

Structural and Electronic Properties of an Alkali Fulleride, Rb_1C_{60}

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Structural and electronic properties of an alkali metal fulleride, Rb_1C_{60} , was studied. In spite of the chain structure with short distance between balls along the crystallographic *a*-direction, the electronic structure calculation study with the X-ray defined crystal structure shows that Rb_1C_{60} is a three-dimensional metal at room temperature. This result is different from the magnetic experiments in which the compound was found to behave as a quasi-one-dimensional metal. Partial Fermi surface nesting is supposed to be the reason for the metal-insulator transition found in Rb_1C_{60} at ~ 50 K.

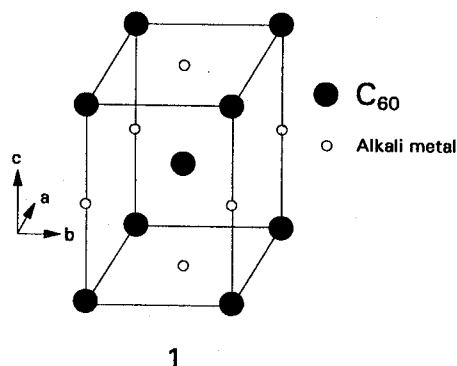
Introduction

Since its discovery from arc-processed graphite,¹ fullerene has attracted considerable interest due to its unusual properties. The production of this molecule in macroscopic quantities² stimulated the study in the solid state properties of this material. Specially the alkali metal-doped fullerene, A_xC_{60} compounds came into focus. Shortly after the synthesis of the superconducting A_3C_{60} compounds³ which were the first known metallic fullerene salts, Rao *et al.*⁴ reported the [2+2] cycloaddition between C_{60} molecules which has been hypothesized to take place during photopolymerization of solid C_{60} . Similar polymeric C_{60} chain structure was found in another alkali metal fullerides A_1C_{60} ($\text{A}=\text{K}, \text{Rb}$ and Cs)⁵ and these compounds were reported to be another metallic fullerene salts.

Rb_1C_{60} is one of the most extensively studied mono alkali metal fulleride and is suggested to be quasi-one-dimensional metal. But it has a phase transition to a spin density wave (SDW) or charge density wave (CDW) at ~ 50 K.⁶ Electronic structure calculation on this compound has been performed by Tanaka *et al.*,⁷ using the model geometry and it has turned out that Rb_1C_{60} is semiconducting with the band gap 1.148 eV. Very recently the crystal structure of Rb_1C_{60} was obtained with X-ray diffraction experiments.⁸ But there has been no systematic study on electronic structure calculation for Rb_1C_{60} with the experimentally defined structure. In this paper we examine the electronic structure of Rb_1C_{60} with the real crystal structure by adopting the extended Hückel tight-binding band calculation⁹ and check plausibility of appearance of the SDW state in the C_{60}^- chain.

Structure

The high temperature (*i.e.*, above ~ 400 K) phase of Rb_1C_{60} has a face-centered cubic (fcc) "rock salt" structure with C_{60} ions surrounded by six alkali metal ions. However, the low temperature structure of Rb_1C_{60} is orthorhombic (*o*- Rb_1C_{60} , see 1) with an unusually short separation of 9.12 \AA between the centers of C_{60} molecules along the crystallographic *a*-direction as shown in Figure 1a.^{5d} Such a short separation originating the [2+2] cycloaddition gives rise to the $\text{C}\cdots\text{C}$ bonds of the order of $1.44 \pm 0.15 \text{ \AA}$ between balls and this interfullerene distance is within the usual range for $\text{C}\cdots\text{C}$



bonds, whereas the intra $\text{C}\cdots\text{C}$ distance of $1.90 \pm 0.15 \text{ \AA}$ in the 4-membered ring is significantly large (see the distance in Figure 1a). Figure 1b represents the projection view of the C_{60} chains along the chain direction (*i.e.*, on the *bc*-plane which is perpendicular to the chain direction). It is clear from Figure 1b that two C_{60} chains are located to form the body-centered orthorhombic structure, and two planes of 4-membered rings constructed by cycloaddition in two nearest balls are perpendicular. The projection view of C_{60} chains on the *ab*-plane is shown in Figure 1c in which the C_{60} chain at the center is located behind the plane. In addition to the short interfullerene distance along the *a*-direction, Figures 1b and 1c suggest that interfullerene distances along the *b*- and diagonal directions are also short (e.g., the separations of fullerene molecules along the *b*- and diagonal directions are 10.10 \AA and 9.86 \AA , respectively) to have interactions between balls, although no chemical bonds are made. These intermolecular distances along the *b*- and diagonal directions are similar to those found in all other alkali-metal doped fullerene compounds.

The band dispersions

The dispersion relations of the highest occupied bands calculated for structure defined Rb_1C_{60} is shown in Figure 2, in which the dashed lines refer to the Fermi level. Since Rb_1C_{60} has body-centered orthorhombic structure, there are two C_{60} molecules in a calculation unit. Including two donated electrons from Rb totally 482 electrons fill up the bands and finally two highest sub-bands are half filled. For simplicity we show the band dispersions from Γ to X (see Figure 2a), Γ to Y (see Figure 2b) and Γ to Z (see Figure 2c) where

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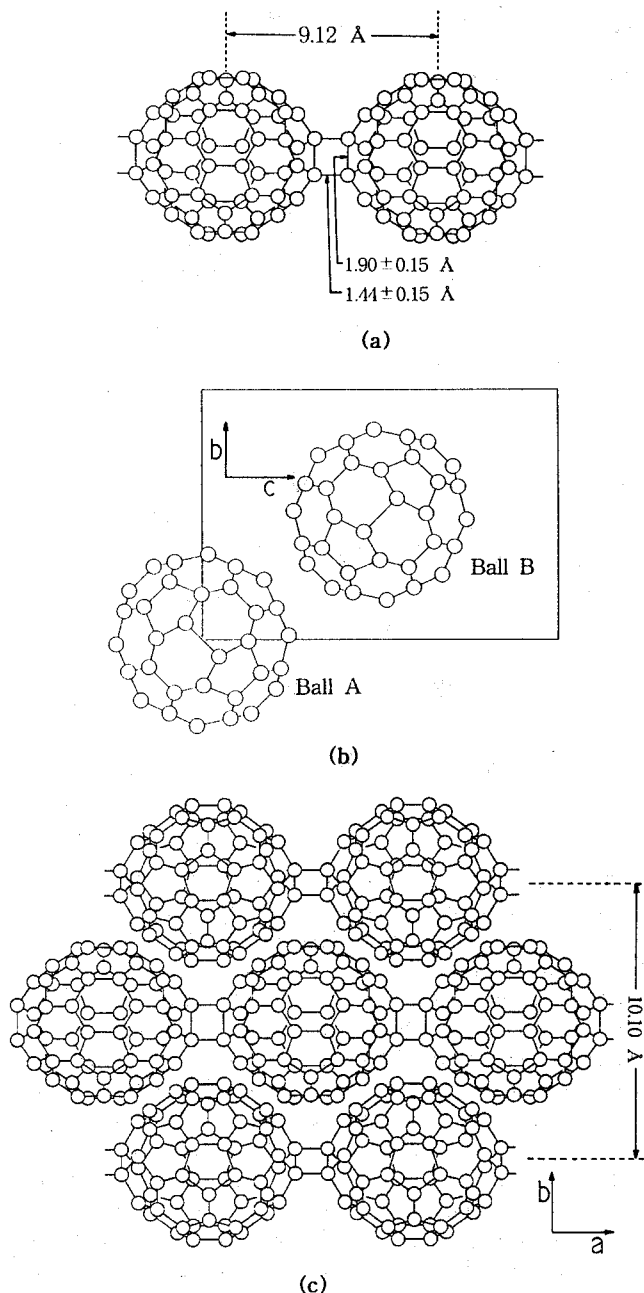


Figure 1. (a) Polymeric chain structure between adjacent C_{60} balls along the crystallographic a -direction in Rb_1C_{60} . (b) Projection view of two C_{60} chains on the bc -plane (Ball B is, in fact, located behind Ball A on the plane). (c) Projection view of C_{60} chains on the ab -plane.

Γ , X, Y and Z represent $(0, 0, 0)$, $(\pi/a, 0, 0)$, $(0, \pi/b, 0)$ and $(0, 0, \pi/c)$ in the reciprocal lattice, respectively. Since each of Figure 2 represents only the part of the total valence and conduction bands, each does not show the exactly half filled situation but still show that one of two subbands is cut by the Fermi level, which means Rb_1C_{60} is metallic. Figure 2 clearly shows that the highest occupied bands are similarly dispersive along three directions, therefore, the compound is likely to be three-dimensional metal. This result is quite striking according to the linear chain structure of

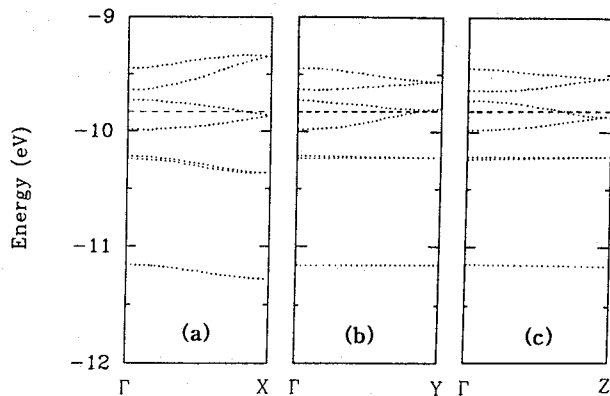


Figure 2. The band dispersion relations calculated for Rb_1C_{60} along (a) Γ to X, (b) Γ to Y, and (c) Γ to Z.

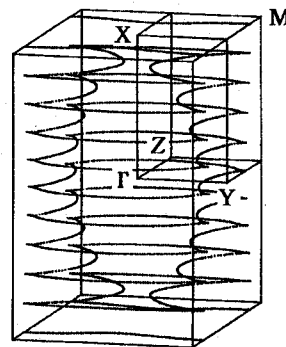


Figure 3. The three-dimensional Fermi surface calculated for Rb_1C_{60} .

C_{60}^- . As mentioned in the structure section, C_{60} molecules are photopolymerized along the a -direction with the short inter $C\cdots C$ distances. Consequently the compound is supposed to be one-dimensional metal and is conductive along the a -direction only. Chauvet *et al.* and Pekker *et al.* also reported $o-Rb_1C_{60}$ is a quasi-one-dimensional metal. However, there are many inter $C\cdots C$ distances within the van der Waals radii sum along the b - and diagonal directions which is essential for the interactions between balls. In A_3C_{60} superconducting compounds the $C\cdots C$ distance between balls within the van der Waals radii sum is crucial for superconductivity.¹⁰ Likewise having many inter $C\cdots C$ distances within the van der Waals radii sum is the reason why the highest bands are similarly dispersive along three directions and consequently $o-Rb_1C_{60}$ becomes a three-dimensional metal.

Fermi surfaces

The three-dimensional Fermi surface associated with the half-filled band is shown in Figure 3. The Fermi surface is drawn on bc -plane changing the wave vector k_x from $-\pi/a$ to π/a . Around the center, Γ , a long pot-like shape is made and on the ab -plane at $k_y = \pi/b$, a tunnel-like surface is shown. For easy understanding the three-dimensional Fermi surface is decomposed into 3 two-dimensional Fermi surfaces which are associated with the band dispersion relations in Figures 2a, 2b, and 2c, as shown in Figure 4. Three Fermi surfaces in Figures 4a, 4b, and 4c are drawn on ab -, bc -

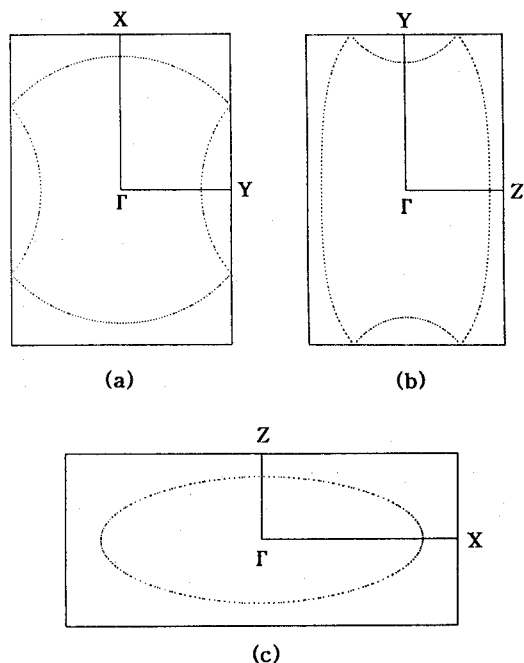


Figure 4. The two-dimensional Fermi surfaces associated with the band dispersions of (a) Figure 2a, (b) Figure 2b, and (c) Figure 2c, respectively.

and ca -planes at $k_z=0$, $k_x=0$ and $k_y=0$, respectively. It is clear from Figures 4a, 4b and 4c that wave vectors from the origin (Γ) to X, Y and Z are crossing the Fermi surfaces, which means the Fermi surfaces are closed along each direction. Thus, $o\text{-Rb}_1\text{C}_{60}$ is conductive along three directions, and this result is consistent with that found in the band dispersion relations. The shapes of Fermi surfaces in Figures 4a and 4c are folded circle and ellipsoid, respectively, with no sign of Fermi surface nesting. However, the Fermi surface in Figure 4b (*i.e.*, the Fermi surface on bc -plane at $k_a=0$) shows partial Fermi surface nesting where the regions described by solid lines. In one-electron band theory, a metallic state may not be stable when its Fermi surface is nested and becomes susceptible to a metal-insulator transition leading to a spin density wave (SDW) state or a charge density wave (CDW) state.¹¹ It is plausible, therefore, the partial Fermi surface nesting shown in Figure 4b is susceptible for the metal-insulator transition found in Rb_1C_{60} at ~ 50 K.

Conclusions

An alkali fulleride, Rb_1C_{60} , has the unique chain structure *via* [2+2] cycloaddition with short separation of 9.12 Å between balls. In spite of the chain structure along the crystallographic a -direction, the electronic structure calculation study with the X-ray defined crystal structure shows that Rb_1C_{60} is a three-dimensional metal at room temperature. This result is different from the magnetic experiments in which the compound was found to behave as a quasi-one-dimensional metal. The experiment to measure the electric resistivity along three directions is, therefore, strongly recommended. Partial Fermi surface nesting is supposed to be the reason for the metal-insulator transition found in Rb_1C_{60}

at ~ 50 K.

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