

## Factors Affecting the Superconducting Transition Temperatures of $\beta$ -Pyrochlore Oxides $\text{AOs}_2\text{O}_6$ (A=K, Rb and Cs)

Dongwoon Jung

Department of Chemistry and Institute of Basic Natural Sciences, Wonkwang University, Iksan, Jeonbuk 570-749, Korea

E-mail: djung@wonkwang.ac.kr

Received October 9, 2010, Accepted November 25, 2010

The traditional BCS superconductors  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs) were investigated to find the relationship between their structures and superconducting transition temperatures. The  $T_c$  decreases with increasing the unit cell parameter of  $\text{AOs}_2\text{O}_6$ . This is in contrast to the case of conventional BCS superconductivity in a single bond model, where  $T_c$  may increase with increasing the the unit cell parameter since the DOS at Fermi level increases as the unit cell parameter increases. Instead, the  $T_c$  of a  $\beta$ -pyrochlore oxide is proportional to the lattice softness of the compound.

**Key Words:**  $\beta$ -Pyrochlore, Crystal structure, Density of states, Lattice softness, Superconducting transition temperature

### Introduction

Pyrochlore oxides have the general chemical formula  $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ , sometimes represented as  $\text{A}_2\text{B}_2\text{O}_7$ , where A is a large cation and B is a smaller transition metal cation.<sup>1</sup> The four crystallographically inequivalent atoms A, B, O, and O' in the face centered cubic unit cell occupy the 16d, 16c, 48f, and 8b sites of the  $\text{Fd}\bar{3}\text{m}$  space group, respectively. The ideal pyrochlore structure is composed of two types of cation-oxygen sublattices: one is a corner sharing tetrahedral network composed of A atoms with an O' atom in the center of each tetrahedron, and the other is another tetrahedral network of B atoms with each B atom coordinated quasi-octahedrally by six O atoms. This type of tetrahedral network is called the pyrochlore lattice. The compounds where A is a trivalent and B a tetravalent cation ( $\text{A}^{3+}$ ,  $\text{B}^{4+}$ ), and also the ( $\text{A}^{2+}$ ,  $\text{B}^{5+}$ ) combination, have been widely studied by various researchers in order to elucidate the effect of geometrical frustration on the properties of localized spin and itinerant electron systems. Recently, Yonezawa *et al.* reported another type of pyrochlore oxides with the general formula  $\text{AB}_2\text{O}_6$  called the  $\beta$ -pyrochlore oxides, where A is a large monovalent alkaline metal cation. It is derived from the parent compound by replacing the O' atoms with K, Rb, or Cs atoms and leaving the 16d site empty.

After the discovery of superconductivity in  $\text{Cd}_2\text{Re}_2\text{O}_7$  at  $T_c = 1$  K for the first time in the family of pyrochlore oxides,<sup>2-5</sup> the interest of the pyrochlore family moved somewhat from their magnetic phenomena<sup>6,7</sup> to superconducting ones. Soon after, a series of superconducting  $\beta$ -pyrochlore oxides showing elevated superconducting transition temperatures, were reported. The  $T_c$ 's of  $\beta$ -pyrochlore oxides  $\text{AOs}_2\text{O}_6$  are 3.3 K, 6.3 K, and 9.6 K when A= Cs, Rb, and K, respectively.<sup>8-12</sup> The  $T_c$  of each compound is decreasing with increasing the size of the alkali metal. The original pyrochlore and  $\beta$ -pyrochlore superconductors are known to be the traditional BCS-type superconductors, which means that the mechanism of the superconductivity appears to be conventional, and may be understood in the framework of the weak-coupling Bardeen-Cooper-Schrieffer (BCS)

theory. The  $T_c$ 's of BCS superconductors are very sensitive to their crystal structures. It is interesting, therefore, to investigate the relationship between the structures and  $T_c$ 's of the pyrochlore compounds. Especially, the difference of  $T_c$  in  $\beta$ -pyrochlore compounds depending upon the change of an alkali metal inside each structure, is worth to examine.

In this paper, the factors affecting the superconducting transition temperatures of  $\beta$ -pyrochlore oxides,  $\text{AOs}_2\text{O}_6$ , are investigated by examining their crystal and electronic structures by using extended Hückel tight-binding band calculation.<sup>13,14</sup>

### Results and Discussion

**Crystal Structure.** The  $\beta$ -pyrochlore structure with space group  $\text{Fd}\bar{3}\text{m}$  has only one adjustable positional parameter and all other atomic coordinates being fixed by symmetry. The variable oxygen x parameter, which is the x-coordinate of the 48f site, determines the detailed geometry of the structure. The deviation from the special value of  $x = 0.3125$  for the ideal octahedron leads to a trigonal distortion with an equal Os-O distance. The value of  $x = 0.3145$  observed for  $\text{KOs}_2\text{O}_6$  are smaller than those for other  $\beta$ -pyrochlore oxides with  $x = 0.32 - 0.33$ , which means that there is a smaller distortion of the octahedron in  $\text{KOs}_2\text{O}_6$  than in  $\text{RbOs}_2\text{O}_6$  and  $\text{CsOs}_2\text{O}_6$ . Crystal structures of  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs) are almost similar each other except the Os-O bond distances, Os-O-Os bond angles, and cell parameters (see Table 1). The Os-O bond distance in  $\text{AOs}_2\text{O}_6$  and the cell parameter of  $\text{AOs}_2\text{O}_6$  become larger as the crystal contains a bigger alkali metal. The differences in Os-O distances

**Table 1.** Cell parameters, Os-O bond distances and Os-O-Os bond angles in  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs)

|                           | Cell parameter (Å) | Os-O distance (Å) | Os-O-Os angle (degree) |
|---------------------------|--------------------|-------------------|------------------------|
| $\text{KOs}_2\text{O}_6$  | 10.099             | 1.9004            | 139.91                 |
| $\text{RbOs}_2\text{O}_6$ | 10.114             | 1.9211            | 137.08                 |
| $\text{CsOs}_2\text{O}_6$ | 10.149             | 1.9469            | 134.30                 |

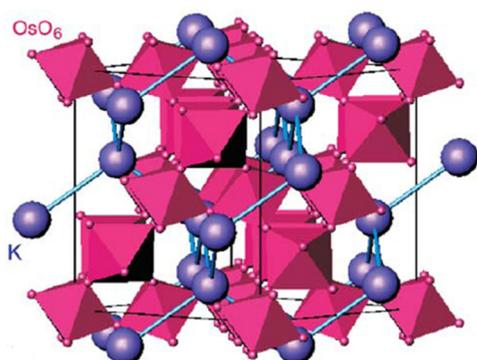


Figure 1. The three-dimensional network of  $\text{KO}_2\text{O}_6$ .

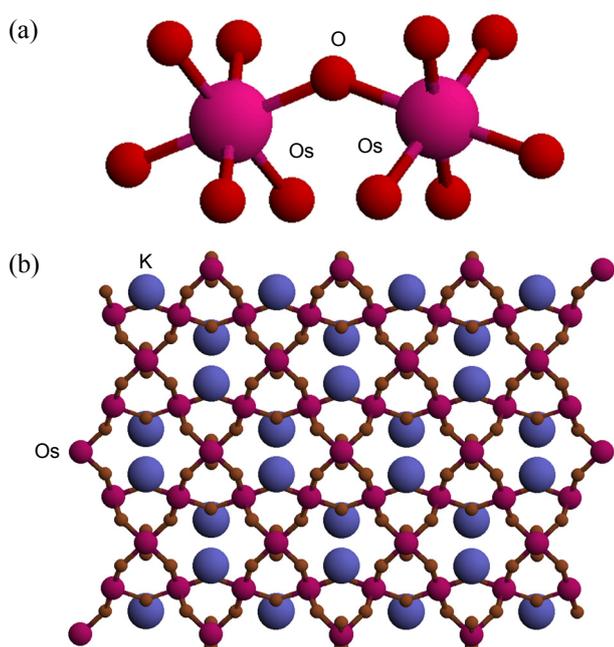


Figure 2. (a) The angle between two connected  $\text{OsO}_6$  octahedra and (b) the projection view of  $\text{KO}_2\text{O}_6$ .

and cell parameters originate from the size of the alkali metal and the  $x$  parameter.

There are eight formula units per unit cell. In each unit cell, the  $\text{OsO}_6$  octahedra share their corners to form a three-dimensional network as shown in Fig. 1. The octahedra are connected along three directions in zig-zag form. The angle of Os-O-Os (see Fig. 2(a)) is within the range of  $134^\circ$  -  $139^\circ$  depending upon the alkali metal. Every two alkali metal atoms sits in the center of cages made of twelve  $\text{OsO}_6$  octahedra as shown in Fig. 2(b).

**Electronic Structure.** Charge carriers of a superconducting states are not individual electron but pairs of electrons (called Cooper pairs) having opposite momenta (i.e., opposite wave vectors).<sup>15</sup> Therefore, the wave functions of Cooper pairs are described by product functions  $\phi(\mathbf{k})\phi(-\mathbf{k})$  and  $\phi(\mathbf{k}')\phi(-\mathbf{k}')$ , where  $\mathbf{k}$  and  $\mathbf{k}'$  refer to the occupied and unoccupied wave vectors of a normal metallic state, respectively.<sup>16</sup> The energy lowering which acts as a driving force to induce a superconducting state

is derived from the interaction between an occupied pair function  $\phi(\mathbf{k})\phi(-\mathbf{k})$  and an unoccupied pair function  $\phi(\mathbf{k}')\phi(-\mathbf{k}')$  i.e.,  $\langle \phi(\mathbf{k})\phi(-\mathbf{k}) | H' | \phi(\mathbf{k}')\phi(-\mathbf{k}') \rangle$ , where the perturbation  $H'$  causing this interaction is lattice vibration in traditional superconductors. According to the BCS theory,<sup>15</sup> Cooper pair formation is induced by electron-phonon coupling: A moving electron in a solid causes a slight, momentary deformation around it, which affects the motion of a second electron in the wake of the first in such a way that, effectively, the two electrons move as an entity as if bound together by an attractive force. The extent of electron-phonon coupling is measured by the electron-phonon coupling constant  $\lambda$ . The relationship between  $T_c$  and  $\lambda$  is governed by the expression:<sup>17</sup>

$$T_c \propto \theta_D \exp\left(-\frac{1+\lambda}{\lambda+\mu^*}\right) \quad (1.1)$$

where  $\theta_D$  is the Debye temperature of the lattice and  $\mu^*$  is the effective Coulomb pseudopotential of the order of 0.1. When  $\lambda$  is small and  $\mu^*$  is neglected, Equation 1.1 is simplified as

$$T_c \propto \theta_D \exp\left(-\frac{1}{\lambda}\right) \quad (1.2)$$

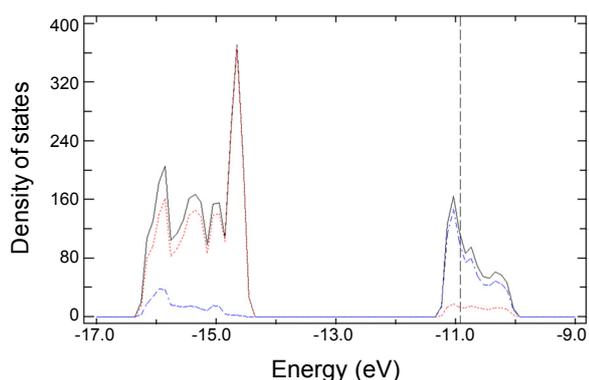
For a lattice having a phonon spectrum effective for electron-phonon coupling,  $\lambda$  is given by

$$\lambda = \frac{n(e_f) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (1.3)$$

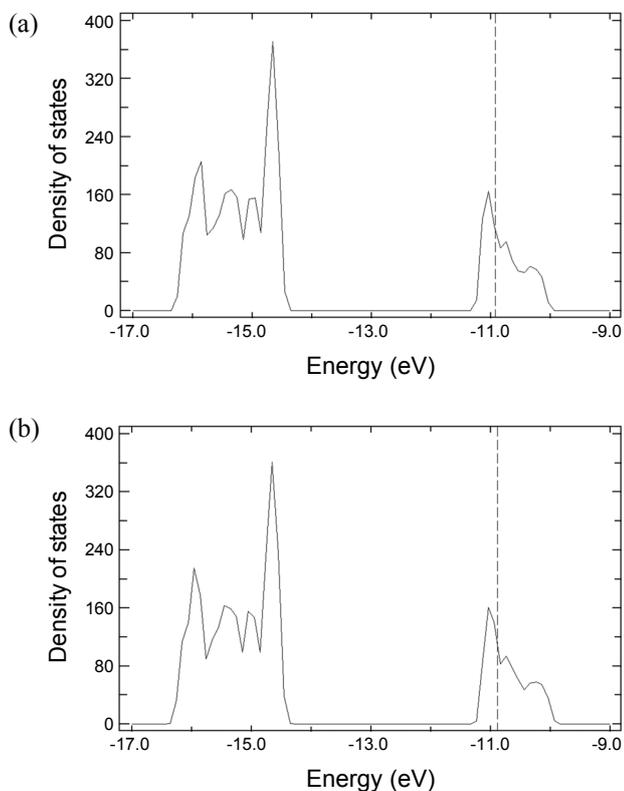
where  $M$  is mass of atoms in the lattice,  $\langle \omega^2 \rangle$  is the square of the phonon frequency averaged over the vibrational band, and  $\langle I^2 \rangle$  is the square of the electron-phonon interaction element averaged over the Fermi surface, and  $n(e_f)$  is the density of states (DOS) at Fermi energy. From equation 1.2 and 1.3, one obtains the expression

$$T_c \propto \exp[-1/n(e_f)] \quad (1.4)$$

which suggests that the  $T_c$  should be raised as the  $n(e_f)$  value increases. Equation 1.4 has been employed in the past two explain the variation in the  $T_c$  values of elemental and alloy metals on the basis of their electronic structures. Fig. 3 shows the projected density of states for  $\text{KO}_2\text{O}_6$  compound where the vertical dashed line represents the Fermi energy. Os 5d-block band contributes most near the Fermi level, while O 2p-block contributes at lower energy. The  $n(e_f)$  values is, therefore, made of Os d-orbital electrons. Although not shown, similar results are obtained from  $\text{RbOs}_2\text{O}_6$  and  $\text{CsOs}_2\text{O}_6$ . Fig. 4(a) and Fig. 4(b) are the density of states calculated for  $\text{KO}_2\text{O}_6$  and  $\text{CsOs}_2\text{O}_6$ . The  $n(e_f)$  values are 111, 110, and 108 electrons/eV, when A is Cs, Rb, and K, respectively. The  $T_c$ 's of  $\beta$ -pyrochlore oxides  $\text{AO}_2\text{O}_6$  are 3.3 K, 6.3 K, and 9.6 K when A = Cs, Rb, and K, respectively. The superconducting transition temperature is, therefore, highest when the  $n(e_f)$  value is smallest. It is con-



**Figure 3.** The projected density of states (PDOS) calculated for  $\text{KOs}_2\text{O}_6$ . The solid line, dashed line, and dotted line represent the total, PDOS of Os 5d orbital, and PDOS of O 2p orbital, respectively.



**Figure 4.** (a) The density of states (DOS) calculated for  $\text{KOs}_2\text{O}_6$  and (b) DOS calculated for  $\text{CsOs}_2\text{O}_6$ . The vertical dashed line represents the Fermi energy.

cluded from the results that the trends in the  $T_c$  values of the  $\text{AOs}_2\text{O}_6$  superconductors cannot be explained on the basis of Equation 1.4.

For a closely related series of superconductors  $\text{AOs}_2\text{O}_6$  ( $A=\text{K, Rb, and Cs}$ ), the  $n(\epsilon_f) \langle I^2 \rangle$  term of Equation 1.3 is expected to be nearly constant. Therefore, Equation 1.3 can be simplified as

$$\lambda \propto \frac{1}{M \langle \omega^2 \rangle} \quad (1.5)$$

**Table 2.** Shortest Os-A and O-A ( $A=\text{K, Rb, and Cs}$ ) contact distances and their  $SI$  values

|                           | Os-A contacts |      | O-A contacts |      |
|---------------------------|---------------|------|--------------|------|
|                           | $r$ (Å)       | $SI$ | $r$ (Å)      | $SI$ |
| $\text{KOs}_2\text{O}_6$  | 4.1868        | 46.6 | 3.1326       | 12.0 |
| $\text{RbOs}_2\text{O}_6$ | 4.1930        | 42.4 | 3.6196       | 4.2  |
| $\text{CsOs}_2\text{O}_6$ | 4.2076        | 37.8 | 3.6246       | -3.6 |

It is noted that the  $M \langle \omega^2 \rangle$  term has a force constant. Thus a low lattice vibrational frequency (i.e., soft phonon derived from vibrations with shallow potential wells) results in a large  $\lambda$  and consequently a higher  $T_c$ . Phonons important for superconductivity are expected to have frequencies of the order of  $\approx 8k_B T_c$ .<sup>17,18</sup> Such low-frequency phonons are associated with the translational and/or librational modes of vibrations. For  $\text{AOs}_2\text{O}_6$  ( $A=\text{K, Rb, and Cs}$ ) superconductors, those phonons are lattice vibrations, and therefore, are strongly governed by the Os-A and O-A interaction states. In general, softer phonons are expected when Os-A and O-A interactions become weaker. In understanding the  $T_c$  variation among the superconducting compounds with similar crystal structures, it is useful to have a semiquantitative method to measure their lattice softness. For an interatomic (or interionic) contact with the actual and ionic radii sums (hereafter it is called as ionic distance)  $r$  and  $r_i$ , respectively, we introduce the softness index ( $SI$ ) as follows:

$$SI = \frac{r - r_i}{r} \times 100 \quad (1.6)$$

Among the numerous interatomic (or interionic) contacts of  $\text{AOs}_2\text{O}_6$  compounds, the most important contacts associated with the lattice hardness are the shortest ones in various categories of Os-A and O-A interactions. From equation 1.6, a larger  $SI$  value means that the difference between the real contact distance and the ionic distance is bigger. In a material having a larger  $SI$  value, elements (or ions) can move within the contact area with more tolerated freedom. A softer lattice, therefore, should have more interatomic (or interionic) contacts with larger  $SI$  values. Table 2 summarizes the  $SI$  values of Os-A and O-A contacts calculated for  $\text{AOs}_2\text{O}_6$  ( $A=\text{K, Rb, and Cs}$ ) on the basis of their crystal structures.

The  $SI$  values of Os-A for isostructural  $\text{AOs}_2\text{O}_6$  compounds are 46.6, 42.4, and 37.8 when  $A=\text{K, Rb, and Cs}$ , respectively. It suggests that the softness in Os-A contact is largest in  $\text{KOs}_2\text{O}_6$  pyrochlore oxide. Same trend is found in the  $SI$  values of O-A contacts. The softness in O-A contact is also largest in the  $\text{KOs}_2\text{O}_6$  pyrochlore oxide. The  $SI$  value of O-A contact is even negative in  $\text{CsOs}_2\text{O}_6$  compound, which means that the real O-Cs contact distance is shorter than the ionic radii sum of O and Cs. This compound has, therefore, large amount of strain which leads to the hard lattice. The result of softness index suggests that the lattice is softest in  $\text{KOs}_2\text{O}_6$  and so it shows the highest  $T_c$ . The  $T_c$  variation in traditional BCS superconductors  $\text{AOs}_2\text{O}_6$  ( $A=\text{K, Rb, and Cs}$ ) oxides is, therefore, related not with the  $n(\epsilon_f)$  (density of states at Fermi energy) values but with the lattice softness of the compound.

### Conclusions

The traditional BCS superconductors  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs) are investigated to find the relationship between their structures and superconducting transition temperatures. The  $n(e_f)$  (density of states at Fermi energy) values of isostructural  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs) oxides are almost similar, so they cannot influence the magnitude of  $T_c$ . This is in contrast to the case of conventional BCS superconductivity in a single bond model, where  $T_c$  may increase with increasing the unit cell parameter since the DOS at Fermi level increases. Instead,  $T_c$ 's of  $\beta$ -pyrochlore oxides is proportional to the lattice softness of each compound. The lattice softness governed by Os-A and O-A (A=K, Rb, and Cs) interaction states, is largest in  $\text{KOs}_2\text{O}_6$  compound among the  $\beta$ -pyrochlore  $\text{AOs}_2\text{O}_6$  (A=K, Rb, and Cs) oxides. Consequently, the highest  $T_c$  found in  $\text{KOs}_2\text{O}_6$  can be explained in terms of its lattice softness.

**Acknowledgments.** This work was supported by Wonkwang Research Grant of 2009.

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