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Physica C 460–462 (2007) 20–27
PHYSICA C
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Chemical trends of superconducting properties in pyrochlore oxides

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Abstract

Chemical trends of fundamental superconducting parameters and normal-state properties are described for a family of pyrochlore oxide superconductors. Particularly, the change of T_c from 1.0 K for α-pyrochlore $Cd_2Re_2O_7$ to 3.3 K (A = Cs), 6.3 K (Rb), and 9.6 K (K) for β-pyrochlore AOs_2O_6 is discussed on the basis of the conventional BCS scheme. Enhanced T_c and anomalous features observed for KOs_2O_6 are ascribed to low-energy phonons probably coming from the rattling of the K cations.

Keywords: Superconductivity; Rattling; Pyrochlore oxide; Specific heat; Resistivity

1. Introduction

Twenty years have already passed after the discovery of Cu-based oxide superconductors in 1986 [1], and many related superconductors have been synthesized successfully. Consequently, it is getting more and more difficult to find a new one. On the other hand, the search for non-Cu-based oxide superconductors has been extended during the last decade, which mainly aims to understand the role of electron correlations in the mechanism of superconductivity or to search for a novel pairing mechanism, hopefully to reach a higher T_c.

An interesting example is a family of pyrochlore oxide superconductors. The first discovered is α-pyrochlore $Cd_2Re_2O_7$ with $T_c = 1.0$ K [2] and the second β-pyrochlore AOs_2O_6 with $T_c = 3.3$, 6.3, and 9.6 K for A = Cs [3], Rb [4–6], and K [7], respectively. They crystallize in the cubic pyrochlore structure of the same space group of $Fd\bar{3}m$ [8] and commonly possess a 3D skeleton made of ReO_6 or OsO_6 octahedra, as illustrated in Fig. 1. The difference between the two types comes from the fact that the O′ atom at the 8b site in the α-pyrochlore $Cd_2Re_2O_6O'$ is replaced by the A atom in the β-pyrochlore AOs_2O_6 [9,10]. Moreover, the Cd 16d site in the former is vacant in the latter. This means, in other words, that a relatively large CdO_4 tetrahedral unit is replaced by a single A atom which must suffer a large size mismatch and can rattle in an oversized atomic cage. It was pointed out that this mismatch causes a peculiar anharmonic vibration, particularly for the smallest K atom [10–12].

The electronic structures of α-$Cd_2Re_2O_7$ and β-AOs_2O_6 have been calculated by first-principle density-functional methods, which reveal that a metallic conduction occurs in the (Re, Os)-O network [12–16]: electronic states near the Fermi level originate from transition metal 5d and O 2p orbitals. Although the overall shape of the density of state (DOS) is similar for the two compounds, the difference in band filling results in different properties; Re^{5+} for α-$Cd_2Re_2O_7$ has two 5d electrons, while $Os^{5.5+}$ for β-AOs_2O_6 has two and a half. It is to be noted that a related α-pyrochlore $Cd_2Os_2O_7$ with Os^{5+} ($5d^3$) exhibits a metal-to-insulator transition at 230 K [17,18].

The mechanism of superconductivity for the pyrochlore oxides has been studied extensively so far. Most of data obtained for $Cd_2Re_2O_7$ have revealed that it is a weak-coupling BCS-type superconductor [19,20]. Experimental efforts to elucidate the nature of the superconductivity of the β-pyrochlores are in progress [11,21–34]. Interestingly to be compared with $Cd_2Re_2O_7$, there are several findings

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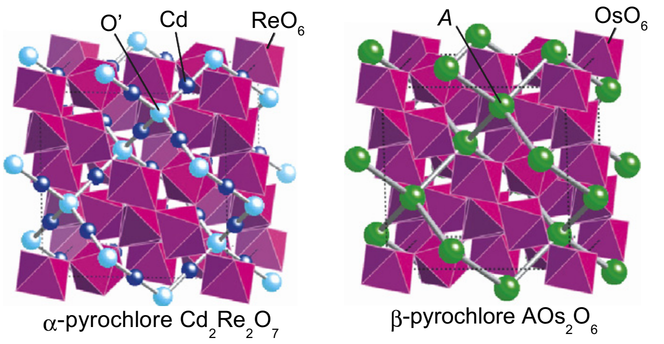
doi:10.1016/j.physc.2007.03.023



α-pyrochlore $Cd_2Re_2O_7$ β-pyrochlore AOs_2O_6

Fig. 1. Comparison of crystal structures between α-pyrochlore $Cd_2Re_2O_7$ (left) and β-pyrochlore AOs_2O_6 (right). They possess the same skeleton made of ReO_6 or OsO_6. The difference comes from the fact that the O′ atom in the former is replaced by the A atom in the latter with the nearby Cd sites vacant.

which suggest unconventional features for AOs_2O_6. For example, resistivity exhibits an anomalous concave-downward curvature, indicating an unusual scattering process involved in the normal state [7]. Moreover, NMR experiments by Arai et al. showed a tiny coherence peak in the relaxation rate below T_c for $RbOs_2O_6$, while no peaks were found for KOs_2O_6 [24]. This is in strong contrast to the result for $Cd_2Re_2O_7$ in which a huge coherence peak was detected [20]. In this paper, we consider systematic variations of various properties over the series, especially of T_c, in order to get meaningful insights on the mechanism of superconductivity and the source of the unconventional properties. The results of band structure calculations are also presented to understand the chemical trends.

2. Experimental

Samples were prepared as reported previously [3,4,7,9]. Single crystals of 1 mm size were obtained for $Cd_2Re_2O_7$ and KOs_2O_6, while only polycrystalline samples were available for $CsOs_2O_6$ and $RbOs_2O_6$, which caused a certain ambiguity for data obtained. The electrical resistivity and specific heat were measured in a Quantum Design physical property measurement system.

3. Results and discussion

3.1. Specific heat

Fig. 2 compares specific heat data for the four compounds [11,19,22]. The superconducting transition is sharp for single crystals of $Cd_2Re_2O_7$ and KOs_2O_6, while is relatively broad for polycrystalline samples of $CsOs_2O_6$ and $RbOs_2O_6$. The magnitude of the jump at T_c, $\Delta C/\gamma T_c$, is 1.15 and 2.83 for $Cd_2Re_2O_7$ and KOs_2O_6, respectively, indicating that the latter is an extremely strong-coupling superconductor.

It is to be noted in Fig. 2 that the magnitude of specific heat above T_c is very different among the four compounds.

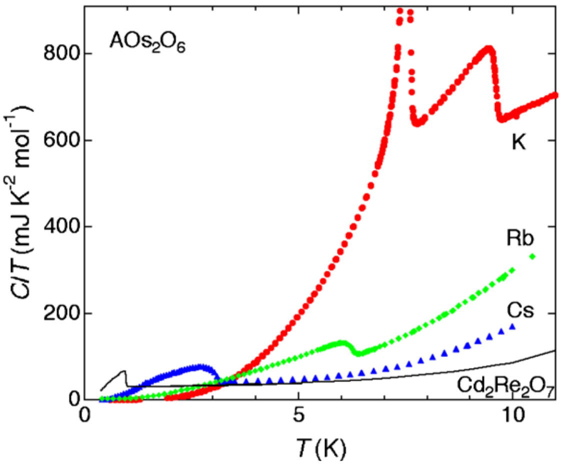


Fig. 2. Specific heat divided by temperature for $Cd_2Re_2O_7$ and AOs_2O_6. The data for $Cd_2Re_2O_7$ and KOs_2O_6 were obtained from single crystals and those for $CsOs_2O_6$ and $RbOs_2O_6$ from polycrystalline samples.

Compared at 10 K, for example, it is a factor of 8 larger for KOs_2O_6 than $Cd_2Re_2O_7$. This must be due to the difference in lattice contributions, not electronic ones, and is surprising because the lattice specific heat of such an identical or closely related structures should be similar. In the case of $Cd_2Re_2O_7$, the electronic and lattice parts could be reasonably separated as $C = \gamma T + \beta T^3$, assuming a Debye-type phonon at low temperature: $\gamma = 30.2$ mJ K^{-2} mol^{-1} and $\beta = 0.222$ mJ K^{-4} mol^{-1} that yields the Debye temperature $\Theta_D = 460$ K [19]. In contrast, it was found that the temperature dependence of the normal-state specific heat for the Cs and Rb compounds is unusually expressed as $C = \gamma T + \beta T^5$ in a wide temperature range between 0.5 and 7 K [11]. Very recently, we found the same T^5 dependence for a single crystalline KOs_2O_6 [35].

Thus, in the β-pyrochlores, usual Debye phonons may be masked by other types of low-energy phonons or other excitations. Possibly related to this, high-temperature specific heat is greatly enhanced due to the contribution from Einstein-like phonons. By fitting the data, Einstein temperature Θ_E was obtained as $\Theta_E = 70$, 61, and 40 K, for A = Cs, Rb, and K, respectively [11]. These must correspond to the specific frequency of the rattling motion of the alkali ions. The second anomaly observed at $T_p = 7.5$ K for the specific heat of the K compound was

Table 1
Summary of superconducting and normal-state properties for α-pyrochlore $Cd_2Re_2O_7$ and β-pyrochlore AOs_2O_6 of A = Cs, Rb, K

	$Cd_2Re_2O_7$	$CsOs_2O_6$	$RbOs_2O_6$	KOs_2O_6
T_c (K)	1.0	3.3	6.3	9.6
$\mu_0 H_{c2}$ (T)	0.29	~3.3	~5.5	30.6
ξ (nm)	34	~10	~7.8	3.3
λ (nm)	460	400	234	270
GL parameter	14	~40	~30	82
$\Delta C/\gamma T_c$	1.15	~1	~1	2.83
γ_{exp} (mJ K^{-2} mol^{-1})	30.2	~40	~40	71
γ_{band} (mJ K^{-2} mol^{-1})	11.5	11.0	10.2	9.6