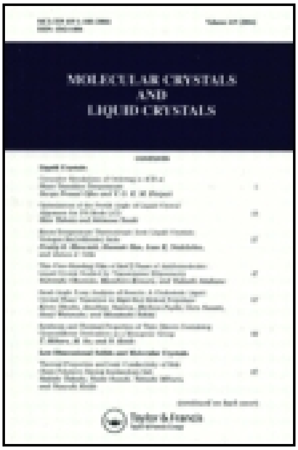

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Hybridization between K and C_{60} Electronic States in Superconducting $K_3Ba_3C_{60}$

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Hybridization between K and C_{60} Electronic States in Superconducting $K_3Ba_3C_{60}$

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We have studied the electronic structure of the superconducting fulleride $K_3Ba_3C_{60}$ using the local density approximation in the density functional theory. We have found the presence of the hybridization not only between Ba and C_{60} states but also between K and C_{60} states. This novel hybridization should have an effect on the electronic properties, including superconductivity. Also in $Rb_3Ba_3C_{60}$, the hybridization between Rb and C_{60} is found as well. In addition, the density of states at Fermi level of $K_3Ba_3C_{60}$ is found to be slightly larger than that of $Rb_3Ba_3C_{60}$, although the lattice constant of $K_3Ba_3C_{60}$ is shorter than that of $Rb_3Ba_3C_{60}$. These results are in sharp contrast to A_3C_{60} superconductors (A=alkali-metal atoms).

Keywords: Electronic structure; $K_3Ba_3C_{60}$; $Rb_3Ba_3C_{60}$; superconductivity; Density-Functional Theory

INTRODUCTION

The face-centered-cubic (fcc) A_3C_{60} superconductors (A=K, Rb, etc.), have been studied intensively. Now it is well known that the larger the lattice constant is, the higher the superconducting transition temperature T_c is[1], e.g., 29K in Rb_3C_{60}, (a=14.384Å)[2] versus 19K in K_3C_{60}, (a=14.240Å)[3]. Accordingly, Cs_2RbC_{60}, which has the largest lattice constant, has the highest Tc (33K) among fcc A_3C_{60}, superconductors[4]. This monotonical relation between the lattice constant and T_c can be explained qualitatively from the density of states at Fermi level, $N(E_F)$, by the standard BCS-type theory based on their electronic structure[5–9].

On the other hand, body-centered-cubic (bcc) $A_3Ba_3C_{60}$ superconductors (A=K, Rb, or their mixture) synthesized recently are found to show a different relationship between the lattice constant and Tc from A_3C_{60} [10–12]. T_c

of $K_3Ba_3C_{60}$ is 5.6 which is higher than that of $Rb_3Ba_3C_{60}$ (2.0K), although the latter has the larger lattice constant than the former. In the case of similar alkaline-earth-doped bcc fullerides, Sr_6C_{60} and Ba_6C_{60} [13,14], it has been shown that C_{60} states are hybridized strongly with the alkaline-earth-metal *d* states[15,16]. the hybridization between C_{60} states and Ba states may play an important role in their electronic properties. In order to clarify the details of the hybridization, we have studied the electronic structure of $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$ from the first-principles calculation.

COMPUTATIONAL METHOD

In $A_3Ba_3C_{60}$ to be studied, A and Ba atoms are experimentally reported to be randomly located in which all C_{60} clusters are orientationally ordered with the highest-symmetry orientation as in the case of K_6C_{60} and Ba_6C_{60}. In order to perform the electronic-structure calculation, we must assume the fixed location of A and Ba atoms, as shown in Fig. 1, which realizes the highest possible symmetry (C_3 point group) under the condition that the unit cell contains one C_{60} cluster. In $K_3Ba_3C_{60}$, atomic coordinates determined experimentally[10] are used. As for $Rb_3Ba_3C_{60}$ of which atomic coordinates have not been reported experimentally, we have optimized the geometry by using the conjugate-gradient procedure [23] under the reported lattice constant of 11.32 Å.

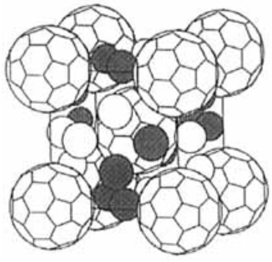

FIGURE 1 Structure of $K_3Ba_3C_{60}$ studied in the present work. Shaded and white spheres denote K and Ba atoms, respectively.

In the present electronic-structure calculations, we use the local density approximation (LDA) within the framework of the density functional theory[18,19] We adopt the Ceperley-Alder exchange-correlation potential in the LDA[20]. The norm-conserving pseudopotentials[21] with the Kleinman-Bylander separable approximation[22] are also adopted. The real-space-partition method[23] is used in order to avoid the breakdown of the separable approximation for K, Rb, and Ba. A plane-wave basis set with a cutoff energy of 50 Ry is used.

RESULTS AND DISCUSSION

In Fig. 2, the band structure and density of states (DOS) of $K_3Ba_3C_{60}$ obtained are shown.

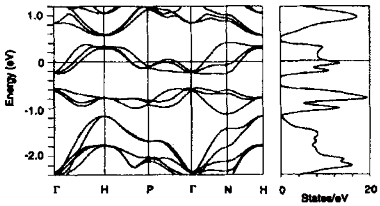

Figure 2 Band structure (left panel) and the density of states (right panel) of $K_3Ba_3C_{60}$. Energy is measured from the Fermi level denoted by the horizontal line. The band where the Fermi level lies is the t_{1g}-derived band. The density of states is broadened by using the Gaussian-distribution function with the width of 0.001eV.

The band in which the Fermi level lies is the t_{1g}-derived band (originating from the t_{1g} state, the second LUMO of the C_{60} cluster) is half-filled with three electrons. The band structure of $K_3Ba_3C_{60}$ is, as will be discussed later, more dispersive than that of the pristine bcc C_{60} having the same lattice constant as that of $K_3Ba_3C_{60}$. It is also the case in the band structure of $Rb_3Ba_3C_{60}$ which we have also calculated[24]. This band broadening clearly indicates the presence of the hybridization. Surprisingly, not only the shapes but also t_{1g}-band widths of $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$ are found to be quantitatively very similar to each other although the lattice constant of $K_3Ba_3C_{60}$ is smaller than that of $Rb_3Ba_3C_{60}$. Moreover, $N(E_F)$ of $K_3Ba_3C_{60}$ is 11.4 (states/eV), which is slightly higher than that of $Rb_3Ba_3C_{60}$, 11.2 (states/eV). From the viewpoint of the BCS theory, this is consistent with the experimental result that T_c of $K_3Ba_3C_{60}$ is higher than that of $Rb_3Ba_3C_{60}$.

These interesting result may be caused by the hybridization. Therefore, in order to study the hybridization behavior more quantitatively, we have calculated t_{1g}-band widths, which are found to be equivalent to their widths at the N point, for several hypothetical bcc fullerides with the fixed lattice constant of $a = 11.246$ Å or 11.32Å. Systems studied are Ba_3C_{60} where K (or Rb) atoms are removed from $K_3Ba_3C_{60}$ ($Rb_3Ba_3C_{60}$), and K_6C_{60} with above a values. The atomic coordinates of K_6C_{60} assumed are identical to those of $K_3Ba_3C_{60}$ for $a = 11.246$ Å, and to those optimized in $Rb_3Ba_3C_{60}$ for $a = 11.32$ Å.

Results are listed in Table I. These results have been obtained by treating K 3p and Ba 5p states as core states. We have also performed the same calculation by treating them as valence states and found the following arguments hold irrespective of the treatment of K $3p$ and Ba $5p$ states[24].

TABLE I Widths of t_{1g}-derived bands at the N point for several hypothetical bcc C_{60} materials and the actual $K_3Ba_3C_{60}$.

	width at $a = 11.246$ Å	width at $a = 11.32$ Å
C_{60}	0.34 eV	0.31 eV
K_6C_{60}	0.56	0.54
Ba_3C_{60}	0.56	0.57
$A_3Ba_3C_{60}$	0.67 (A=K)	0.66 (A=Rb)

A considerable difference in t_{1g}-band widths of $K_3Ba_3C_{60}$ and bcc Ba_3C_{60} at a =11.246Å indicates the presence of the hybridization between K and C_{60} states in the $K_3Ba_3C_{60}$ superconductor. Also, the difference in t_{1g}-band widths of bcc Ba_3C_{60} and bcc C_{60} at a =11.246Å indicates the presence of the hybridization between Ba and C_{60} states. The magnitude of these differences show that the degree of the hybridization between K and C_{60} states is about half of that between Ba and C_{60} states; this can be confirmed as well by the fact that the t_{1g}-band width of K_6C_{60} is almost identical to that of Ba_3C_{60} at a =11.246Å. Similarly, the difference in t_{1g}-band widths of $Rb_3Ba_3C_{60}$ and Ba_3C_{60} at a =11.32Å has been obtained, indicating the presence of the hybridization between Rb and C_{60} states.

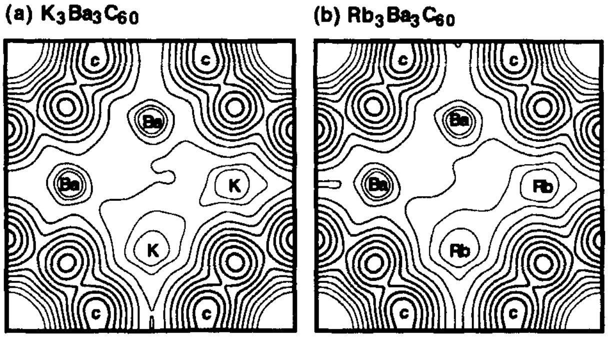

FIGURE 3 (a) Valence electron density on the (100) plane of $K_3Ba_3C_{60}$, (b) that of the pristine C_{60}. The center of the C_{60} cluster is located at each corner. Each contour line indicates twice (half) the density of the neighboring thinner (thicker) contour lines. The highest-density contour lines correspond to 0.2 in atomic units.

This hybridization between alkali states and C_{60} states is implied also by the valence-electron densities of $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$ as shown in

Fig. 3. Figure 3 indicates that there remain considerable electrons around not only Ba but also alkali sites. Similarly, due to this hybridization, the superconducting carriers should appear not only on C_{60} clusters and around Ba sites but also around alkali sites[24]. Because the carriers should be coupled with the optical phonon involving alkali-ion displacements, the mass difference between K and Rb may cause the T_c difference.

The similar hybridization between C_{60} between K states and C_{60} states is found to be the present also in the actual K_6C_{60} ($a = 11.39$ Å)[25].

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