

Evidence for Distinct Polymer Chain Orientations in KC_{60} and RbC_{60}

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(Received 7 July 1998)

The KC_{60} and RbC_{60} polymer phases exhibit contrasting electronic properties while powder diffraction studies have revealed no definite structural difference. We have performed single crystal x-ray diffraction and diffuse scattering studies of these compounds. It is found that KC_{60} and RbC_{60} possess different chain orientations about their axes, which are described by distinct space groups $Pmnn$ and $I2/m$, respectively. Such a structural difference will be of great importance to a complete understanding of the physical properties. [S0031-9007(98)07594-2]

PACS numbers: 61.48.+c, 61.10.Nz

The recently discovered alkali-fullerides AC_{60} [$A = \text{K, Rb, Cs}$] exhibit a phase transition from a high temperature cubic phase [2] to an orthorhombic one in which the molecules form one-dimensional polymer chains [3–6] at about 350 K. Despite extensive studies, the physical properties of the latter phase are still the subject of controversy. They have been investigated by ESR [3,7–9], μSR [10], NMR [8,11–13], and optical and electrical conductivity measurements [7,14]. RbC_{60} and CsC_{60} possess a magnetic transition towards an insulating phase below ~ 50 K, whereas KC_{60} does not. The exact nature of the magnetic low temperature phase is not yet understood; several scenarios for quasi-one-dimensional [3,4,7,9,12] or three-dimensional [8,15,16] magnetic ordering are being debated. The different behavior of KC_{60} relative to RbC_{60} and CsC_{60} is also not understood. Recent theoretical calculations show that the chain orientations influence the dimensionality of the electronic properties [17]. However, powder diffraction studies [5] revealed no definite structural difference between KC_{60} and RbC_{60} . Accordingly, a better knowledge of the details of the AC_{60} structures, especially the chain orientations, is needed. We present the first single crystal diffraction study of KC_{60} and RbC_{60} , and we show that KC_{60} and RbC_{60} possess different relative chain orientations.

The main structural results [3,5,6] obtained for KC_{60} and RbC_{60} are summarized in the following. The unit cell is orthorhombic, with parameters a , b , and c equal to 9.11, 9.95, 14.32 Å and 9.14, 10.11, 14.23 Å for KC_{60} and RbC_{60} , respectively [5]. C_{60} molecules are centered at $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ positions, and alkali ions at $(0, 0, 1/2)$ and $(1/2, 1/2, 0)$. Polymerization occurs via $[2 + 2]$ cycloaddition along the shortest parameter a [Fig. 1(a)]. The most plausible orthorhombic space groups compatible with the molecular symmetry are $Immm$ and $Pmnn$. The orientation of a C_{60} chain about its axis a can be characterized by the angle μ of the planes

of cycloaddition with c . For the body-centered space group $Immm$, two configurations must be considered: an ordered one, with $\mu = 0$ or 90° [Fig. 1(b)], where chains passing through the origin and the center of the unit cell have the same orientation, and a disordered one if $\mu \neq 0$ or 90° ; the mirror planes perpendicular to b and c constrain the chains to take orientations μ or $-\mu$, with equal probabilities [Fig. 1(c)]. Such a disorder would give rise to diffuse planes perpendicular to a^* in reciprocal space. The $Pmnn$ structure has glide planes, so that, if the orientation of the chain passing

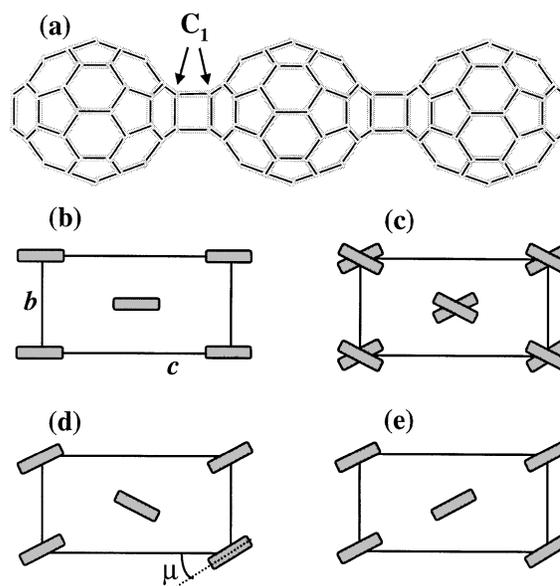


FIG. 1. (a) Linear polymer chain formed by $[2 + 2]$ cycloaddition. Schematic drawing of chain orientations for (b) ordered $Immm$, (c) disordered $Immm$, (d) $Pmnn$, and (e) $I2/m$. The shaded bars indicate the orientation of the polymer chains; they represent the projection of the cycloaddition planes defined by the C_1 atoms onto the crystallographic (b, c) plane.

through the unit cell origin is μ , the orientation of that passing through its center is $-\mu$ [Fig. 1(d)]. In diffraction, $Immm$ can be distinguished from $Pmnn$ by the extinction of the reflections for $h + k + l$ odd. From Rietveld refinements, Stephens *et al.* [5] found $\mu = 45 \pm 5^\circ$ for both KC_{60} and RbC_{60} samples, but they could not discriminate between $Immm$ and $Pmnn$. A pair distribution function analysis performed by Fox *et al.* [6] indicated a possible orientational chain disorder.

For the present study, KC_{60} and RbC_{60} crystals (typical size: 10^{-2} mm³) were prepared by stoichiometric doping of C_{60} single crystals at 400 °C; the polymer phase was obtained by subsequent slow cooling (the detailed procedure is described in Ref. [14]). The samples were first characterized by x-ray powder diffraction [14(b)] and electron beam analysis [18]; their electrical transport properties were reported in Ref. [14]. The sample crystallinity suffered from the insertion and polymerization process, but it was still acceptable for our diffraction studies (mosaic spread $\approx 2^\circ$, full width at half maximum, for KC_{60} and $\approx 2.5^\circ$ for RbC_{60}).

The single crystal x-ray experiments combined photographic (precession and fixed crystal) and diffractometer techniques. The precession method, which gives undistorted sections of the reciprocal space, enabled us to check the body-centered extinctions mentioned above and to study the domain structure of the crystal. The latter information cannot be accessed by powder diffraction techniques. The fixed-crystal, fixed-film monochromatic technique was employed to detect the x-ray diffuse scattering possibly due to orientational disorder of the C_{60} chains. This technique, where the crystal is under vacuum, is particularly efficient as it maximizes the signal-to-noise ratio. Finally, the diffractometer technique enabled us to make quantitative measurements of the Bragg peak intensities used for structure refinements.

Precession photographs (CuK_α radiation) have been taken on different crystals to ascertain general results. Complex precession patterns similar to those presented for pressure polymerized C_{60} in Ref. [19] were obtained. They show the coexistence of orientational variants due to the cubic-orthorhombic symmetry lowering. These variants are related by the lost symmetry operations. We have determined the orientational relationships between the variants, which gives information regarding the structural polymerization mechanism. In KC_{60} , the polymerization involves the sliding of dense $(111)_c$ cubic planes whose orientation is preserved, as in pressure polymerized C_{60} [19]. The situation is somewhat different for RbC_{60} because the orientation of $(111)_c$ planes is not preserved. 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 imposed by the larger Rb ions. The symmetry elements preserved by the cubic-orthorhombic transformation are (i) in KC_{60} the $[110]_c = \mathbf{b}$ twofold axis and (ii) in RbC_{60} the $[\bar{1}\bar{1}0]_c = \mathbf{a}$

and the $[110]_c = \mathbf{b}$ twofold axes. This transformation generates 12 variants for KC_{60} and only 6 for RbC_{60} . A careful analysis of the precession patterns reveals that KC_{60} presents a primitive (P) lattice while RbC_{60} is body centered (I , absence of $h + k + l = 2n + 1$ reflections).

Experiments using the fixed-crystal, fixed-film method were performed for KC_{60} and RbC_{60} . They revealed no diffuse scattering. Calculations showed that the diffuse scattering intensity expected for chain disorder should have the same order of magnitude as that produced by the rotating molecules in pure C_{60} , which can be easily detected by the fixed-crystal, fixed-film method. We thus conclude that the polymer chains are ordered in both KC_{60} and RbC_{60} .

The Bragg peak intensity measurements on KC_{60} and RbC_{60} were performed on a three-circle diffractometer, using CuK_α radiation. AC_{60} crystals often present $\{111\}_c$ twins originating from the parent C_{60} crystals, and we selected samples with negligible twin volumes ($\leq 1\%$). The unit cell parameters are found to be equal to those in Ref. [5] within experimental accuracy. In order to refine the structure, we had to measure diffraction peaks from a single domain. This task required a selection procedure to exclude overlapping reflections. We computed the Bragg peak positions for all variants and selected isolated reflections; we then scanned these reflections towards neighboring ones (typically within 0.8 \AA^{-1}) to ensure the absence of contamination. The remaining Bragg peaks were fitted using Gaussian profiles, yielding peak intensities $I_0(hkl)$. We obtained the following data set of unique and isolated reflections: 177 reflections, among which 107 reflections with $h + k + l = 2n + 1$ and 70 reflections with $h + k + l = 2n$, and for KC_{60} , 82 reflections with $h + k + l = 2n$ for RbC_{60} . Their intensities are relatively weak: only 111 peaks for KC_{60} (63 peaks with $h + k + l = 2n + 1$ and 48 peaks with $h + k + l = 2n$) and 39 peaks for RbC_{60} verify the relation $I > \sigma$ [20]. We also checked (i) the $h + k + l = 2n + 1$ extinctions for RbC_{60} , and (ii) the glide plane extinctions in KC_{60} .

The structural analysis is based on the minimization of the reliability factor [20]

$$R = \sum \left| \frac{|F_{\text{obs}}|}{\sum |F_{\text{obs}}|} - \frac{|F_{\text{calc}}|}{\sum |F_{\text{calc}}|} \right|, \quad (1)$$

where F_{obs} and F_{calc} are observed and calculated structure factors. $|F_{\text{obs}}(h, k, l)|$ is the square root of the integrated intensity given by $I = I_0(hkl)Q^2$ (the mosaic broadening of the reflection is considered to be proportional to Q^2), and corrected for polarization effects. The limited intensity data lead us to restrict the number of refined parameters to the chain orientation angle μ , an isotropic carbon Debye-Waller (DW) parameter U_C , anisotropic alkali DW parameters U_{11}, U_{22}, U_{33} , and the molecular distortion; we relaxed the C_1 atom positions only, which most affects the reliability factor [5]. We

varied these parameters simultaneously over broad ranges using a step by step procedure which required reasonably small computing times due to the limited data set. The set of parameter values that gave the lowest R (R_{\min}) was retained. In comparison with the usual least-squares refinement method, this procedure enables us to test all possible combinations of the parameters, but its drawback is that uncertainties are not easily evaluated.

The R values obtained by minimization over the molecular distortion and over the DW factors are plotted versus orientation angle μ in Fig. 2. For $Pmnn$ KC_{60} , we obtain $R_{\min} \approx 0.16$ for $U_C \approx 0.01 \text{ \AA}^2$, $U_{11}, U_{22}, U_{33} \approx 0.24, 0.02, 0.3 \text{ \AA}^2$, $d_{C_1\text{-inter}} \approx d_{C_1\text{-intra}} \approx 1.55 \text{ \AA}$, and $\mu \approx 51^\circ$. The DW factor for carbon is normal, while those of potassium are unusually large; preliminary experiments as a function of temperature indicate that they probably conceal alkali ion displacements [21]. For RbC_{60} a refinement was first attempted within the $Immm$ space group, leading to $R_{\min} \approx 0.24$ for $\mu \approx 48^\circ$ (Fig. 2). However, this implies, as indicated before, a $(+\mu)/(-\mu)$ orientational chain disorder which is 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 C_{60} polymer chains. We were thus forced to consider monoclinic body-centered arrangements. The space group compatible with the symmetry of C_{60} chains is $I2/m$, with the chain axis parallel to the twofold axis; the corresponding chain orientations are depicted in Fig. 1(e). In this case, the (\mathbf{b}, \mathbf{c}) angle is not constrained to 90° . However, we have not detected a deviation of this angle value from 90° (within an estimated experimental uncertainty of 0.5°). It

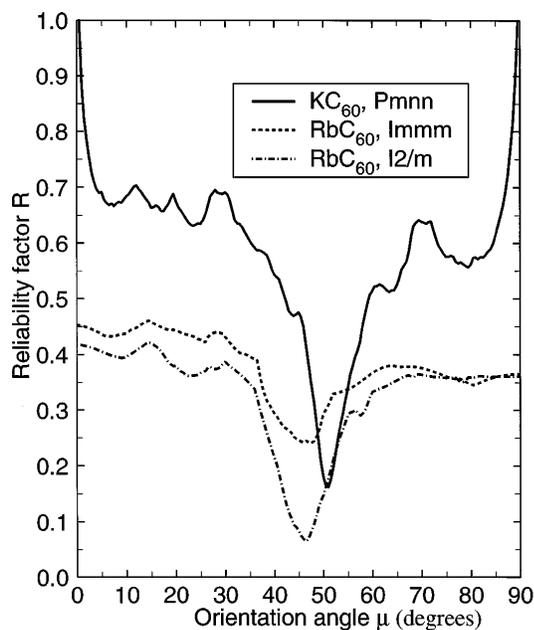


FIG. 2. Reliability factor R calculated for peaks satisfying $I > \sigma$, as a function of the chain orientation μ (see the text).

may be very weak because of the relatively homogeneous distribution of the atoms on a chain around its axis [if it were fully homogeneous, the (\mathbf{b}, \mathbf{c}) angle would be equal to 90°]. Within the $I2/m$ hypothesis, the reliability factor minimum $R_{\min} \approx 0.06$ corresponds to $U_C \approx 0.01 \text{ \AA}^2$, $U_{11}, U_{33} \approx 0.16, 0.09 \text{ \AA}^2$ [22] (U_{22} cannot be determined because all measured h, k, l peaks have small k values), $d_{C_1\text{-inter}} \approx 1.5 \text{ \AA}$, $d_{C_1\text{-intra}} \approx 1.6 \text{ \AA}$, and $\mu \approx 47^\circ$ (Fig. 2) [23]. This model is highly attractive because the chain orientations are ordered (in agreement with the absence of diffuse scattering) and it greatly improves R_{\min} , as compared to $Immm$. The chain orientations in KC_{60} and RbC_{60} ($\mu \approx 51^\circ$ and 47°) are in agreement with the results of Stephens *et al.* ($45 \pm 5^\circ$) [5], and the molecular distortions are found to be similar in KC_{60} and RbC_{60} [6]. However, the different space groups obtained for KC_{60} and RbC_{60} , namely, $Pmnn$ and $I2/m$, imply completely different relative orientations of the chains.

It is interesting to compare the structural environments in KC_{60} and RbC_{60} . The first-neighbor C_{60} - C_{60} interchain (8.73 \AA) and intermolecular (9.85 \AA) distances are remarkably similar for both compounds, while the second-neighbor distance (equal to b) increases from 9.95 \AA (KC_{60}) to 10.11 \AA (RbC_{60}). The A - C_{60} distance increases for the first neighbors (6.74 \AA for KC_{60} and 6.81 \AA for RbC_{60}) while it decreases slightly for the second neighbors (7.16 \AA for KC_{60} and 7.12 \AA for RbC_{60}). The above distances depend on the unit cell parameters only. The chain orientation comes into play for the interatomic A - C or C - C environments. In both compounds the alkali ions roughly face carbon hexagons from the first neighbors C_{60} (along $[110]$ and $[1\bar{1}0]$) and “single” C - C bonds from their second neighbors (along $[001]$) [24]. The influence of the different values of μ ($\mu_K \approx 51^\circ$ and $\mu_{Rb} \approx 47^\circ$) is small and no clear distinction between KC_{60} and RbC_{60} can be identified at this point. In contrast, the intermolecular C_{60} environments are different. There is only one type of environment in KC_{60} (along $[111]$ and $[1\bar{1}\bar{1}]$) where a “double” bond approximately faces a pentagon from the neighboring C_{60} , as shown in Fig. 3(a). In RbC_{60} the lower space group symmetry implies that the $[111]$ and $[1\bar{1}\bar{1}]$ intermolecular environments are different, as shown in Figs. 3(b) and 3(c). It is possible that alkali- C_{60} interactions favor roughly the same chain orientation angle in KC_{60} and RbC_{60} ($\sim 45^\circ$ – 50°), while the C_{60} - C_{60} interactions determine the relative chain orientations and thus the space group symmetry. Preliminary calculations [21] have indeed shown that the C_{60} - C_{60} intermolecular potential varies appreciably with the chain orientations, the symmetry of their arrangement, and the unit cell parameters. This should be kept in mind when analyzing pressure effects and pressure-induced transitions in AC_{60} compounds [8,14,25].

MAS-NMR spectra of RbC_{60} and CsC_{60} are very similar and differ from that of KC_{60} [11,13]. Alloul *et al.* [11]

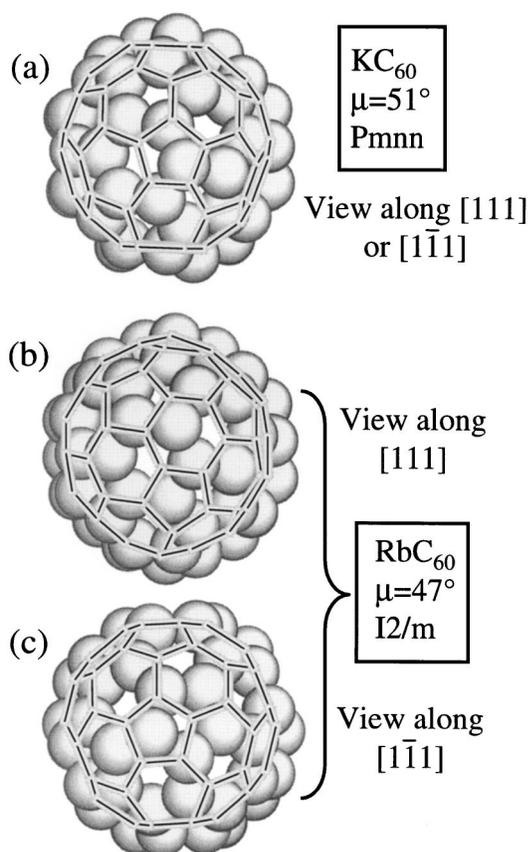


FIG. 3. Molecular environments viewed along the axes $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ joining centers of nearest-neighbor molecules in KC_{60} and in RbC_{60} . The C atoms (spheres) of the more distant molecule are viewed through a portion of the C-C bond skeleton of the nearer one.

suggested that the distribution of spin density along a chain is influenced by its neighbors. With the present results, we can now attribute the difference between the KC_{60} and RbC_{60} spectra to the distinct relative chain orientations in the two compounds [Figs. 1(d) and 1(e)]. The similarity of the RbC_{60} and CsC_{60} spectra suggests that the chain orientations are likely the same in RbC_{60} and CsC_{60} . As discussed in the introduction, the physical properties of RbC_{60} and CsC_{60} are very similar and differ markedly from those of KC_{60} . A strong correlation between physical properties and relative chain orientations can thus be inferred in polymerized AC_{60} . Electronic structure calculations have already been performed by Erwin *et al.* [15] and by Tanaka *et al.* [17] for $I2/m$ RbC_{60} . Further theoretical investigations taking into account the distinct chain orientations in AC_{60} are much awaited.

J.H. and A.Z. acknowledge support from the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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