Distinct polymer chain orientations in KC_{60} and RbC_{60}

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Polymerized alkali fullerides KC_{60} and RbC_{60} display different electronic properties. Single crystal X-ray diffraction and diffuse scattering studies show that the C_{60} chains possess different relative orientations about their axes. We will discuss this result in relation with electronic band structure calculations. The influence of pressure will also be discussed.

Alkali fullerides AC_{60} (A=K, Rb) exhibit a transition around 350K from a high temperature cubic phase towards an orthorhombic one where the molecules form polymer chains (1-3). The unit cell parameters are $a_K \approx a_{Rb} \approx 9.12$ Å, $b_K = 9.95$ Å, $b_{Rb} = 10.11$ Å, $c_K = 14.32$ Å, $c_{Rb} = 14.23$ Å. Polymerization occurs by [2+2] cycloaddition along the shortest **a** axis (fig.1(a)). Powder diffraction studies showed that: i) the intrachain C-C bond lengths are similar in KC_{60} and RbC_{60} (4,5), and ii) the angle μ formed by the cycloaddition planes of a chain and the **c** axis, which characterizes the chain orientation, satisfies $|\mu| = 45° \pm 5°$, in both KC_{60} and RbC_{60} (3). No definite structural difference has been evidenced between the two compounds, although the relative chain orientations have not been unambiguously determined in any of them. MAS-NMR studies (6) revealed differences between the spin distributions in KC_{60} and in RbC_{60}, suggesting that orientational chain ordering may differ. The AC_{60} compounds have also been investigated by ESR, μSR, NMR and electrical or optical conductivity measurements, and the electronic properties of KC_{60} and RbC_{60} are different. For instance, between 50K and 25K, RbC_{60} exhibits a magnetic transition, unlike KC_{60} (see e.g. (7,8); the possibility of coexistence with a spin-singlet phase has also recently been reported (9)).

In this paper, we present the results of a single-crystal X-ray diffraction study of KC_{60} and RbC_{60}. The relative chain orientations are different in the two compounds, which probably influences the electronic properties. This is discussed in light of ab-initio band structure calculations.

X-RAY DIFFRACTION RESULTS

KC$_{60}$ and RbC$_{60}$ single crystals (typical volume 10^{-2} mm^3) were obtained by stoichiometric doping of C$_{60}$ crystals at 400°C. A solid state transformation to the polymer phase was obtained by subsequent slow cooling to room temperature. The X-ray diffraction experiments (10) were performed using precession, fixed-film and diffractometer techniques.

Precession photographs, which give a global view of the reciprocal space, were taken first. They reveal the existence of orientational domains, which appear at the transition from the cubic to the polymer phase. These domains are related by the point symmetry operations lost at the transition and their orientational relationships could be determined from analysis of the photographs. Additionally, we have shown that Bragg peaks satisfying the relation h+k+l odd are present in KC$_{60}$ but not in RbC$_{60}$. Thus, the Bravais lattice of polymerized KC$_{60}$ is primitive, while that of RbC$_{60}$ is body-centered.
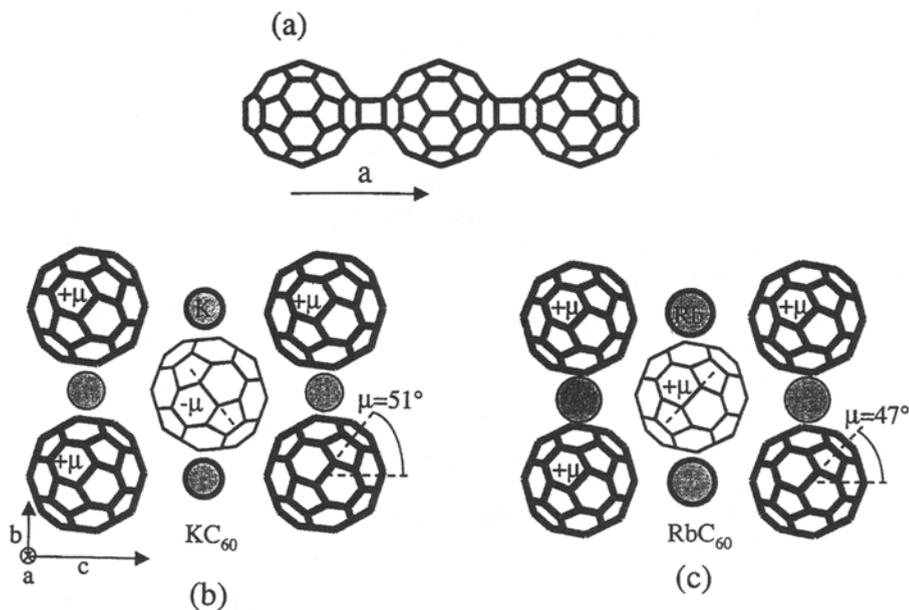
FIGURE 1. (a) Linear polymer chain running along **a**. (b) KC$_{60}$ and (c) RbC$_{60}$ unit cells. In (b) and (c), light lines indicate out of plane C$_{60}$ and alkali ions.

The two orthorhombic space groups compatible with the C$_{60}$ chain symmetry are Pmnn and Immm (3). Thus, one may infer that KC$_{60}$ space group is Pmnn, while RbC$_{60}$ is Immm. For the Immm space group, if the chains are not oriented with their cycloaddition rings in the mirror planes perpendicular to **b** or to **c** ($\mu=0°$ or 90°), they should take orientations μ and $-\mu$ with equal probability. In a diffraction experiment,

this disorder would produce some diffuse scattering localized between the Bragg reflections. Careful search for such diffuse scattering, using the fixed-crystal fixed-film method under vacuum, to maximize signal-over-noise ratio, was carried out (fig.2). The results showed that there is no diffuse scattering in RbC_{60}, contrary to what would be expected for Immm.
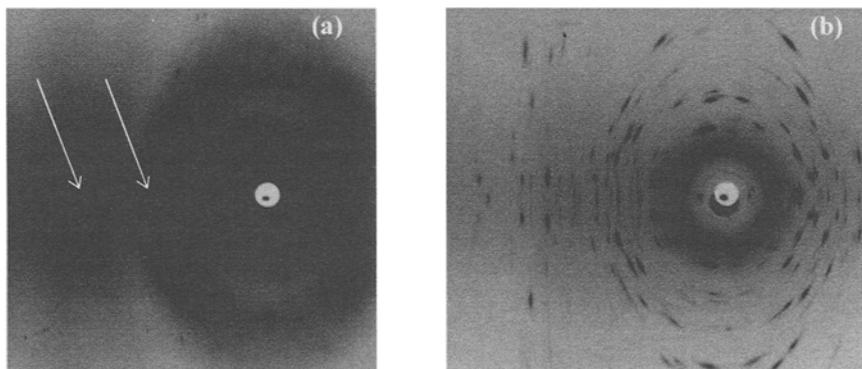
FIGURE 2. Monochromatic fixed-crystal fixed-film photographs from (a) a C_{60} crystal, (b) a RbC_{60} crystal. In (a) and (b), the central ring, from background contributions, should be ignored. In (a), the arrows point toward the diffuse scattering due to the rotating molecules in pure C_{60} at room temperature. The diffuse scattering expected for orientational chain disorder in RbC_{60}, which should be of the same order of magnitude, is absent in (b).

Finally, Bragg peak intensity measurements on KC_{60} and RbC_{60} were performed on a three-circle diffractometer. Despite the existence of orientational variants, we succeeded in measuring a sufficient number of isolated peaks from a single variant. A single crystal structure refinement was then performed, minimizing the reliability factor i.e. the difference between calculated and measured structure factors (fig.2 in ref.(10)). For Pmnn KC_{60}, we obtain a minimum value of the reliability factor $R_{min} \approx 0.16$ for $\mu \approx 51°$. An attempt to refine the RbC_{60} data for the Immm space group gives $R_{min} \approx 0.24$ for $\mu \approx 48°$. This configuration is in conflict with the absence of diffuse scattering, so that we were lead to consider a space group of lower symmetry than orthorhombic. The convenient space group compatible with the symmetry of the C_{60} chains is the monoclinic space group I2/m. A refinement within I2/m leads to an improved value of the reliability factor : $R_{min} \approx 0.06$, for $\mu \approx 47°$. This validates the I2/m structure. We note that no deviation from 90° (allowed by the monoclinic symmetry) has been detected within an experimental resolution of 0.5°. In any case, this deviation is expected to be small due to the rather homogeneous distribution of the C atoms around the chain axes.

In summary, the chain orientation angles are similar in KC_{60} and RbC_{60} (51° and 47°), in agreement with ref.(3), but these compounds are found to possess different space groups, Pmnn and I2/m, respectively. This implies different relative chain orientations; the chain orientations alternate (μ and $-\mu$) in KC_{60} while they are parallel

in RbC_{60}, as shown in fig.1(b) and (c). The single-crystal X-ray diffraction and diffuse scattering study has thus evidenced an important structural difference between KC_{60} and RbC_{60}.

ELECTRONIC BAND STRUCTURE CALCULATIONS

We now address the question of whether the different magnetic properties of KC_{60} and RbC_{60} can be explained by their different relative chain orientations. In ref. (11), first-principles electronic-structure calculations within Local Density Approximation (LDA) were used to calculate the single-particle band structure of the paramagnetic state. A tight-binding fit of the conduction bands (fig.3(a)) was then used as the input to a many-body model Hamiltonian in order to study magnetic fluctuations around the paramagnetic state. The orientational state was taken (for computational simplicity) to be I2/m, with $\mu = 45°$, which has now been found to be the correct space group for RbC_{60}; unit cell parameters were those of RbC_{60}.
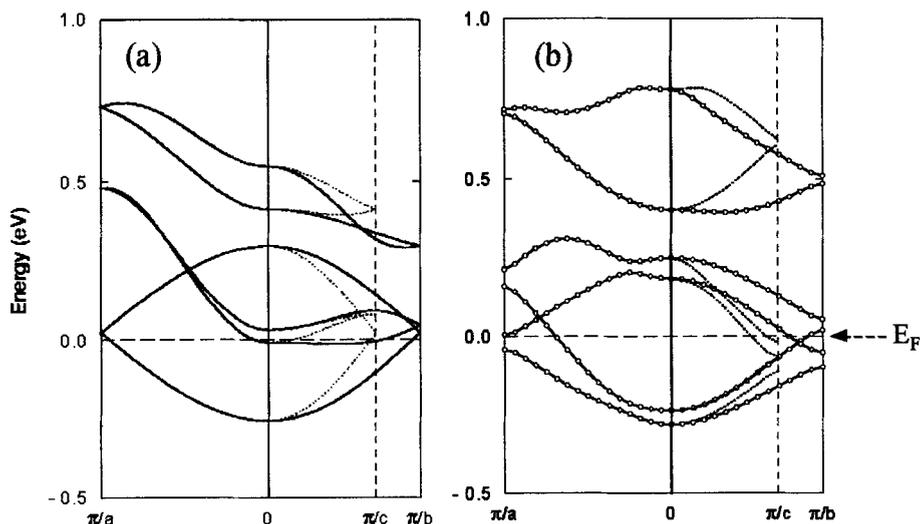
FIGURE 3. (a) Tight-binding fit to the LDA conduction-band structure of RbC_{60} with space group I2/m; the bands are folded into the corresponding doubled Pmnn unit cell. (b) Full LDA band structure for the space group Pmnn.

To repeat that calculation for the Pmnn space group describing KC_{60} is beyond the scope of this paper. Instead, we examine the input to the many-body calculation - namely, the conduction band dispersion within the LDA. We focus here solely on the differences between RbC_{60} and KC_{60} relative chain orientations. To make the comparison simpler, all other parameters are kept fixed. Fig. 3(b) shows the LDA band structure for the Pmnn space group, appropriate for KC_{60}. The electronic dispersion of the lowest band is three-dimensional (11), despite the quasi-one-dimensional polymer

50

chains, for both I2/m and Pmnn chain orientations. For the I2/m space group, the rather flat band near the Fermi level (E_F) in fig. 3(a) may contribute to the stabilization of a magnetically ordered ground state, in which a splitting of 0.1 eV results in a pseudo-gap near E_F (fig.3 in ref.(11)). For the Pmnn space group, this flat band at E_F is completely absent. Without the peak at E_F, the energy gain from exchange splitting is considerably reduced. We speculate that it is in fact insufficient to stabilize a magnetic ground state. This is consistent with the experimental findings (7,8).

PRESSURE EFFECTS

KC_{60} and RbC_{60} possess different chain orientations while their unit cell parameters are close. This may be related to the strong sensitivity of the orientational potential of the C_{60} chains with the interchain distances (12). Significant pressure effects may thus be expected. Indeed, resistivity measurements have shown that around 5kbar and 180K, RbC_{60} exhibits a transition (13); NMR studies also show that the magnetic ground state disappears under pressure (8). Our present results about (i) the influence of the chain orientations on the electronic properties and (ii) the sensitivity of the orientational potential with the interchain distances, suggest that the transition evidenced in ref.(13) may be associated to changes in the chain ordering. Structural investigations under pressure would thus be very interesting.

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