

## Neutron diffraction study of the polymeric structure of $\text{Na}_2\text{RbC}_{60}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 371

(<http://iopscience.iop.org/0953-8984/11/2/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:24

Please note that [terms and conditions apply](#).

## Neutron diffraction study of the polymeric structure of $\text{Na}_2\text{RbC}_{60}$

Alexandros Lappas<sup>†</sup>, Craig M Brown<sup>†‡</sup>, Konstantinos Kordatos<sup>†</sup>,  
Emmanuelle Suard<sup>‡</sup>, Katsumi Tanigaki<sup>§</sup> and Kosmas Prassides<sup>†</sup>

<sup>†</sup> School of Chemistry, Physics and Environmental Science, University of Sussex,  
Brighton BN1 9QJ, UK

<sup>‡</sup> Institute Laue Langevin, F-38042 Grenoble, France

<sup>§</sup> Department of Materials Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku,  
Osaka 558-8585, Japan

Received 1 September 1998

**Abstract.** High-resolution neutron powder diffraction is used to authenticate that the  $\text{Na}_2\text{RbC}_{60}$  fulleride undergoes on cooling an incomplete structural phase transition from a primitive cubic to a monoclinic phase (space group  $P2_1/a$ , lattice constants at 2.5 K:  $a = 13.707(2)$  Å,  $b = 14.466(2)$  Å,  $c = 9.366(1)$  Å,  $\beta = 133.64(1)^\circ$ ). Very short interfullerene C–C contacts are identified, providing evidence for the presence of bridging bonds whose distances refine to  $\sim 1.7$  Å. The C–C bonds are inclined to the  $c$  axis by  $\sim 7.7^\circ$  and lie within the  $bc$  plane. The stability of the ground state polymeric structure and the kinetics of the monomer  $\rightarrow$  polymer transformation are influenced by the charge state of the fulleride ions, the steric crowding associated with the dopant alkali ions and the relative orientational state adopted by neighbouring fullerides in the precursor monomer phase.

### 1. Introduction

The origin of the unusually fast depression of  $T_c$  with decreasing interfullerene separation in superconducting fullerides,  $\text{Na}_2(\text{A},\text{A}')\text{C}_{60}$  (where A, A' = alkali metal) has attracted particular interest. Empirically it appears that the modified structure and intermolecular potential encountered in these primitive cubic fullerides sensitively affect the electronic and conducting properties [1]. Structural work at elevated pressures for  $\text{Na}_2\text{RbC}_{60}$  [2] has also identified a low-symmetry phase with short  $\text{C}_{60}^{3-}-\text{C}_{60}^{3-}$  distances ( $\sim 9.35$  Å), reminiscent of polymerized  $\text{AC}_{60}$  salts ( $\sim 9.11$  Å) [3]. However, recent synchrotron x-ray diffraction [4] and susceptibility measurements together with  $^{13}\text{C}$  and  $^{23}\text{Na}$  NMR [5] have revealed, even at ambient pressure, a more complicated situation than hitherto appreciated. The properties of ternary,  $\text{Na}_2\text{AC}_{60}$  and quaternary,  $\text{Na}_2(\text{A},\text{A}')\text{C}_{60}$  fullerides were found to be highly sensitive to cooling protocols. While upon rapid cooling, the salts remain strictly cubic, slow cooling stabilizes the same low-symmetry phase as that found at high pressures, comprising of quasi-one-dimensional  $\text{C}_{60}^{3-}$  chains with short interball centre-to-centre distances of  $\sim 9.38$  Å. Although single carbon–carbon interfullerene bonds have been reported before in the dimer phases of both  $\text{AC}_{60}$  fullerides [6] and the  $(\text{C}_{59}\text{N})_2$  heterofullerene solid [7], it was only recently that this type of bonding was proposed as the way of linking together the  $\text{C}_{60}^{3-}$  units in the case of  $\text{Na}_2\text{RbC}_{60}$  [8, 9] and the  $\text{C}_{60}^{4-}$  units in  $\text{Na}_4\text{C}_{60}$  [10] to produce polymeric structures of varying dimensionality. Here we report the results of temperature dependent high-resolution neutron

powder diffraction studies of the crystal structure of  $\text{Na}_2\text{RbC}_{60}$  at ambient pressure. Such experiments were performed in an attempt to characterize the interfullerene C–C bonding interaction more accurately than it had been possible before by synchrotron x-ray powder diffraction. As the x-ray scattering power of C is weak, such details have eluded earlier structural work [4, 9].

## 2. Experiment

The single-phase  $\text{Na}_2\text{RbC}_{60}$  sample of mass 1.2 g, used in the present study, was prepared by direct solid-state reaction of stoichiometric quantities of  $\text{C}_{60}$ , Na and Rb contained in a Ta cell, sealed inside a glass tube filled with 500 Torr of He gas. The heat treatment followed included heating at 480 K for 3 h, 570 K for 12 h, and 620 K for 72 h. Further annealing was carried out at 673 K with intermediate regrindings for a period of four weeks. Phase purity was established by solid state NMR and synchrotron x-ray powder diffraction measurements.

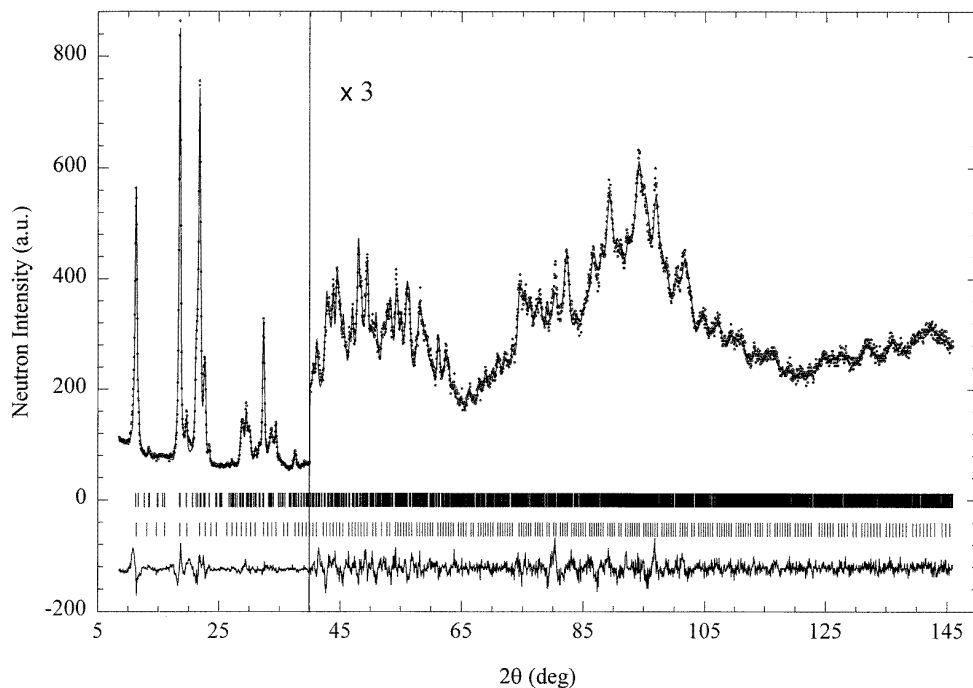
The neutron powder diffraction experiments were undertaken with the high-flux, high-resolution diffractometer D2b ( $\lambda = 1.5938 \text{ \AA}$ ), at the Institute Laue Langevin, Grenoble, France. The  $\text{Na}_2\text{RbC}_{60}$  sample, from the same batch used for the synchrotron x-ray [4, 9] studies, was loaded in a cylindrical vanadium can ( $\varnothing = 4 \text{ mm}$ ) sealed with indium wire and then placed in a standard ILL ‘orange’ liquid-helium cryostat. The sample was first cooled from room temperature to 180 K at a rate of  $5 \text{ K h}^{-1}$ . The temperature was then held at 180 K for 17 hours before further cooling to liquid helium temperatures. Data were collected on warming at temperatures of 2.5, 100 and 200 K. The instrument was operated in its high-resolution mode and the data were collected for the angular range,  $2\theta = 0\text{--}162.5^\circ$  in steps of  $0.05^\circ$ . Full diffraction profiles were obtained with counting times of 22 hours at 2.5 K, 14 hours at 100 K and 9 hours at 200 K. The raw data were merged and normalized to a standard vanadium run using standard ILL programs. The data analysis was performed with the FULLPROF [11] suite of powder diffraction software.

## 3. Results and discussion

### 3.1. Optimization of the structural model

Figure 1 presents the neutron powder diffraction profile of  $\text{Na}_2\text{RbC}_{60}$  obtained at 2.5 K, following the cooling protocol described earlier. Detailed inspection of the profiles at all temperatures investigated in the present study shows that the Bragg reflections can be indexed with the monoclinic space group  $P2_1/a$ . However, refinement of the profiles using the LeBail [12] pattern decomposition technique in  $P2_1/a$  symmetry fails to reproduce the necessary intensity for a number of Bragg peaks in the  $2\theta$  range  $8\text{--}35^\circ$ . This is in agreement with our earlier experimental work [4, 8] where synchrotron x-ray diffraction studies found that a minority cubic (space group  $P\bar{a}3$ ) phase also survives at low temperatures. Two-phase LeBail profile analysis of the neutron diffraction data further confirmed that a fraction of the high-temperature primitive cubic phase was frozen in, despite the extremely slow cooling.

Accordingly the neutron powder diffraction profiles at 2.5, 100 and 200 K were refined by the Rietveld method using a two-phase model of coexisting monoclinic and cubic phases. The monoclinic unit cell ( $a = 13.707(2) \text{ \AA}$ ,  $b = 14.466(2) \text{ \AA}$ ,  $c = 9.366(1) \text{ \AA}$ ,  $\beta = 133.64(1)^\circ$  at 2.5 K) with the fullerene molecules at  $(0, 0, 0)$  and  $(1/2, 1/2, 0)$  is shown in figure 2. The nearest interfullerene distance is  $9.37 \text{ \AA}$  within the  $ac$  plane, in good agreement with the values obtained from our synchrotron x-ray studies [4, 9]. It is considerably shorter than the nearest neighbour centre-to-centre distance of  $10.02 \text{ \AA}$  in  $\text{C}_{60}$ , but compares well with earlier observations in

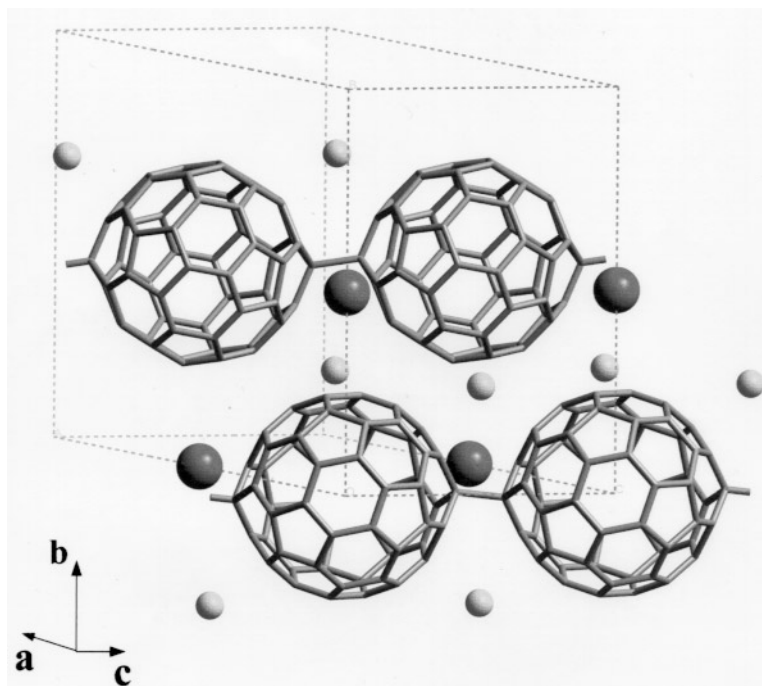


**Figure 1.** Observed (points), calculated (solid line) and difference (lower panel) plots for the final two-phase Rietveld refinement of the high-resolution powder neutron diffraction data of  $\text{Na}_2\text{RbC}_{60}$  at 2.5 K. Reflection positions are shown as tick marks. The tick marks show the reflection positions for the monoclinic (top set) and primitive cubic (bottom set) cells.

fullerides with C–C interfullerene connections, like the two-dimensional  $\text{Na}_4\text{C}_{60}$  [10] and the one-dimensional  $\text{AC}_{60}$  ( $A = \text{Rb}, \text{Cs}$ ) [3] polymers, in which the shortest centre-to-centre distances are 9.28 and 9.11 Å, respectively. The gradual loss of the superconducting cubic and the appearance of the non-superconducting monoclinic phase on cooling agrees well with the fact that the diamagnetic response of  $\text{Na}_2\text{RbC}_{60}$  is strongly suppressed [13] in SQUID susceptibility studies following slow cooling treatments. The superconducting volume fraction remaining at low temperatures correlates well with the amount of the untransformed cubic phase.

Our starting structural model was based on the monoclinic structure reported in [8, 9] (space group  $P2_1/a$ ) in which 30 symmetry-inequivalent carbon atoms were needed to generate the two  $\text{C}_{60}$  molecules in the unit cell. The alkali metals were initially located at  $(1/2, 0, 0)$  and  $(0, 1/4, 1/2)$  positions, derived from the high-symmetry tetrahedral and octahedral sites of the parent cubic structure. For the minority cubic phase, we employed the  $Pa\bar{3}$  structural model already documented in the literature [1, 14], in which the  $\text{C}_{60}$  units adopt two distinct orientational states, rotated anticlockwise about the  $[111]$  direction of the cubic cell by either  $\phi \sim 98$  or  $38^\circ$ , and the  $\text{Na}^+$  and  $\text{Rb}^+$  ions are placed in the tetrahedral and octahedral interstices, respectively. Rietveld refinements were then performed with this two-phase model.

At first, the two  $\text{C}_{60}^{3-}$  ions present in the monoclinic unit cell were allowed to rotate about the  $[001]$  direction anticlockwise and the resulting quality-of-fit factors ( $R_{wp}$ ) were monitored. Figure 3 presents the evolution of  $R_{wp}$  with the rotation angle  $\psi$  which was varied between 0 and  $180^\circ$ , in increments of  $4^\circ$ . The initial  $\text{C}_{60}$  orientation of  $\psi = 0^\circ$  corresponds to that of the



**Figure 2.** The crystal structure of polymerized  $\text{Na}_2\text{RbC}_{60}$ , as determined by the present neutron diffraction study. The fullerenes form polymeric chains connected by single C–C bonds with an inclination of  $7.7^\circ$  to the  $c$  axis of the monoclinic cell.  $\text{Na}^+$  and  $\text{Rb}^+$  ions are depicted as small and large spheres, respectively.

standard orientation, located at the origin of an orthorhombic cell defined by the relationships:  $a_o = c_m$ ,  $c_o = b_m$  and  $(a_o/b_o) = \tan(\theta_m - \pi/2)$ . The refinements were stable throughout the  $\psi$ -range with a deep minimum  $A$  in  $R_{wp}$  ( $= 5.61\%$ ) evident at an angle  $\psi = 82 \pm 1^\circ$ . At this angle, the relative orientation of the molecules is such that pairs of carbon atoms, located on the  $c$  axis, from neighbouring fullerenes are brought in close proximity. Another well defined, but more shallow, minimum  $B$  with  $R_{wp} = 6.53\%$  is also observed at an angle  $\psi = 64 \pm 1^\circ$ . The precise position of the two minima was established by a set of smaller stepwise rotations in increments of  $1^\circ$ . The appearance of a secondary orientational state ( $B$ ) may be indicative of molecular disorder in the polymeric phase of  $\text{Na}_2\text{RbC}_{60}$ , which warrants further investigation, especially on the grounds of the intrinsic orientational disorder present in fulleride solids.

Subsequent two-phase Rietveld refinements of the 2.5 K neutron diffraction profile were performed with starting coordinates for  $\text{C}_{60}^{3-}$  corresponding to the  $\psi_A \sim 82^\circ$  orientation of the  $\text{C}_{60}$ – $\text{C}_{60}$  linear arrays. These resulted in excellent quality fits ( $R_p = 3.23\%$ ,  $R_{wp} = 4.28\%$ ,  $R_{exp} = 2.46\%$ ) [15]. The results of these Rietveld refinements are plotted in figure 1 and selected structural parameters for the monoclinic and primitive cubic phases of  $\text{Na}_2\text{RbC}_{60}$  derived from the present analysis, at different temperatures, are presented in table 1. The incomplete nature of the transition is clearly apparent, as at all temperatures the monoclinic phase is dominant with the frozen-in volume fraction of the primitive cubic tending to gradually increase at elevated temperatures. This is in agreement with our earlier observations which also revealed the existence of hysteresis [16], as this slow transformation showed different onset temperatures in the course of cooling ( $T_{pc \rightarrow m} \sim 250$  K) and heating ( $T_{m \rightarrow pc} \sim 270$  K) sequences.

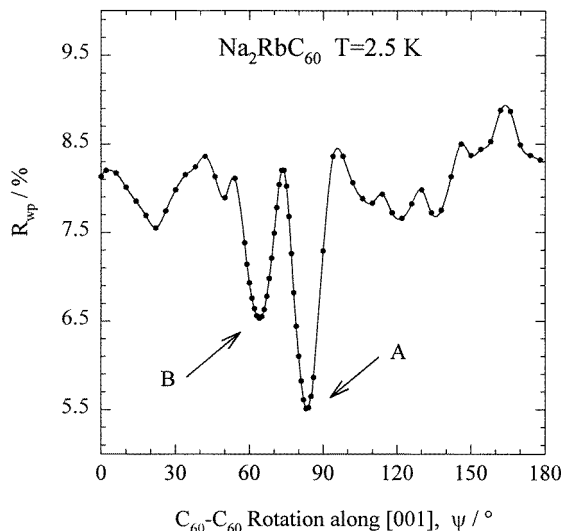
**Table 1.** Final structural parameters for  $\text{Na}_2\text{RbC}_{60}$  derived from two-phase Rietveld refinements of the neutron data at 2.5, 100 and 200 K.  $B_{\text{iso}}(\text{C})$  is the isotropic temperature factor for the carbon atoms. In the monoclinic cell,  $\text{C}_{60}$  is located at the 2a (0, 0, 0), Na at the 4e ( $x$ ,  $y$ ,  $z$ ), and Rb at the 2c (1/2, 0, 0) sites. In the primitive cubic cell,  $\text{C}_{60}$  is located at the 4a (0, 0, 0), Na at the 8c ( $x$ ,  $x$ ,  $x$ ), and Rb at the 4b (1/2, 1/2, 1/2) sites.

	$T = 2.5 \text{ K}$ Counting time = 22 h	$T = 100 \text{ K}$ Counting time = 14 h	$T = 200 \text{ K}$ Counting time = 9 h
<b>Polymer Phase</b>			
Space group	$P2_1/a$ (cell choice 3)		
$a$ (Å)	13.707(2)	13.705(2)	13.710(3)
$b$ (Å)	14.466(2)	14.495(2)	14.520(3)
$c$ (Å)	9.366(1)	9.363(2)	9.358(2)
$\beta$ (°)	133.64(1)	133.60(1)	133.56(1)
% content	70.7(1)	66.3(1)	68.4(1)
Fullerene orientation	$\psi \sim 82^\circ$	$\psi \sim 82^\circ$	$\psi \sim 82^\circ$
$B_{\text{iso}}(\text{C})$ (Å <sup>2</sup> )	1.27(7)	1.18(8)	1.41(8)
Bridging carbon & 'on-ball' neighbours	C4-C4: 1.70(7) Å C4-C3: 1.54(5) Å C4-C12: 1.50(5) Å C4-C14: 1.42(8) Å		
<b>Cubic phase</b>			
Space group	$Pa\bar{3}$		
$a$ (Å)	14.0163(8)	14.0254(10)	14.0399(13)
% content	29.3(1)	33.7(1)	31.6(1)
$B_{\text{iso}}(\text{C})$ (Å <sup>2</sup> )	3.44(16)	1.82(18)	2.31(23)
Major fullerene orientation & % fractional occupancy	$\phi \sim 98^\circ$ 0.8	$\phi \sim 98^\circ$ 0.8	$\phi \sim 98^\circ$ 0.8
$R_{\text{wp}}$ (%), $R_{\text{exp}}$ (%)	4.28, 2.46	4.61, 3.06	5.19, 3.99
$R_{\text{Bragg}}$ (%)—polymer phase	3.99	5.57	5.40
$R_{\text{Bragg}}$ (%)—cubic phase	3.08	4.02	3.57

The refinement results presented in figure 1 and table 1 were derived following an exhaustive series of Rietveld refinements in which the molecular orientation and geometry of the  $\text{C}_{60}$  units were systematically varied. Our methodology is presented in detail below. The work was carried out using the diffraction profile at 2.5 K for which we had the best signal to noise ratio, and then applied to the datasets at higher temperatures. First we explored the significance of the secondary minimum in  $R_{\text{wp}}$  at  $\psi_B \sim 64^\circ$  (figure 3). A series of Rietveld refinements was performed in which it was assumed that both fullerene orientations with  $\psi_A \sim 82^\circ$  and  $\psi_B \sim 64^\circ$  were present simultaneously. Allowing the relative fractions  $\eta_A$  and  $\eta_B$  to vary in the course of the refinement led to no statistically significant improvement in  $R_{\text{wp}}$  with  $\eta_A$  converging to a value of 0.972(7). As a result, we conclude that there is no evidence for a partially disordered structural model. In all these Rietveld refinements, the major and minor fractions of  $\text{C}_{60}^{3-}$  orientations in the primitive cubic phase were kept constant at the value of 80% for  $\phi \sim 98^\circ$  already reported in the literature [1, 14, 17, 18].

### 3.2. Bridging and frontier carbon atom geometry

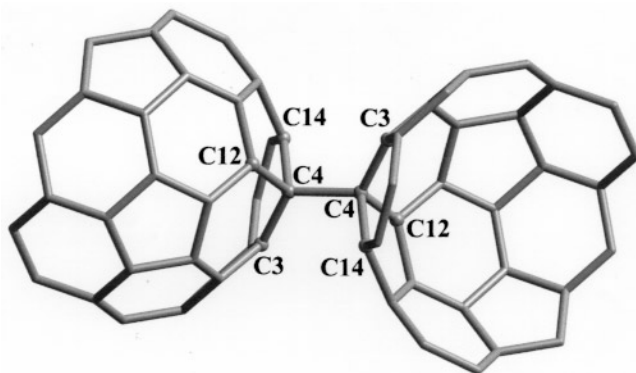
Having established the absence of orientational disorder in the monoclinic phase, we turned our attention to the issue of chemical bonding in  $\text{Na}_2\text{RbC}_{60}$ , as implied by the short lattice



**Figure 3.** Variation of the weighted profile  $R$  factor ( $R_{wp}$ ) for the Rietveld refinement of the neutron data of  $\text{Na}_2\text{RbC}_{60}$  at 2.5 K as a function of the anticlockwise rotation of the  $\text{C}_{60}^{3-}$  ions about the [001] direction of the monoclinic cell (space group  $P2_1/a$ ).

constant of 9.37 Å. In the beginning, we employed an undistorted structural model for the  $\text{C}_{60}$  units with alternating short (1.39 Å) and long (1.45 Å) C–C bonds. Bearing in mind the short interball separation along the  $c$  axis, we attempted to define as accurately as possible the position of the frontier C atom (C4) which was the most likely to be involved in the bonding interactions along the  $c$  axis. In the beginning, we assumed an interfullerene close contact,  $\text{C4–C4} = 1.55$  Å, close to the ideal  $\text{sp}^3$  bonding configuration postulated by local density functional (LDA) calculations [19]. We then allowed this carbon atom to move first only along the  $c$  axis in order to test the magnitude of the closest C–C contacts. In the course of these refinements, we constrained its position so that the  $\text{C4–C4}$  distance did not exceed 1.6 Å, the single C–C intermolecular bonding distance in the  $(\text{C}_{59}\text{N})_2$  dimer [20]. This did not result in statistical improvement of  $R_{wp}$ , but it provided a good starting point to explore the effect on its nearest neighbour carbon atoms (C3, C12, C14). We thus attempted to refine, in a stepwise fashion, the fractional coordinates of the three nearest neighbours of C4, while keeping the rest of the  $\text{C}_{60}$  shell as a ‘rigid body’ and the distance  $\text{C4–C4} = 1.60(5)$  Å. Stable refinements were quickly achieved with this fully ordered model, while improved  $R$  factors were obtained when the bridging carbon C4 was also allowed to move freely away from the  $c$  axis— $R_{wp}$  decreased from 5.71 to 5.61% [21]. The intermolecular  $\text{C4–C4}$  bond tended to become somewhat longer, converging to a value of 1.70(7) Å. At the same time, the  $\text{C4–C4}$  bond was now inclined by  $7.7^\circ$  with respect to the  $ac$  plane. The on-ball C–C bond distances converged to values of  $\text{C4–C3} = 1.54(5)$  Å,  $\text{C4–C12} = 1.50(5)$  Å, and  $\text{C4–C14} = 1.42(8)$  Å (figure 4).

Following this, we allowed the  $\text{C4–C4}$  bond to move on the  $bc$  plane by rotating the fullerene molecules about the [100] direction of the unit cell, while keeping the interchain contacts at the optimum orientation angle of  $\psi \sim 82^\circ$ . In figure 5, we present the values of the weighted profile  $R$  factor, as monitored during the stepwise rotation of  $\text{C}_{60}$  anions by an angle,  $\varepsilon$  in both a clockwise (negative values) and an anticlockwise (positive values) manner. The additional left-hand side vertical axis displays how the intermolecular single



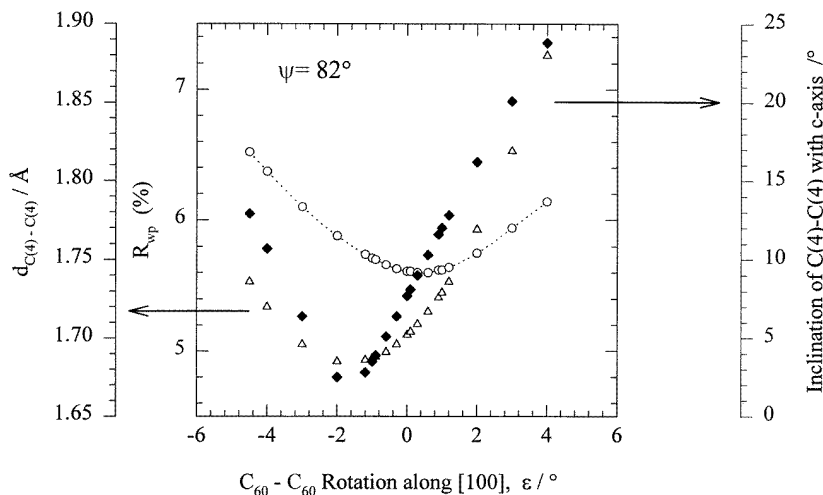
**Figure 4.** Geometry of the frontier (C3, C12, C14) and bridging (C4) carbon atoms on adjacent fullerenes, showing the optimum orientation and distortion of the molecules along the direction of polymerization ( $c$  axis).

C–C bond ( $d_{C(4)-C(4)}$ ; open ‘triangle’ symbols) varies when the C4 contact carbon atoms on neighbouring fullerenes move away from each other. At the same time, the right-hand vertical axis also shows the variation of the inclination angle (full ‘diamond’ symbols) of this bond with respect to the short  $c$  axis. It was found that rotations even by small increments ( $0.3^\circ$ ) of  $\varepsilon$  lead to statistically significant deterioration of the quality of the refinements. The minimum in  $R_{wp}$  is attained for a C4–C4 bond length of  $\sim 1.7 \text{ \AA}$  and an inclination of about  $\sim 7.7^\circ$  from the  $c$  axis within the  $bc$  plane, thus setting an upper limit for this bonding distance.

### 3.3. Dopant alkali ion optimized environment

We now turn our attention to the optimized geometry of the alkali ions ( $A^+$ ) with respect to the  $C_{60}^{3-}$  molecular orientational state. Initial refinements were performed with  $\text{Na}^+$  placed in the pseudo-tetrahedral  $(0, 1/4, 1/2)$  interstice. Subsequent refinements allowed it to move to the general  $4e$  position with coordinates  $(-0.018, 0.266, 0.482)$ . This displacement led only to a marginal improvement in the quality of the fit, but it was in agreement with the predictions of the LDA calculations [19] for the relaxed  $\text{Na}_2\text{RbC}_{60}$  geometry. The large isotropic temperature factor for  $\text{Na}^+$ , of the order of  $\sim 10 \text{ \AA}^2$  even at 2.5 K, suggests the existence of static disorder, possibly related to steric crowding. In addition, the number of nearest C neighbours of  $\text{Na}^+$  is reduced to eight in the polymer phase from 12 found in the orientationally ordered primitive cubic phase (figure 6(a)). In the  $\psi_A \sim 82^\circ$  orientation, the  $C_{60}^{3-}$  ions have rotated in such a way that each  $\text{Na}^+$  coordinates optimally to three 6:5 C–C bonds (fusing hexagons and pentagons) and one 6:6 C–C bond (fusing two hexagons). This kind of arrangement is reminiscent of that found in the minor configuration ( $\phi \sim 38^\circ$ ) of fulleride anions in the primitive cubic structure, in which  $\text{Na}^+$  coordinates to three 6:5 fusions as well as to the C atoms of a hexagonal face [1]. The shortest  $\text{Na}^+ - C_{60}^{3-}$  approach is  $\sim 2.50 \text{ \AA}$ , somewhat smaller than the sum of the van der Waals radius of C ( $1.65 \text{ \AA}$ ) and the  $\text{Na}^+$  ionic radius ( $0.95 \text{ \AA}$ ), but the average  $\text{Na}^+ - \text{C}$  distance is  $\sim 2.75 \text{ \AA}$  (figure 6(a)). Finally, the  $\text{Rb}^+$  ions which occupy the octahedral holes are coordinated to four 6:5 and two 6:6 C–C bonds of the six neighbouring fulleride ions. This results in little steric  $\text{Rb}^+ - \text{C}$  crowding as the closest contact is  $\sim 3.30 \text{ \AA}$  (figure 6(b)).



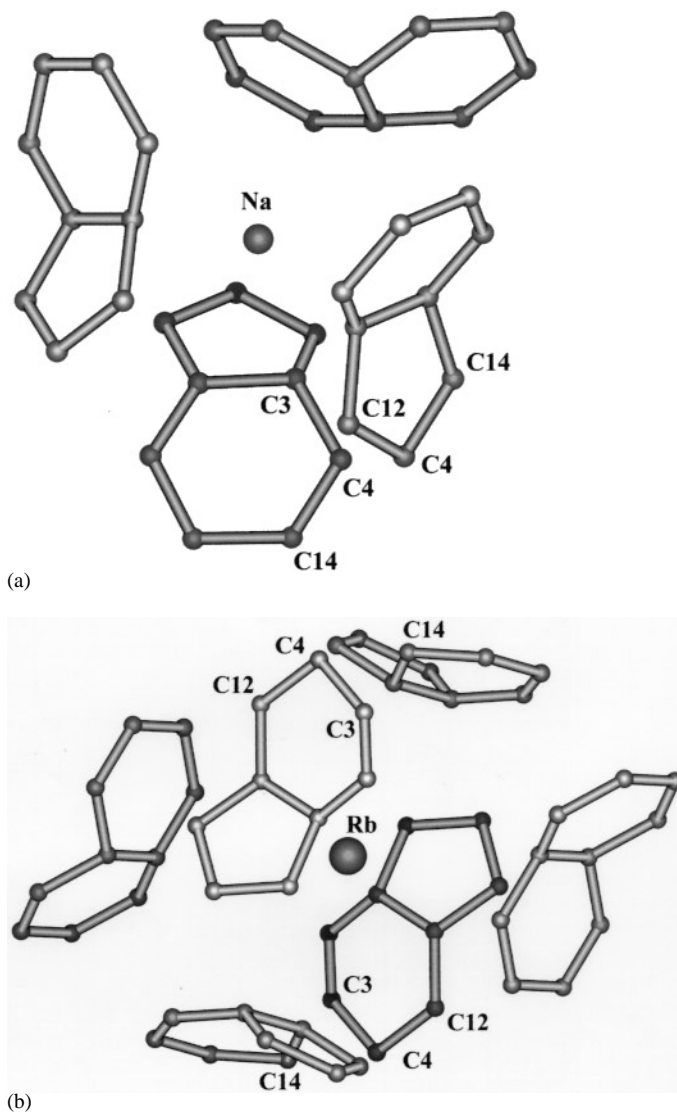


**Figure 5.** Dependence of the reliability factor,  $R_{wp}$  (open circles) of the Rietveld refinement of the 2.5 K neutron diffraction data of  $\text{Na}_2\text{RbC}_{60}$  on clockwise (negative values) and anticlockwise (positive values) rotations of  $\text{C}_{60}^{3-}$  ions by an angle  $\varepsilon$  about the [100] direction of the monoclinic cell. The additional left-hand side vertical axis shows the accompanying variation of the bridging C–C bond ( $d_{\text{C}(4)-\text{C}(4)}$ , open triangles) and the right-hand vertical axis that of the inclination angle (full diamonds) of this bond with respect to the  $c$  axis.

### 3.4. The differing structural behaviour of $\text{RbC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$

The origin of the differing structures adopted by  $\text{RbC}_{60}$  (chains bridged by two C–C bonds) and  $\text{Na}_2\text{RbC}_{60}$  (chains bridged by one C–C bond) has generated considerable interest [8]. A recent microscopic theory of the phase changes in  $\text{RbC}_{60}$  [22] has identified two competing orientations for the low-temperature structure when rotations,  $\Phi$  about the cubic [110] axis are considered, one corresponding to the formation of a doubly bonded polymer at  $\Phi = 45^\circ$  and the other to the formation of singly bonded dimer (or polymer) at  $\Phi = 9^\circ$ . We have argued before that the origin of the differing structural behaviour between  $\text{RbC}_{60}$  and  $\text{Na}_2\text{RbC}_{60}$  is strongly associated with the different charged states of the fulleride ions [9]. In  $\text{C}_{60}^-$  salts, the presence of a single unpaired electron per ball allows only the formation of dimers, with polymer formation occurring via a different mechanism, namely a [2 + 2] cycloaddition reaction. However, in the case of  $\text{C}_{60}^{3-}$  salts, the availability of additional electrons allows the bridging of each fulleride unit with two nearest neighbours through single C–C bond formation, leading to a polymeric structure. Comparative studies of the stabilities of a variety of bridging structures for  $\text{C}_{60}^-$  and  $\text{C}_{60}^{3-}$  have confirmed these arguments [23, 24]. The present structural determination also reveals a steric factor that appears to disfavour the [2 + 2] cycloaddition route for polymer formation in  $\text{Na}_2\text{RbC}_{60}$ . If  $\text{Na}_2\text{RbC}_{60}$  were to adopt a structure similar to that of the  $\text{RbC}_{60}$  polymer,  $\text{Na}^+$  would encounter severe steric crowding, as the shortest approach between  $\text{C}_{60}^{3-}$  and  $\text{Na}^+$  is now of the order of  $\sim 2.35$  Å (the average  $\text{Na}^+$ –C distance is  $\sim 2.65$  Å) and as a result the formation of the singly bonded polymer is accompanied by considerable steric relief.

An additional difference between the polymer phases of  $\text{Na}_2\text{RbC}_{60}$  and  $\text{RbC}_{60}$  arises from the different precursor phases. The  $\text{RbC}_{60}$  polymer is formed at  $T < 400$  K from the orientationally disordered face-centred cubic (fcc) rocksalt (space group  $Fm\bar{3}m$ ). On the other hand, the  $\text{Na}_2\text{RbC}_{60}$  polymer forms from the orientationally ordered primitive cubic  $Pa\bar{3}$  phase at much lower temperature,  $\sim 250$  K. Quasi-free molecular rotations in the fcc precursor phase



**Figure 6.** Coordination environments of (a) the  $\text{Na}^+$  ions in the tetrahedral and (b) the  $\text{Rb}^+$  ions in the octahedral interstices of the monoclinic structure of  $\text{Na}_2\text{RbC}_{60}$  for the optimum interfullerene orientation at  $\psi_A \sim 82^\circ$ . The bridging C4 atoms and their on-ball neighbours (C3, C12, C14) are also labelled.

of  $\text{RbC}_{60}$  allow frequent optimal contact between fullerenes for polymer formation through [2+2] cycloaddition. This contrasts with the extremely slow kinetics exhibited by the monomer  $\rightarrow$  polymer transformation in  $\text{Na}_2\text{RbC}_{60}$ . The primitive cubic precursor is characterized by fullerene orientations in which 6:6 carbon bonds nest over pentagonal faces of neighbouring molecules [1]. Carbon bonds can form during orientational jumps, as the fullerenes perform small amplitude librational motion [25], but the resulting kinetics are extremely slow [26] and the transformation does not go to completion with the monomer phase surviving to low temperatures. One can also conclude that formation of additional C–C bridging bonds from the orientationally ordered cubic phase will be even slower.

#### 4. Conclusions

In conclusion, high-resolution neutron powder diffraction has confirmed that at low temperatures the ground state structure of  $\text{Na}_2\text{RbC}_{60}$  is monoclinic, comprising singly bonded polymeric chains of  $\text{C}_{60}^{3-}$  units. The monomer  $\rightarrow$  polymer transition is incomplete with a sizeable fraction of the cubic phase ( $\sim 30\%$ ) surviving to low temperatures. We find that the bridging C–C bond distance refines to  $\sim 1.7 \text{ \AA}$ , somewhat longer than a typical covalent single bond but still implying a bonding interaction between neighbouring fulleride units. Furthermore, the C–C bridge is not perfectly aligned with the  $c$  axis and is inclined by  $\sim 7.7^\circ$  with respect to it within the  $bc$  plane of the monoclinic cell. The  $\text{Na}^+ - \text{C}_{60}^{3-}$  interaction is also optimized for the adopted orientation ( $\psi_A \sim 82^\circ$ ) of the fulleride ions; the coordination of the  $\text{Na}^+$  ion, which resides in distorted tetrahedral interstices, is reduced from 12 in the primitive cubic to eight in the monoclinic phase with steric crowding significantly relieved. While electronic considerations are paramount in selecting the particular structural type of bridging geometry adopted for different charge states of the  $\text{C}_{60}^{n-}$  ions, we find that geometric factors related to the fulleride orientational state in the precursor monomer phase and the location of the intercalated alkali ions also play a sensitive role in the determination of both the ground state geometry and the kinetics of the transformation.

#### Acknowledgments

Financial support from the TMR Programme of the European Commission (Research Network 'FULPROP' ERBFMRXCT970155) is acknowledged. KP thanks the Leverhulme Trust for a 1997–98 research fellowship. We also thank the ILL for the provision of neutron beamtime and Dr J Rodriguez-Carvajal for help with the Rietveld refinements.

#### References

- [1] Prassides K, Christides C, Thomas I M, Mizuki J, Tanigaki K, Hirose I and Ebbesen T W 1994 *Science* **263** 950
- Yildirim T, Fischer J E, Dinnebier R, Stephens P W and Lin C L 1995 *Solid State Commun.* **93** 269
- [2] Zhu Q 1995 *Phys. Rev. B* **52** 723
- [3] Chauvet O, Oszlanyi G, Forro L, Stephens P W, Tegze M, Faigel G and Janossy A 1994 *Phys. Rev. Lett.* **72** 2721
- Stephens P W, Bortel G, Faigel G, Tegze M, Janossy A, Pekker S, Oszlanyi G and Forro L 1994 *Nature* **370** 636
- [4] Prassides K, Vavakis K, Kordatos K, Tanigaki K, Bendele G M and Stephens P W 1997 *J. Am. Chem. Soc.* **119** 834
- [5] Cristofolini L, Kordatos K, Lawless G, Prassides K, Tanigaki K and Waugh M P 1997 *J. Chem. Soc., Chem. Commun.* 375
- [6] Oszlanyi G, Bortel G, Faigel G, Granasy L, Bendele G M, Stephens P W and Forro L 1996 *Phys. Rev. B* **54** 11 849
- [7] Brown C M, Cristofolini L, Kordatos K, Prassides K, Bellavia C, Gonzalez R, Keshavarz-K M, Wudl F, Cheetham A K, Zhang J P, Andreoni W, Curioni A, Fitch A N and Pattison P 1996 *Chem. Mater.* **8** 2548
- [8] Prassides K 1997 *Curr. Opinion Solid State Mater. Sci.* **2** 433
- [9] Bendele G M, Stephens P W, Prassides K, Vavakis K, Kordatos K and Tanigaki K 1998 *Phys. Rev. Lett.* **80** 736
- [10] Oszlanyi G, Baumgartner G, Faigel G and Forro L 1997 *Phys. Rev. Lett.* **78** 4438
- [11] Rodriguez-Carvajal J 1997 *Program FULLPROF* version 3.5 ILL (unpublished)
- [12] LeBail A, Duroy H and Fourquet J L 1988 *Mater. Res. Bull.* **23** 447
- [13] Prassides K, Tanigaki K and Iwasa Y 1997 *Physica C* **282–287** 307
- [14] Lappas A, Kosaka M, Tanigaki K and Prassides K 1995 *J. Am. Chem. Soc.* **117** 7560
- [15] In order to account for the complicated background shape especially at high  $2\theta$ , the background was treated with a Fourier filtering technique implemented in the FULLPROF suite of Rietveld refinement programs, and it was not further refined but read from a file during subsequent refinements.

- [16] Margadonna S, Brown C M, Kordatos K, Lappas A, Prassides K, Kosaka M and Tanigaki K 1998 *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* vol 6, ed K M Kadish and R S Ruoff (Pennington, NJ: Electrochemical Society) pp 650–8
- [17] David W I F, Ibberson R M, Dennis T J S, Hare J P and Prassides K 1992 *Europhys. Lett.* **18** 219
- [18] Kniaz K, Fischer J E, Zhu Q, Rosseinsky M J, Zhou O and Murphy D W 1993 *Solid State Commun.* **88** 47
- [19] Ogitsu T, Margadonna S, Prassides K, Tanigaki K, Kusakabe K and Tsuneyuki S 1998 *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* vol 6, ed K M Kadish and R S Ruoff (Pennington, NJ: Electrochemical Society) pp 666–72
- [20] Andreoni W A, Curioni A, Holzer K, Prassides K, Keshavarz-K M, Hummelen J C and Wudl F 1996 *J. Am. Chem. Soc.* **118** 11 335
- [21] A difference in  $R_{wp}$  greater than 0.08% is considered as statistically significant; see E Prince and C H Spiegelmann 1992 *International Tables for Crystallography* vol C, ed A J C Wilson (Boston: Kluwer) p 618
- [22] Nikolaev A V, Prassides K and Michel K H 1998 *J. Chem. Phys.* **108** 4912
- [23] Ogitsu T, Prassides K, Tanigaki K, Kusakabe K and Tsuneyuki S 1998 *Electronic Properties of Novel Materials Materials—Progress in Molecular Nanostructures (AIP CP442)* ed H Kuzmany, J Fink, M Mehring and G Roth (Woodbury, NY: American Institute of Physics) pp 331–4
- [24] Pekker S, Oszlanyi G and Faigel G 1998 *Chem. Phys. Lett.* **282** 435
- [25] Christides C, Prassides K, Neumann D A, Copley J R D, Mizuki J, Tanigaki K, Hirose I and Ebbesen T W 1993 *Europhys. Lett.* **24** 755
- [26] Margadonna S, Brown C M, Lappas A, Kordatos K, Tanigaki K and Prassides K 1998 *Electronic Properties of Novel Materials—Progress in Molecular Nanostructures (AIP CP442)* ed H Kuzmany, J Fink, M Mehring and G Roth (Woodbury, NY: American Institute of Physics) pp 327–30