POLYMER CHAIN ORIENTATIONS IN KC_{60} AND RbC_{60}: STRUCTURAL ANALYSIS AND RELATION WITH ELECTRONIC PROPERTIES

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Abstract

First single crystal X-ray diffraction studies of polymerized KC_{60} and RbC_{60} are presented. While powder diffraction studies showed no definite structural differences, the single crystal diffraction data analysis reveals different relative chain orientations in the two compounds. They are discussed in relation with semi-empirical energy calculations. The structural difference between KC_{60} and RbC_{60} may be a key feature for the understanding of their contrasted conducting and magnetic properties.

Keywords: Fullerenes and derivatives, X-ray diffraction and scattering, computer simulations

1. Introduction

With the discovery of the fullerenes C_{2n} in 1985 [1] and their elaboration in macroscopic quantities since 1990 [2], a new and wide field of investigations has been offered to chemists and physicists. The most abundant member of the family, the C_{60} molecule, is an electron acceptor and numerous salts have now been synthesised with electronic properties such as ferromagnetism or superconductivity for instance. The C_{60} molecule being nearly spherical, these compounds present many interesting orientational order and disorder phenomena. Such structural phenomena are in close connection with electronic properties, as was shown for superconductivity for instance [3]. C_{60} molecules also present the remarkable property to bound covalently and form polymers. In this letter, we present the first single crystal study of polymerized KC_{60} and RbC_{60}, with special emphasis on polymer chain orientations.
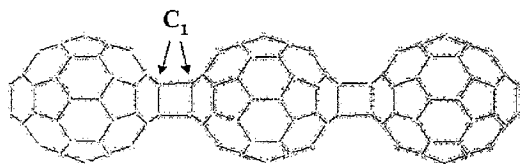

Fig.1 : linear C_{60} polymer chain formed by [2+2] cycloaddition.

Alkali fullerides AC_{60} [4] (A=K, Rb, Cs) present around 350K a transition from a high temperature cubic phase [5] towards an orthorhombic one in which the molecules form one-dimensional polymer chains [6-9]. KC_{60} and RbC_{60} exhibit contrasted conducting and magnetic properties (see part 4), while powder diffraction studies have revealed no structural difference [8]. The present single-crystal diffraction study allows a new careful search for possible differences. The main structural results obtained before [6,8,9] are summarized in the following. The orthorhombic unit cell parameters a, b and c are equal to 9.11, 9.95, 14.32Å and 9.14, 10.11, 14.23Å for KC_{60} and RbC_{60},

respectively. C_{60} molecules are centered at (0,0,0) and (1/2,1/2,1/2), and alkali ions at (0,0,1/2) and (1/2,1/2,0). Polymerization occurs via [2+2] cycloaddition along a (fig.1).
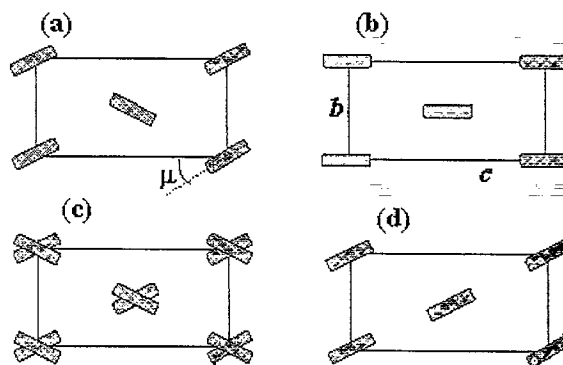

Fig.2 : Sketch of the chain orientations for space groups : (a) Pmnn, (b) ordered Immm, (c) disordered Immm, (d) I2/m. The shaded bars represent the projection of the cycloaddition planes defined by the C_1 atoms onto the crystallographic (b,c) plane. They indicate the orientation of the polymer chains.

The orthorhombic space groups naturally compatible with molecular symmetry are Pmnn and Immm. The orientation of a C_{60} chain about its axis a can be defined by the angle μ of the plane of cycloaddition with c. The Pmnn structure has glide planes, so that if the orientation of the chain passing through the unit cell origin is μ, the orientation of that passing through its center is $-\mu$ (fig.2(a)). The mirror planes of the body-centered Immm structure impose an ordered structure with $\mu=0$ or 90° for all chains (fig.2(b)). However, a disordered Immm structure can also be considered for any other μ value if the chains take orientations μ and $-\mu$ with equal probability (fig.2(c)). In a diffraction experiment, i) Immm can be distinguished from $\overline{P}$mnn by the extinction of the Bragg reflections for h+k+l odd, ii) disordered Immm is characterized by diffuse sheets perpendicular

to a*. Stephens et al. [8] found $\mu=45\pm5°$ for both KC_{60} and RbC_{60}, they could not distinguish between Immm and Pmnn. Fox et al [9] found indications for a possible chain disorder.

2. Experimental results from single crystal X-ray diffraction

KC_{60} and RbC_{60} crystals ($\sim10^{-1}$-$10^{-2}mm^3$) were prepared by stoichiometric doping of C_{60} single crystals at 400°C and then slowly cooled into the polymer phase (detailed procedure is described in ref.[10]). The crystals have been first characterized by electron beam analysis [11] and powder X-ray diffraction [12]. Their electrical transport properties were studied in [10,12].

The AC_{60} crystals often present natural faces which are the crystallographic faces of the original C_{60} crystal, and thus of high temperature cubic AC_{60}. Samples were first studied using the precession technique, which allows one to obtain photographs of reciprocal planes without deformation. $CuK\alpha$ radiation precession photographs have been performed for the main cubic directions. Several crystals were studied to ascertain general results. The crystallinity of the samples is acceptable for diffraction studies (mosaic spread ~2° full-width at half-maximum for KC_{60} and ~2.5° for RbC_{60}). The diffraction patterns display a number of Bragg reflections forming intricate arrangements with overall cubic symmetry for their positions (fig.3). One has to consider different orientational variants whose diffraction patterns superimpose. They result from the phase transition from the cubic phase towards the orthorhombic one of lower symmetry; their orientational relationships are given by the symmetry elements lost at the transition. All variants should have the same volume as they are energetically equivalent. This is not the case as can be seen from some intensity dissymmetries (fig.3), which suggests that an anisotropic factor inferred during the cubic to orthorhombic transformation. Further sample cooling experiments under uniaxial pressure may be of great interest to reduce the number of variants and even to get a true single crystal of the orthorhombic phase. Using computer-generated simulations of the precession patterns, we confirm the unit cell parameters of Stephens et al. [8] and we can determine the orientational relationships between the variants (a similar analysis is detailed in [13] for pressure polymerized C_{60}). In KC_{60}, the polymerization involves the sliding of dense $(111)_c$ planes whose orientation is preserved, as in pressure polymerized C_{60} [13]. Such a sliding may indeed have a low energy cost. This structural polymerization mechanism explains the formation of $(KC_{60})_n$ fibers where ribbons of twinned $(111)_c$ lamellas are joined by the polymer chains [14]. The $(111)_c$ planes are not preserved anymore in RbC_{60}: the structural polymerization mechanism observed for pressure polymerized C_{60} and for KC_{60} does not apply to RbC_{60} possibly due to steric constraints from the larger Rb ions. Precession photographs also allowed us to establish that h+k+l=2n+1 reflections are observed for KC_{60} but not for RbC_{60}, as is illustrated in fig.3. A first structural difference between KC_{60} and RbC_{60} is evidenced : KC_{60} has a primitive structure, while RbC_{60} is body-centered .

We looked for possible diffuse scattering that would be produced by orientational chain disorder. $CuK\alpha$ radiation fixed-crystal fixed-film experiments were performed and they revealed no diffuse scattering in KC_{60} nor in RbC_{60}. Having calculated that the expected diffuse scattering intensity should be of the same order of magnitude as that produced by rotating molecules in pure C_{60}, we performed the same experiment with a small C_{60} crystal, in which case the diffuse scattering was easily detected. We thus conclude in the orientational order of the chains in KC_{60} and RbC_{60}.
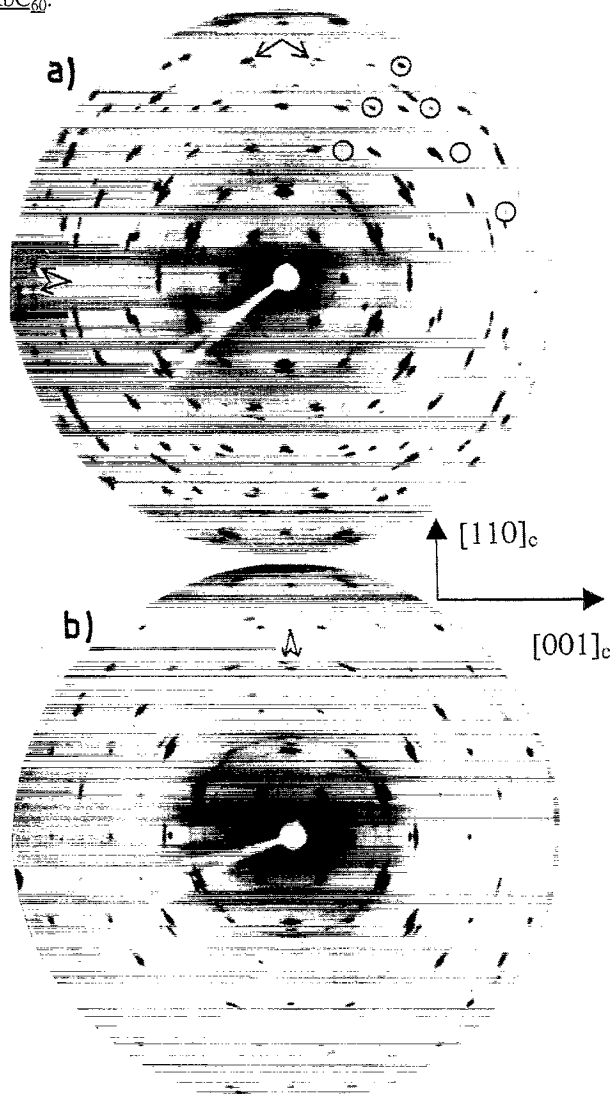

Fig.3. $CuK\alpha$ $(hhl)_c$ precession photographs for (a) KC_{60} and (b) RbC_{60}. Some peaks with equivalent positions under cubic symmetry operations but with different intensities are marked by arrows. Several h+k+l=2n+1 reflections are encircled.

The Bragg peak intensity measurements were performed on a three-circle diffractometer for KC_{60} and RbC_{60}. In order to refine the structure, we had to measure diffraction peaks from a single domain. The original experimental procedure developed to measure isolated reflections from a single orientational variant and the refinement method are described in ref. [15]. The refinement was performed over a limited parameter set : the chain orientation angle μ, an isotropic carbon Debye-Waller (DW) parameter, anisotropic alkali DW parameters, and the molecular distortion due to polymerization (positions of the C_1 atoms in fig.1). In both KC_{60} and RbC_{60}, i) the carbon DW value is standard ($\approx0.01Å^2$), ii) large alkali DW parameters are determined, as in Stephens et al. [8], iii) molecular distortions appear similar in KC_{60} and RbC_{60}, in agreement with Fox et al. [9]. KC_{60} is found to have Pmnn space group, the chain orientation angle value being $\mu\approx51°$. Within the Immm

hypothesis, μ was found equal to 48° in RbC$_{60}$. This would imply, as indicated before, a $+\mu/-\mu$ orientational chain disorder actually ruled out by the absence of diffuse scattering. Aside from Immm, no body-centered orthorhombic space group is convenient to describe the orientational ordering of the C$_{60}$ chains. We thus resolved to consider monoclinic body-centered arrangements. The monoclinic space group compatible with the symmetry of the C$_{60}$ chains is I2/m, with the chain axis parallel to the 2-fold axis and the corresponding chain orientations are depicted in fig.2(d). The (**b**,**c**) angle should not be strictly equal to 90°, but this monoclinic distortion has not been observed within experimental resolution. It may actually be very small due to the relatively homogeneous distribution of the carbon atoms around a chain : if it were fully homogeneous, the (**b**,**c**) angle would be equal to 90°. Within the I2/m hypothesis, we found $\mu \approx 47°$. This new proposed space group appears highly attractive because the chains present orientational order (no diffuse scattering expected, as observed) and because it greatly improves the minimum value of the reliability factor as compared to Immm (R_{min}=0.06 to be compared to 0.24). To summarize, we find relatively close values of the chain orientation angle in KC$_{60}$ and RbC$_{60}$ ($\approx$51° and 47°) in agreement with [8]. However, we have determined different space groups for the two compounds : Pmnn and I2/m, namely, which imply completely different arrangements of the chain orientations, as illustrated in fig.2(a) and (d).

Table 1. Measured and calculated h,k,l reflection intensity ratios between 18K and 300K. Uncertainties are about 25% for the measured ratios.

h,k,l	I_{18K}/I_{300K} (observed)	I_{18K}/I_{300K} (calculated)
3,0,3	1.7	4.3
3,1,4	1.1	0.4
3,0,5	1.7	3.4
3,2,5	1.3	1.8
4,0,4	1.2	0.7
3,1,6	1.5	3.3
4,1,5	1.4	2.5

In KC$_{60}$, the alkali ion DW parameters are found to be [15]: $U_{11} \approx 0.24$Å^2, $U_{22} \approx 0.02$Å^2 and $U_{33} \approx 0.3$Å^2. These large DW parameters may in fact conceal displacements of the K ions from their ideal positions (0,0,1/2) and (1/2,1/2,0). A comparison of the room and low temperature peak intensities can help distinguish between large thermal vibrations and atomic displacements. Preliminary diffractometer measurements performed at room temperature and at 18K are in favor of the second hypothesis. Table 1 gives the measured and calculated ratios of peak intensities at 18K and 300K for a set of reflections. The calculation was made using the above DW parameters (assuming a crude linear dependence of these parameters with temperature). They reveal a profound disagreement with the measured ratios. On the contrary we point out that the measured ratios are all within the same range (between 1.1 and 1.7) which appears to be compatible with standard DW factors (<0.06Å^2) thus supporting the possibility of K displacements from their ideal positions. This result is also interesting in relation with a debated question in

superconducting A$_3$C$_{60}$: are alkali ions centered in octahedral sites or not [17,18]?

3. Molecular environments and energy calculations

KC$_{60}$, RbC$_{60}$ and CsC$_{60}$ compounds present cubic phases at high temperature, with alkali into the octahedral sites, and they all present a phase transition under slow cooling towards an orthorhombic phase formed of polymer chains of C$_{60}$ molecules. A rather natural hypothesis would thus be that the polymer phases are isostructural. This is not the case for KC$_{60}$ and RbC$_{60}$, as demonstrated above.
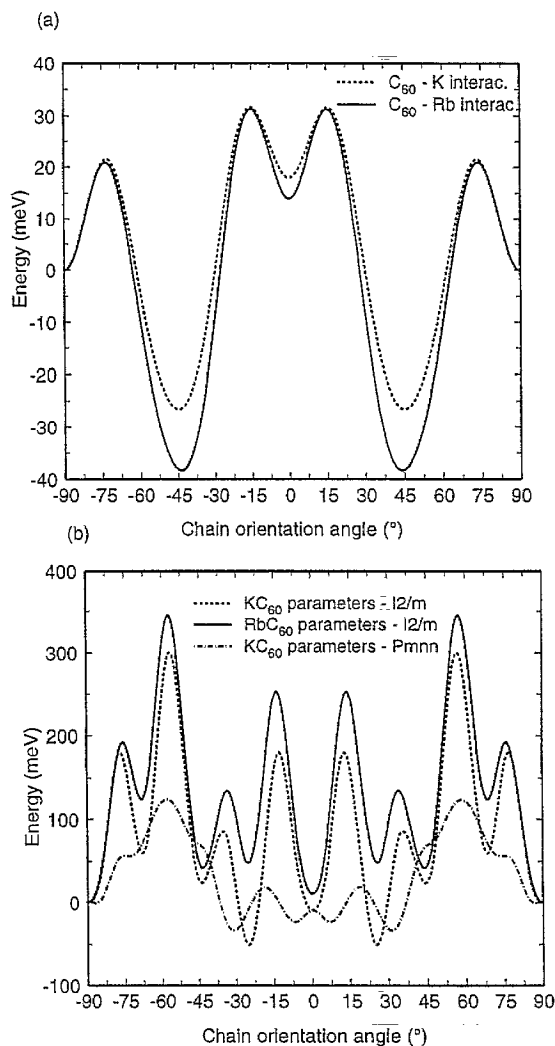
(a)

(b)

FIG.4. (a) C$_{60}$-alkali ions and (b) C$_{60}$-surrounding C$_{60}$ chains interaction energy as a function of the orientation angle μ (see the text). Energies are normalized to zero for μ=90° to facilitate comparisons.

In both compounds, the alkali ions roughly face carbon hexagons from the first neighbors C$_{60}$ (along [110] and [1-10]) and 'single' C-C bonds from their second neighbors (along [001]) [16]. However the intermolecular environments are different. There is only one type of environment in Pmnn KC$_{60}$ (along [111] and [1-11]) where a 'double' C-C bond approximately faces a pentagon from neighboring C$_{60}$, and two different intermolecular environments along [111] and [1-11] in I2/m RbC$_{60}$ [15]. To try to understand why intermolecular environments are different in

KC_{60} and RbC_{60}, we present here preliminary energy calculations. They are performed for carbon atoms and alkali ions interacting through van der Waals forces (van der Waals parameters for alkali ions and for carbon atoms are given in [18] and [19](a)). Electrostatic interactions are calculated with a point charge (+e) on the alkali ion, at (0,0,1/2) and (1/2,1/2,0) positions, and with the partial atomic charges optimized from AM1 calculations for the C_{60} molecule [20]. Simple carbon-carbon van der Waals interactions do not account correctly for orientational ordering in pure C_{60} ([19] and references therein). Thus we do not expect our calculations to be relevant to determine the true energy minima; however they can allow us to understand why KC_{60} and RbC_{60} are not isostructural. The interaction energy between a C_{60} molecule and all neighboring alkali ions is shown in fig.4(a), as a function of its orientation μ around **a**. Interaction energies between a C_{60} molecule and molecules of the surrounding chains are shown in fig.4(b), as a function of μ. All the chains are rotated and their relative orientations are defined by the space group Pmnn or I2/m. Fig.4(a) shows that alkali-C_{60} interactions favors the same μ (~ 45°). Fig.4(b) shows that interactions between C_{60} polymer chains are strongly dependent on the inter-chain distances (compare RbC_{60}, I2/m and KC_{60}, I2/m, which differ by the unit cell parameters only). This may explain why KC_{60} and RbC_{60} are not isostructural. The differences between the RbC_{60} I2/m and Pmnn curves also show that the energy minimisation is highly sensitive to the relative chain orientations i.e. to the space group. In summary, a plausible scenario is that alkali-C_{60} interactions favor roughly the same chain orientation (45-50°) in KC_{60} and RbC_{60}, while the C_{60}-C_{60} interactions impose different relative chain orientations. Finally, the strong influence of the inter-chain distances on their orientational ordering (fig.4(b)) should be kept in mind when analyzing pressure effects and pressure induced transitions in AC_{60} compounds [12,21,22].

4. Polymer chain orientations and electronic properties

The physical properties of the AC_{60} compounds (A=K, Rb, Cs) have been investigated by ESR [6,21,23,24], μSR [25], NMR [21,26-28], and electrical or optical conductivity measurements [10,12,23]. KC_{60} presents a metal-to-semiconductor phase transition near 50K [10,12] and the low temperature phase is not magnetic. On the contrary, RbC_{60} and CsC_{60} present a transition near 50K towards an insulating magnetic phase [6,21,23-25,27,28]. The exact natures of these low temperature phases are not elucidated. For RbC_{60} and CsC_{60}, it has tentatively been attributed to random spin freezing [25(b)], quasi-one dimensional spin density or charge density waves [6,23,25(a)], quasi-one dimensional (1D) [24,27] or three-dimensional (3D) [21] antiferromagnetic ordering. Theoretical arguments in favor of the 1D or 3D character of this phase have also been developed [7,29]. The different behavior of KC_{60} relative to RbC_{60} and CsC_{60} is not yet understood.

It is worth recalling that the MAS-NMR spectra of RbC_{60} and CsC_{60} are very similar, while they differ from that of KC_{60} [26,28]. Alloul et al. [26] suggested that the spin density distribution on a chain depends on the ordering of its neighbors. With the present results, the differences between the KC_{60} and RbC_{60} spectra can be attributed to the distinct relative chain orientations in the two compounds (fig. 2(a) and (d)). It is also tempting to consider that RbC_{60} and CsC_{60} have similar chain orientations. The distinct chain orientations in KC_{60} and RbC_{60} may be a key feature for the understanding of the electronic properties of these compounds. This point of view is supported

by the recent calculations of Tanaka et al. on the influence of relative chain ordering on the band structure [30]. We also note that the I2/m RbC_{60} structure with $\mu \approx 45°$ has been studied by Erwin et al. [29] (it was considered as a structural simplification made to reduce calculations). The electronic structure was found to be 3D and the spin configuration in the low temperature magnetic phase was described as possibly ferromagnetic within each chain and antiferromagnetic between nearest-neighbor chains. Further theoretical studies are necessary.

6. References

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