

Structure of Rb:C<sub>60</sub> compounds

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We report x-ray-diffraction studies on Rb<sub>x</sub>C<sub>60</sub> samples of nominal composition ranging from  $x=1.5$  to 6. After six weeks of annealing at 200°C, we observe well-defined stoichiometric compounds Rb<sub>n</sub>C<sub>60</sub> with  $n=0$  (pure C<sub>60</sub>), 3, 4, and 6, and refine the corresponding face-centered cubic, body-centered tetragonal, and body-centered cubic structures. Evidence is found for a fifth compound as well. The  $n=3$  and 6 structures are analogous to the corresponding K<sub>n</sub>C<sub>60</sub> compounds.

The solid-state reaction resulting in the superconducting alkali-metal-C<sub>60</sub> compounds<sup>1-3</sup> typically leads to inhomogeneous materials with ill-defined stoichiometry. For the potassium compounds the preparation methods were rapidly refined and the composition K<sub>3</sub>C<sub>60</sub> was identified<sup>3</sup> shortly after the initial report of its superconductivity.<sup>1</sup> The isolation of a pure superconducting phase is a prerequisite for further characterization of physical properties, such as the London penetration depth and coherence length,<sup>4</sup> and pressure dependence.<sup>5</sup> The crystal structure was determined to be fcc (Ref. 6) as in the pure C<sub>60</sub> material, with cations in octahedral and tetrahedral interstitial sites. In contrast, the kinetics of the Rb reaction is slower and more complex, and the isolation of the superconducting phase, Rb<sub>3</sub>C<sub>60</sub>, was accomplished only very recently by Holczer *et al.*<sup>7</sup> and Fleming *et al.*<sup>8</sup>

Here we report results of extensive x-ray-diffraction studies on a series of Rb<sub>x</sub>C<sub>60</sub> samples of different composition. The structural parameters are summarized in Table I. At a nominal composition of Rb<sub>6</sub>C<sub>60</sub>, we observe a bcc structure reported earlier for K<sub>6</sub>C<sub>60</sub> and Cs<sub>6</sub>C<sub>60</sub> by

Zhou *et al.*<sup>9</sup> At lower Rb concentration, the majority phase is always the fcc phase isostructural with superconducting K<sub>3</sub>C<sub>60</sub>.<sup>6</sup> Based on the results of Ref. 7, it is clear that this is the superconducting phase. In some samples of low Rb concentration, the presence of the undoped (pure) C<sub>60</sub> fcc phase is evident. Besides these three phases that were expected on the basis of previous results, we have detected two other structures. There is a tetragonal phase, with nominal composition Rb<sub>4</sub>C<sub>60</sub>, the structure of which we discuss here. This compound was independently discovered by Fleming *et al.*<sup>10</sup> Finally, there is one other phase, from which we have found so few diffraction lines that we are not able to hypothesize a structure.

The samples, sealed since preparation in glass tubes, were identical with the ones in Ref. 7, where the preparation is described in detail. The x-ray powder-diffraction measurements were made at the State University of New York X3A beam line at the National Synchrotron Light Source. X-rays of wavelength 0.83 Å were monochromatized by flat Si(111) crystals, and the diffracted beam was analyzed with a Ge(111) crystal. The system resolution,

TABLE I. Unit-cell dimensions, bond distances, and temperature factors in A<sub>x</sub>C<sub>60</sub> phases. The temperature factor is defined as  $2B = 12\pi^2\langle u^2 \rangle$ , where  $u$  is the thermal motion amplitude.

Composition	Space group	Cell dimension (Å)	Closest C <sub>60</sub> -C <sub>60</sub> (Å)	Closest A-C <sub>60</sub> (Å)	Volume per C <sub>60</sub> (Å <sup>3</sup> )	Thermal factor (Å <sup>2</sup> )	
						C <sub>60</sub>	A
C <sub>60</sub>	<i>Fm</i> $\bar{3}m$	14.18	10.03	· · ·	713		
Rb <sub>3</sub> C <sub>60</sub>	<i>Fm</i> $\bar{3}m$	14.425	10.20	3.33	750	1.0 ± 0.3	2.0 ± 0.5 <sup>a</sup> 15 ± 3 <sup>b</sup>
Rb <sub>4</sub> C <sub>60</sub>	<i>I4/mmm</i>	$a=11.96$ $c=11.04$	10.10	3.13	789	1 ± 1	10 ± 2
Rb <sub>6</sub> C <sub>60</sub>	<i>Im</i> $\bar{3}$	11.54	9.99	3.42	768	0.7 ± 0.2	1.1 ± 0.2
K <sub>3</sub> C <sub>60</sub>	<i>Fm</i> $\bar{3}m$	14.24	10.06	3.27	722	1.2 ± 0.5	6.5 ± 2 <sup>a</sup> 16 ± 6 <sup>b</sup>

<sup>a</sup>Tetrahedral site.<sup>b</sup>Octahedral site, A = Rb or K.

measured on  $\text{Al}_2\text{O}_3$  standards, was  $0.04^\circ$  full width at half maximum. We used a standard Rietveld profile analysis with an anomalous dispersion correction for the Rb of  $f' = -5.0$  electrons.

Figure 1(a) shows the profile of  $\text{Rb}_6\text{C}_{60}$ . The diffraction peak widths are  $0.1^\circ$ , corresponding to a crystal-line coherence length of at least  $250 \text{ \AA}$ . All of the lines can be indexed to a bcc structure, with lattice constant  $11.54 \pm 0.01 \text{ \AA}$ . This is clearly isostructural with  $\text{K}_6\text{C}_{60}$  and  $\text{Cs}_6\text{C}_{60}$ , described by Zhou *et al.*<sup>9</sup> The best fit ( $R_I = 6.1\%$  and  $R_{wp} = 8.3\%$ ) has bond lengths ranging from  $1.42$  to  $1.54 \text{ \AA}$ , but the quality of fit degrades only marginally if the bond lengths are constrained to the average values  $1.37 \text{ \AA}$  and  $1.45 \text{ \AA}$ , determined in more accurate single-crystal determinations of fullerenes and derivatives.<sup>11</sup> Therefore we do not regard the variation from our fits as significant, and believe that the  $1.37 \text{ \AA}$  and  $1.45 \text{ \AA}$  values are probably more correct. In this structure (space group  $\text{Im}\bar{3}$ ), all of the fullerenes have the same orientation. The Rb atoms are located at fractional unit-cell po-

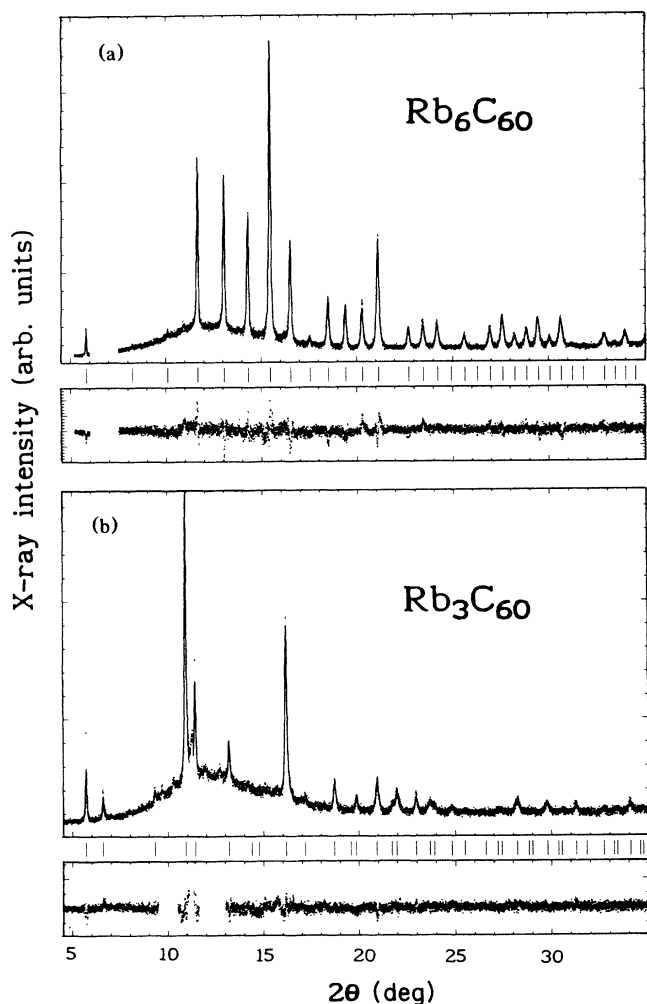


FIG. 1. Rietveld fits to powder x-ray-diffraction profiles of (a)  $\text{Rb}_6\text{C}_{60}$  and (b)  $\text{Rb}_3\text{C}_{60}$  phases. In  $\text{Rb}_3\text{C}_{60}$ , regions not shown in difference plot were excluded due to weak contaminant phases.

sitions  $(0.5, 0.282, 0)$ , nearly identical to those found for the K and Cs analogs by Zhou *et al.*<sup>9</sup>

Except for the  $x=6$  specimen, all of our  $\text{Rb}_x\text{C}_{60}$  samples consist of mixtures of two or more phases, complicating the analysis of the data. Nevertheless, measuring and comparing the spectra of eight samples (of nominal composition from  $x=1.5$  to  $3$ ) allowed us to assign sets of diffraction peaks to separate phases. Therefore we were able to perform Rietveld refinement for selected phases by excluding regions of peaks from competing phases. In the spectra of Figs. 1 and 2 these regions are indicated by gaps in the difference panel. We emphasize that any peak so removed was found more prominently in other spectra.

Figure 1(b) shows the spectrum for a sample of nominal composition  $\text{Rb}_3\text{C}_{60}$ . The sample, obtained in a two-stage doping process from  $\text{Rb}_{2.5}\text{C}_{60}$ , as described in Ref. 7, has a superconducting diamagnetic fraction of 45% at 4.2 K; a relatively high value for a loose powder sample.<sup>7</sup> Nearly all of the visible peaks are those of an fcc phase, isostructural to the  $\text{K}_3\text{C}_{60}$  phase described earlier;<sup>6</sup> impurity phases represent less than 5% of the material. The peak widths are similar to those measured for  $\text{Rb}_6\text{C}_{60}$ . Satisfactory fits are obtained with all C-C bonds equal to  $1.43 \text{ \AA}$ . The quality of the fit improves slightly if the carbon positions are unconstrained, leading to bond lengths from  $1.38$  to  $1.51 \text{ \AA}$ . Rb ions occupy both octahedral  $(\frac{1}{2}, 0, 0)$  and tetrahedral  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  interstitials in the fcc lattice. As in  $\text{K}_3\text{C}_{60}$ , the tetrahedrally coordinated Rb atoms nest into the hexagonal faces of the fullerenes, apparently impeding their rotation; the octahedral Rb has a very large Debye-Waller factor. Likewise, similar to  $\text{K}_3\text{C}_{60}$ ,<sup>6</sup> we find that the fullerenes are randomly distributed between the two orientations consistent with hexagonal faces pointing in the  $(111)$  directions, i.e., space group  $\text{Fm}\bar{3}m$  is preferred over  $\text{Fm}\bar{3}$ .

The highest superconducting fractions were reported<sup>7</sup> for compounds with nominal compositions slightly off the ideal  $\text{Rb}:\text{C}_{60} = 3:1$  ratio, and, therefore, it is clearly important to determine if the compound truly has stoichiometric composition. The Rietveld refined site occupancies are  $100\% \pm 20\%$ . An even stronger argument for a stoichiometric composition for this phase comes from measurements of the lattice constant. We observe that the position of the  $(311)$  peak from this phase varies by no more than  $0.01^\circ$  ( $0.1\%$ ) in all of the samples studied for Rb concentrations  $x=1.5$ – $3.0$ , despite the widely differing amounts of coexisting impurity phases. In comparison, the lattice expands by  $1.7\%$  from  $\text{C}_{60}$  to  $\text{Rb}_3\text{C}_{60}$ . It is also worth pointing out that if the material had a non-stoichiometric composition, one would expect the superconducting transition temperature  $T_c$  to depend on sample preparation history, contrary to observation.<sup>7</sup> Based on all of these arguments, we conclude that the  $\text{Rb}_3\text{C}_{60}$  phase is stoichiometric.

The remaining  $\text{Rb}_x\text{C}_{60}$  phases are detected only as minority phases coexisting with the fcc  $\text{Rb}_3\text{C}_{60}$  material. Figure 2(b) shows the spectrum of a sample of nominal composition  $\text{Rb}_{2.8}\text{C}_{60}$ . The comparison to the spectrum of  $\text{Rb}_3\text{C}_{60}$  [replotted in Fig. 2(a)] reveals relatively strong lines at  $7.94^\circ$ ,  $10.30^\circ$ ,  $11.25^\circ$ , and  $12.70^\circ$ ; the linewidths are  $0.12^\circ$ , slightly wider than  $\text{Rb}_3\text{C}_{60}$  and  $\text{Rb}_6\text{C}_{60}$ . These

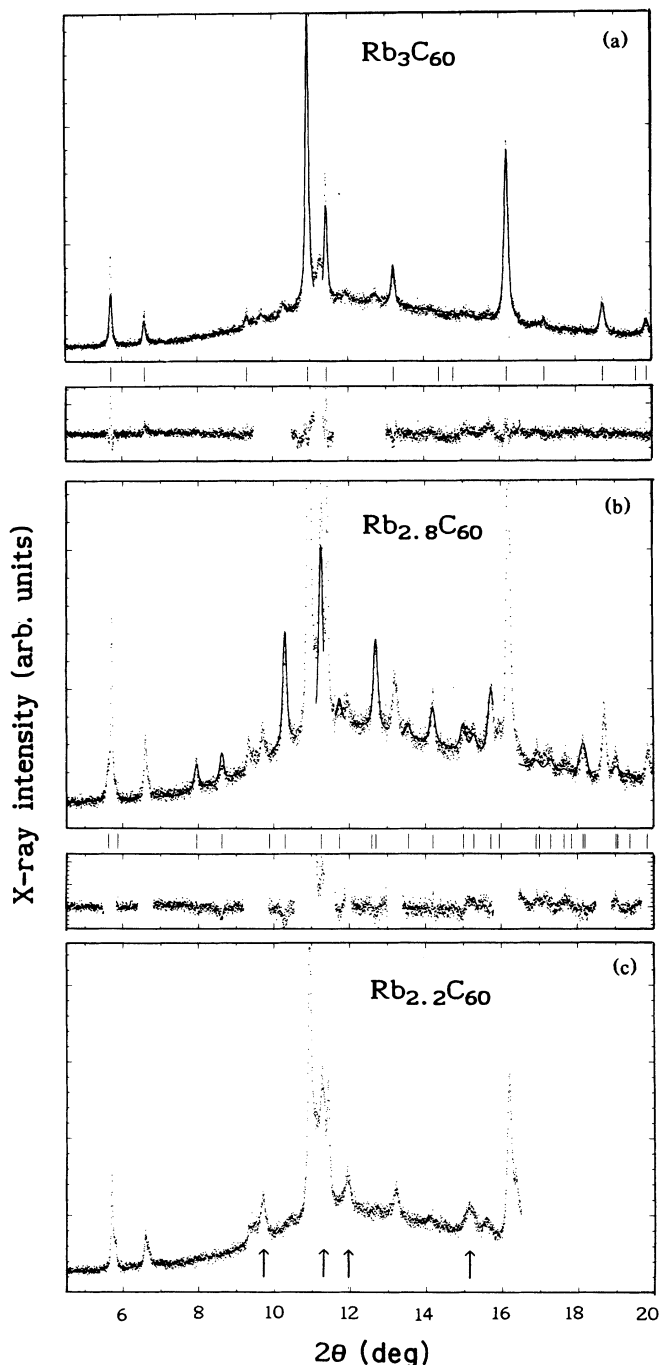


FIG. 2. Powder x-ray-diffraction profiles of samples of composition (a) Rb<sub>3</sub>C<sub>60</sub>, (b) Rb<sub>2.8</sub>C<sub>60</sub>, and (c) Rb<sub>2.2</sub>C<sub>60</sub>. (b) A Rietveld fit to the tetragonal Rb<sub>4</sub>C<sub>60</sub> phase (fcc Rb<sub>3</sub>C<sub>60</sub> peaks excluded). (c) The four diffraction peaks assigned to the unknown, Rb-deficient phase.

lines are also visible in other samples and their strengths scale together from sample to sample. We are able to index these, and several other weaker peaks, with a body-centered tetragonal lattice<sup>10</sup> with lattice constants  $a=b=11.96$  Å,  $c=11.04$  Å. The lattice constants suggest a distorted bcc structure. Trying several possible locations for Rb atoms leads to the best agreement with the x-ray-

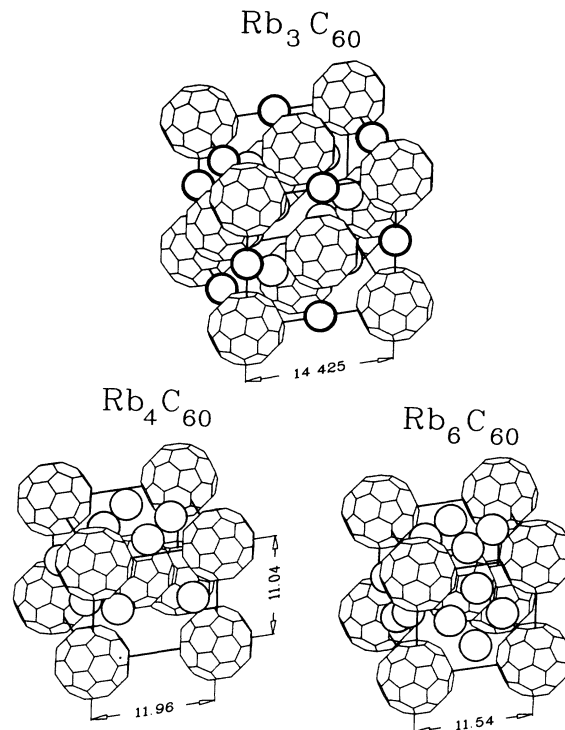


FIG. 3. Schematic view of three Rb:C<sub>60</sub> structures. Rb atoms at the octahedral sites of Rb<sub>3</sub>C<sub>60</sub> are indicated by double circles.

diffraction spectrum if they are at  $(0.23, 0.5, 0)$  in the space group  $I4/mmm$ , as illustrated in Fig. 3. We find that the Rb occupancy is close to 100%, leading to a nominal composition of Rb<sub>4</sub>C<sub>60</sub> for this phase. Based on the nominal composition of Rb<sub>2.8</sub>C<sub>60</sub>, one expects the presence of some Rb deficient material in this sample, but it is apparently not in the form of pure C<sub>60</sub>, since its sharp diffraction peaks would show up in the spectra.

In the diffraction spectrum of Rb<sub>4</sub>C<sub>60</sub> there are enough regions overshadowed by the Rb<sub>3</sub>C<sub>60</sub> phase that we are not able to determine C-C bond lengths. Consequently, for the purpose of the refinement, we have put in the values determined in other phases. It is likewise difficult to come to any specific conclusions about the orientation of the C<sub>60</sub> molecules from this spectrum. However, we can afford to speculate based on the geometrical environment of the fullerene molecules. Each C<sub>60</sub> is surrounded by eight Rb in the  $a$ - $b$  plane, at a distance of 6.58 Å from the center, and eight Rb in the  $a$ - $c$  and  $b$ - $c$  planes, at a distance of 6.39 Å. For freely rotating C<sub>60</sub> of radius 3.57 Å, the nearest Rb-C distance would be 2.82 Å, which is impossibly short. On the other hand, even if rigid C<sub>60</sub> are oriented as they are in the two cubic (bcc and fcc) phases, the Rb-C distances range from a comfortable 3.13 to 3.78 Å. The icosahedral C<sub>60</sub> do not have the fourfold axes required in space group  $I4/mmm$ , and so we infer that they must be orientationally disordered between two states, as we previously showed for K<sub>3</sub>C<sub>60</sub>.<sup>6</sup> This structure may be derived from the bcc Rb<sub>6</sub>C<sub>60</sub> structure by removing two of the cations on the vertical faces. This distorts the lattice, and moves the remaining cations relative to the C<sub>60</sub>.

There are several weak peaks in Fig. 2(b) which do not index to either the fcc  $\text{Rb}_3\text{C}_{60}$  or the tetragonal  $\text{Rb}_4\text{C}_{60}$  structures, notably at  $9.70^\circ$  and  $11.93^\circ$ . We believe that they come from yet another phase. For some samples, like the  $\text{Rb}_{2.2}\text{C}_{60}$  shown in Fig. 2(c), these lines are clearly stronger than the  $\text{Rb}_4\text{C}_{60}$  peaks. Aside from the fact that it is Rb deficient, we cannot identify this phase. Note that it also has strong peaks at  $11.26^\circ$  and  $15^\circ$ , which may help explain the discrepancies seen in Fig. 2(b) at these angles, and that the peaks are somewhat broader.

In conclusion, we found at least five phases, four of stoichiometric composition  $x=0,3,4,6$  in the  $\text{Rb}:\text{C}_{60}$  system. The samples in this study were made in a slow diffusion process, over a time of about six weeks. As a result of this, the superconducting phase transition is always sharp, at  $T_c=29.6\text{ K}$ .<sup>7</sup> The x-ray-diffraction peaks belonging to the superconducting phase  $\text{Rb}_3\text{C}_{60}$  are relatively narrow, indicating good crystalline coherence. The other, minority phases, are the natural coproducts of the staged diffusion process described in Ref. 7. This is supported by the observation that the corresponding x-ray peaks are broader. In view of the fact that the strongest  $\text{Rb}_4\text{C}_{60}$  peaks are seen in a sample of composition

$\text{Rb}_{2.8}\text{C}_{60}$ , it is evident that some of these samples have not yet reached equilibrium.

The refinement of the  $\text{Rb}_3\text{C}_{60}$  structure shows that the distance between the  $\text{C}_{60}$  molecules is about 1.3% larger than in  $\text{K}_3\text{C}_{60}$ . A growing body of evidence, including the pressure dependence of the critical temperature,<sup>5</sup> points to the correlation between the superconducting  $T_c$  and the  $\text{C}_{60}$ - $\text{C}_{60}$  distance.

After this work was completed we learned of a study with similar overall results.<sup>12</sup>

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