Evidence of a structural anomaly at 14 K in polymerised CsC$_{60}$

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Abstract

We report the results of a high-resolution synchrotron X-ray powder diffraction study of polymerised CsC$_{60}$ in the temperature range 4 to 40 K. Its crystal structure is monoclinic (space group $I2/m$), isostructural with RbC$_{60}$. Below 14 K, a spontaneous thermal contraction is observed along both the polymer chain axis, $a$ and the interchain separation along [111], $d_1$. This structural anomaly could trigger the occurrence of the spin-singlet ground state, observed by NMR at the same temperature.

PACS.61.48+c Fullerenes and fullerene-related materials.
PACS.61.10Nz Single crystal and powder diffraction.

Introduction. - Alkali fullerides with stoichiometry AC$_{60}$ ($A$= K, Rb, Cs) undergo a structural transition from a high-temperature monomer to a polymer phase in the vicinity of 350 K [1, 2]. Polymerisation occurs by a [2+2] cycloaddition mechanism, leading to the formation of one-dimensional C-C bridged C$_{60}$ chains [3]. The AC$_{60}$ polymers exhibit interesting structural properties and form a variety of conducting and magnetic phases. A
metal-insulator transition below 50 K is accompanied by the stabilisation of a magnetic state in RbC$_{60}$ and CsC$_{60}$, whereas KC$_{60}$ remains metallic to low temperatures [4]. The nature of the magnetic transition has remained controversial, as both quasi-one dimensional electronic instabilities [4, 5, 6, 7, 8] and three-dimensional magnetic ordering [9, 10] have been proposed. Initial X-ray powder diffraction studies [3] have described the structure of the polymers as orthorhombic (space group *Pmnn*) with the orientation of the C$_{60}$ chains about the short axis *a* described by $\mu = 45 \pm 5^\circ$, where $\mu$ is the angle between the cycloaddition planes and the *c* axis. However, recent single crystal X-ray diffraction and diffuse scattering studies [11] on KC$_{60}$ and RbC$_{60}$ have revealed that they are not isostructural. They adopt different relative chain orientations (Figure 1) and their crystal structures are described by distinct space groups, *Pmnn* (orthorhombic) and *I2/m* (body-centred monoclinic), respectively. The difference in their respective physical properties can thus be attributed to the distinct relative chain orientations. Moreover the angle $\mu$ was determined as 51$^\circ$ for KC$_{60}$ and 47$^\circ$ for RbC$_{60}$, the difference also affecting the electronic band structure [12].

CsC$_{60}$ exhibits overall similar physical properties to RbC$_{60}$. However, recent NMR measurements have detected the appearance of a spin-singlet ground state below $T_S = 13.8$ K which coexists with the long range ordered magnetic state [13]. It was proposed that the development of the non-magnetic phase may be correlated either with a structural change, tentatively ascribed to the occurrence of a spin-Peierls transition or with an electronic instability. We note that earlier $\mu$SR data had described the low-temperature state of CsC$_{60}$ as comprising of co-existing static magnetic and fluctuating paramagnetic domains [14]. In this paper, we report the crystallographic characterisation of the CsC$_{60}$ polymer by synchrotron X-ray powder diffraction in the temperature range 4-40 K. This reveals that CsC$_{60}$ is isostructural with RbC$_{60}$, adopting a body-centred monoclinic structure (space group *I2/m*). In addition, our results show that a spontaneous strain appears along both the polymer chain axis and the interchain [111] direction below $T_S$, providing the signature of magnetoelastic coupling.

**Experimental.** - The CsC$_{60}$ sample was prepared by solid state reaction of stoichiometric quantities of Cs metal and C$_{60}$ in sealed quartz tubes at 800 K for four weeks with intermittent shaking. High-resolution synchrotron X-ray powder diffraction measurements were performed on a CsC$_{60}$ sample sealed in a 0.5-mm diameter glass capillary. Data were collected in continuous scanning mode using nine Ge(111) analyser crystals on the BM16 beamline
at the European Synchrotron Radiation Facility (ESRF), Grenoble, France in
the temperature range 4-40 K ($\lambda = 0.79972$ Å). Data were rebinned in the 2θ
range 5°- 45° to a step of 0.01°. Analysis of the diffraction data was performed
with the GSAS suite of powder diffraction programmes [15]. In the course
of the Rietveld refinements, the characteristic modulated background was
fitted to a 15th-order Chebyshev polynomial. It arises from diffuse scattering,
probably due to the static rotational disorder of residual C$_{60}$ molecules and/or
to the different orientational domains arising from the symmetry lowering at
the monomer- polymer transition. The initial refinements included the scale
factor, the background coefficients, the lattice constants, the zero point and
the peak width parameters. The final refinements incorporated the isotropic
temperature factors, the positional parameters of the bridging C atoms and
the occupation number of Cs.

**Results.** - We first performed detailed Rietveld refinements of the diffrac-
tion profile of CsC$_{60}$ at 20 K. We used three starting structural models,
derived from those reported before for the AC$_{60}$ polymers. In all cases, the
C$_{60}^-$ ions are located at the (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) positions, while the Cs$^+$ ions
at the (0,0,$\frac{1}{2}$) and ($\frac{1}{2}$,$\frac{1}{2}$,0) positions in the unit cell. However, in each case
a different polymer chain orientation ordering is adopted, as illustrated in
Figure 1. For space group $Pmnn$, the orientation of the chains at the origin
and the centre of the unit cell are $\mu$ and -$\mu$, respectively, while for $I2/m$,
they are identical ($\mu$). The third model is described by space group $Immm$
and involves a disordered arrangement of chains with $\mu$ or -$\mu$ (≠0° or 90°)
orientations. In the course of the refinements, we monitored the resulting
quality-of-fit factors ($R_{wp}$) as a function of the orientation of the chains for
all three space groups. Figure 2 presents the evolution of $R_{wp}$ with the ro-
tation angle $\mu$ which was varied between 40° and 50°. The refinements were
stable throughout this $\mu$-range with a minimum in all cases at $\mu \approx 46^\circ$. How-
ever, the deepest minimum is clearly obtained for the monoclinic $I2/m$ space
group, in a similar fashion to RbC$_{60}$ [11]. Subsequent refinements concen-
trated on this structural model and resulted in excellent quality fits ($R_{wp} =
3.97\%, R_{exp} = 1.44\%$). The final results are plotted in Figure 3. The re-
sulting lattice parameters at 20 K are $a = 9.0968(3)$ Å, $b = 10.1895(3)$ Å, $c =
14.1351(4)$ Å and $\alpha = 89.820(6)^\circ$. The intra- and inter-molecular C$_1$-C$_1$
bond distances also refined to 1.72(1) Å and 1.60(1) Å, respectively, where C$_1$
is the bridging C atom between two C$_{60}$ molecules.

Following the successful determination of the structure of the CsC$_{60}$ poly-
mer at 20 K, we attempted Rietveld refinements of the datasets at other
temperatures. In the course of these refinements, the positional and thermal atomic parameters and the peak width functions were kept fixed. The resulting variation of the monoclinic lattice constants in the temperature range 4-40 K is strongly anisotropic (Figure 4). While the lattice constants, \( b \) and \( c \) vary smoothly with temperature, a clear anomaly occurs below \( \approx 14 \) K along the polymer chain axis \( a \). A spontaneous contraction of the \( a \) constant, \( \Delta a/a \approx 1.5 \times 10^{-4} \) is evident between 14 and 4 K. At the same time, the monoclinic angle \( \alpha \) also increases by roughly the same proportion, leading to an overall contraction in the volume of the unit cell of \( \Delta V/V \approx 2 \times 10^{-4} \). The observed anomaly is also mirrored in the interfullerene chain separations. In space group \( I2/m \), there are two types of intermolecular environments, \( d_1 \) along the [111] and \( d_2 \) along the [\( 1\overline{1}1 \)] directions of the unit cell. These are not affected equally below 14 K (Figure 5) with a sharp decrease in interchain separation occurring only for \( d_1 \) along [111] (\( \Delta d_1/d_1 \approx 1.0 \times 10^{-4} \)).

**Discussion.** - The temperature-dependent synchrotron X-ray data have shown that the low-temperature structure of \( \text{CsC}_{60} \) is identical to that of \( \text{RbC}_{60} \) with similar orientational angles \( \mu \). Thus both polymers have comparable electronic structures \([9, 12]\) and show the appearance of a low-temperature magnetic insulating phase, in contrast to the non-isostuctural \( \text{KC}_{60} \) whose metallic state is robust and shows no low-temperature instabilities. The difference in size between \( \text{K}^+ \), \( \text{Rb}^+ \) and \( \text{Cs}^+ \) also leads to increased nearest-neighbour separations between the polymer chains (successively by \( \approx 0.11\% \) and 0.12\%) and increased quasi-one-dimensional character of the electronic structure, as we progress from \( \text{KC}_{60} \) to \( \text{RbC}_{60} \) to \( \text{CsC}_{60} \). In the related family of fulleride polymers, \( \text{Na}_2\text{Rb}_{1-x}\text{Cs}_x\text{C}_{60} \) (\( 0 \leq x \leq 1 \)), the electronic properties were also shown to be very sensitive to such subtle size effects \([16]\).

The details of the electronic structure of the \( \text{RbC}_{60} \) and \( \text{CsC}_{60} \) polymers remain controversial. While many experiments reveal one-dimensional characteristics \([4, 8]\), electronic band structure calculations predict three-dimensional energy bands \([2, 7]\). In addition, recent \(^{13}\text{C}\) magic angle spinning NMR experiments on \( \text{CsC}_{60} \) have shown that the conduction electron density is concentrated along the equator of the \( \text{C}_{60} \) ions and away from the \( \text{C}-\text{C} \) bridging bonds \([18]\). This indicates that the band structure is dominated by strong transverse coupling between the polymer chains rather than a strong one-dimensional coupling along them. Nonetheless, \(^{13}\text{C}\) and \(^{133}\text{Cs}\) NMR measurements also revealed a transition to a non-magnetic (spin-singlet) ground state at \( T_S = 13.8 \) K, ascribed to a structural or electronic instability \([13]\).
The former was interpreted as a spin-Peierls transition, consistent with the presence of strong 1D features in the electronic description of the CsC$_{60}$ polymer.

A highly significant result of the present diffraction experiments is the observation of a spontaneous thermal contraction along both the chain axis, $a$ and the interchain separation along [111], $d_1$ below a transition temperature of about 14 K, which coincides with the spin-singlet state transition temperature, $T_S$ and unambiguously points to the structural origin of the instability. This result is certainly reminiscent of the situation encountered for the linear chain compound, CuGeO$_3$ in which the magnetic transition to a spin-Peierls state is accompanied by shifts of the Cu$^{2+}$ ions along the chain direction and oxygen displacements perpendicular to the chains [19]; the magnetoelastic coupling was evident in diffraction experiments as a spontaneous thermal contraction along the axis $b$, perpendicular to the chain direction, of comparable magnitude to that observed for CsC$_{60}$. However, no evidence of any superstructure peaks is established in CsC$_{60}$, while the quality of the powder diffraction data is not such as to allow us to determine whether the spontaneous strain is accompanied by a structural phase transition. In this respect, it is also interesting to note that the $b$ and $c$ axes parameters of CsC$_{60}$ and the interchain distance along [111], $d_2$ show no anomalies at $T_S$.

The current structural evidence is certainly consistent with the occurrence of a structural transition in CsC$_{60}$. However, while a spin-Peierls scenario is possible, it is equally likely that the observed structural changes may arise from a CDW (commensurate or incommensurate) transition. An appealing simple interpretation of the structural anomaly at 14 K could be that a soft phonon mode along the polymer chain may be responsible for the lattice contraction along $a$ which then induces a local structural rearrangement through the variation of the interchain distance $d_1$. In this respect, it would be of interest to perform high-resolution structural measurements at elevated pressures. The intermolecular distance $d_1$ should vary the most, while contraction along $a$ should be limited because of the rigidity of the polymer chain. Band structure calculations should then give valuable insight on the influence of the $d_1$ variation on the nature of the non-magnetic phase, especially as it has been found experimentally that application of pressure gradually suppresses the magnetic order in favour of the spin-singlet state in both CsC$_{60}$ and RbC$_{60}$ [13, 10].

**Conclusions.** - In conclusion, high-resolution synchrotron X-ray powder diffraction has established that the structure of CsC$_{60}$ is monoclinic (space
group $I2/m$), isostructural with that of RbC$_{60}$. The similarity in the orientational ordering of the polymer chains in these systems explains their comparable electronic and conducting properties. A structural anomaly is observed below $\approx 14$ K, coincident with the appearance of a non-magnetic state. The observed structural changes provide the signature of magnetoelastic coupling between the $C_{60}$ localised spins and the phonon degrees-of-freedom.

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Figure 1: Schematic drawing of the $\text{C}_{60}$ chain orientations for space groups (a) $Pmnn$ and (b) $I2/m$. The shaded bars indicate the orientation of the polymer chains by projection onto the crystallographic $bc$ plane. The disordered $Immm$ space group discussed in the text corresponds to a random distribution of the chain orientation $\mu/ - \mu$ ($\neq 0^\circ$ or $90^\circ$).

Figure 2: Dependence of the reliability factor, $R_{wp}$ of the Rietveld refinement of the synchrotron X-ray diffraction data of CsC$_{60}$ at 20 K on the chain orientation $\mu$ for the three space groups $Pmnn$, disordered $Immm$ and $I2/m$.

Figure 3: Observed (points), calculated (solid line) and difference (lower panel) synchrotron X-ray powder diffraction profiles of CsC$_{60}$ at 20 K (space group $I2/m$). The positions of the reflections are shown as tick marks.

Figure 4: Temperature dependence of the monoclinic lattice parameters, $a$, $b$, $c$ and $\alpha$ of polymerised CsC$_{60}$. The dotted lines are guides to the eye.

Figure 5: Temperature dependence of the interchain distances, $d_1$ (along [111]) and $d_2$ (along [1T1]) in polymerised CsC$_{60}$. The dotted line is a guide to the eye.
\[ \Delta a/a \sim 1.5 \times 10^{-4} \]

- \( a (\text{Å}) \)
- \( b (\text{Å}) \)
- \( c (\text{Å}) \)
- \( \alpha (°) \)

\( T (\text{K}) \)
