma_w$. In fact, for the same model to reproduce both $S(T)$ and $\rho(T)$ one condition is that this temperature dependence be negligible. A sizeable temperature dependence of $\sigma_n$ and $\sigma_w$ parameters would affect directly the $\rho(T)$, whereas the additional temperature dependent factors would cancel in the expression for $S(T)$. Thus most of the temperature dependence comes exclusively from the existence of two distinct parts in the electronic spectrum. Second observation is linked to the strong increase of the resistivity in the low temperature range, which implies that the rise in temperature renders the charge carriers propagation more difficult. This is contrary to what would happen if the low energy electronic states were localized in space and it was the delocalized states that became more populated as the temperature increased. The model suggests that the mean free path $l_w$, for the states in the enhanced part of DOS, is greater than the one related to the wide part of the DOS, $l_w$. This is the consequence of the parameters $\sigma_n$ and $\sigma_w$ being of similar order of magnitude, i.e. $v_{th}l_w \sim v_{th}l_w$, and a rather natural assumption that the velocity in the wide portion of the electronic spectrum is significantly larger than in the narrow part, $v_w \gg v_w$. Good spatial coherence of the low lying states rules out a bad metal or a localized transport limit. As the effective single particle states close to $E_F$ are spatially coherent, one may speak of an effective, renormalized electronic dispersion at low temperature, which is not destroyed by the weak residual interaction. This situation, where the renormalization is strong while the effective electronic band picture is preserved, is often encountered in heavy fermion systems.

The pressure dependence observed in the experiments may be transferred into the pressure dependence of the model parameters. Experiments unambiguously suggest that the pressure mostly affects the low energy electronic spectrum. The model parameters related to that part of the spectrum are the low energy DOS, $g_n$, and the scattering parameter $\sigma_n$. The rattling of potassium atom is supposed to weaken under pressure. This should mostly be reflected in the gradual decrease of the DOS enhancement around the $E_F$. Indeed, reducing $g_n$ by 20% qualitatively reproduces the observed shifts, both in the resistivity and TEP, under the maximum pressure of 2.3 GPa.

One final comment is due on the relation between the model and the reported, almost temperature-independent magnetic susceptibility $\chi$. It should be noted that a dynamically formed enhancement in the DOS originating from the electron-phonon interaction should generally not show up in $\chi$. The DOS enhancement near the $E_F$ forms separately for spin-up and spin-down electrons. Hence, it cannot be regarded as a construct that would stably move in energy in opposite directions for spin-down and spin-up electrons when the magnetic field is applied. The $E_F$ is the same for spin-up and spin-down electrons in a spin polarized system, therefore the DOS enhancement should not move at all. As expected, no enhancement was observed in the electronic energy as a result of the applied magnetic field.

To conclude, we have studied the transport properties of KO$_2$O$_6$ under pressures up to 2.3 GPa. A strong evidence for a narrow enhancement in the DOS around the $E_F$ comes from the TEP data, which shows a non-metallic behavior persisting to very high temperatures. A simple model is able to account for the unusual features of both the thermopower and the resistivity over a wide temperature range. We infer that the pressure behavior of the transport coefficients is mainly influenced by the decrease in rattling of the K ions.

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1. S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, J. Phys.: Condens. Matter 16, L9 (2004).
2. Z. Hiroi, S. Yonezawa, and Y. Muraoka, J. Phys. Soc. Jpn. 73, 1651 (2004).
3. H. Aoki, J. Phys.: Condens. Matter 16, V1 (2004).
4. J. Kuneš, T. Jeong, and W. E. Pickett, Phys. Rev. B 70, 174510 (2004).
5. S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, J. Phys. Soc. Jpn. 73, 819 (2004).
6. S. Yonezawa, Y. Muraoka, and Z. Hiroi, J. Phys. Soc. Jpn. 73, 1655 (2004).
7. Z. Hiroi, S. Yonezawa, J.-I. Yamaura, T. Muramatsu, and Y. Muraoka, J. Phys. Soc. Jpn. 74, 1682 (2005).
8. M. Brühlwiler, S. M. Kazakov, J. Karpinski, and B. Batlogg, Phys. Rev. B 73, 094518 (2006).
9. R. Saniz, J. E. Medvedeva, L.-H. Ye, T. Shishidou, and A. J. Freeman, Phys. Rev. B 70, 100505(R) (2004).
10. A. R. Bishop, D. Mihailovic, and J. Mustre de Len, J. Phys.: Condens. Matter 15, L169 (2003).
11. W. E. Pickett, Rev. Mod. Phys. 61, 433 (1989); K. Gofron, J. C. Campuzano, A. A. Abrikosov, M. Lindroos, A. Bansil, H. Ding, D. Koelling, and B. Dabrowski, Phys. Rev. Lett. 73, 3302 (1994); A. Ino, C. Kim, M. Nakamura, T. Yoshida, T. Mizokawa, A. Fujimori, Z.-X. Shen, T. Kakeshita, H. Eisaki, and S. Uchida, Phys. Rev. B 65, 94504 (2002).
12. T. Muramatsu, N. Takeshita, C. Terakura, H. Takagi, Y. Tokura, S. Yonezawa, Y. Muraoka, and Z. Hiroi, Phys. Rev. Lett. 95, 167004 (2005).
13. G. Schuck, S. M. Kazakov, K. Rogacki, N. D. Zhigadlo, and J. Karpinski, Phys. Rev. B 73, 144506 (2006).
14. N. Barišić, L. Forró, D. Mandrus, R. Jin, J. He, and P. Fazekas, Phys. Rev. B 67, 245112 (2003).
15. J.M. Ziman, Electrons and Phonons (Oxford University Press, 1972), § 9.11.
16. J.-S. Zhou and J.B. Goodenough, Phys. Rev. B 51, 3104 (1995).
17. Z. Hiroi, S. Yonezawa, T. Muramatsu, J.-I. Yamaura, and Y. Muraoka, J. Phys. Soc. Jpn. 74, 1255 (2005).
18. T. Hotta, Phys. Rev. Lett. 96, 197201 (2006); K. Hattori, Y. Hi-
rayama, and K. Miyake, J. Phys. Soc. Jpn. 14, 3306 (2005).

19 R. Hott, R. Kleiner, T. Wolf, and G. Zwicknagl, in A. Narlikar "Frontiers in Superconducting Materials", Springer (2005), cond-mat/0408212.