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Unusual thermal stability of a site-ordered MC_{60} rocksalt structure ($M = K, Rb, \text{ or } Cs$)

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X-ray diffraction and differential scanning calorimetry of M_xC_{60} , with $x \sim 1$ and $M = K, Rb, \text{ or } Cs$, reveal an unusual T -dependent phase sequence. A low-symmetry ground state is found, while the high- T limit is an ordered rocksalt structure in which only the octahedral sites are occupied. The unusual high- T stability of this ordered phase is attributed to the entropy of molecular orientational disorder and/or thermal disorder of the alkali-metal ions within the octahedral sites. Unique to K_xC_{60} with $x \geq 1.4$, we find at intermediate temperatures an fcc site-disordered lattice gas phase with random occupancy of tetrahedral and octahedral sites, which is thus isostructural with superconducting K_3C_{60} .

Alkali-metal-intercalated C_{60} has been widely studied.¹ For K, Rb, and Cs, x-ray refinements at 300 K reveal three stoichiometric compounds: face-centered cubic M_3C_{60} (with the exception of Cs), body-centered tetragonal M_4C_{60} , and body-centered cubic M_6C_{60} .²⁻⁴ Non-stoichiometric Rb_xC_{60} samples showed the existence of a dilute fcc phase with $0 < x \leq 1$, as well as the possibility of finite Rb vacancy concentration in the bcc phase at high temperature.⁵ The fcc lattice of C_{60} contains one octahedral site per molecule, roughly twice the size of the two tetrahedral sites. Thus for $x < 3$ one might expect to find ordered ground-state structures with selective site occupancy. Two recent studies suggest that such phases indeed exist, subject to proper matching of ionic radii within the different site volumes. RbC_{60} and CsC_{60} , with one Rb or Cs per octahedral site, have been identified by core-level spectroscopy,⁶ and Na_2C_{60} with one Na in each tetrahedral site has been identified by x-ray diffraction.⁷ These structures might be expected to transform to high- T lattice gas phases with random occupancy of both sites, driven by the mixing entropy of filled and empty sites, by analogy to restaging transitions in dilute layer intercalates.⁸

Other results reveal potential complications. First, the octahedral site can accommodate multiple small ions, the apparent limit being a Na_9 cluster.⁹ Second, Na_3C_{60} , with a single small ion in the large octahedral site, undergoes a distortion from fcc at 300 K to a low- T lattice of lower symmetry (which evidently destroys the expected superconductivity). Similar distortions have not been observed in the heavy alkali-metal M_3C_{60} superconductors, nor in Na_6C_{60} (Ref. 7) nor $Na_{11}C_{60}$,⁹ although the M_3C_{60} x-ray refinements yield an unphysically large thermal factor for the octahedral ion.² The implication is that addi-

tional factors might come into play in determining phase stability when the mismatch between ion and site volumes exceeds some critical value.^{7,10}

In this paper we present T -dependent x-ray diffraction and differential scanning calorimetry (DSC) results for K-, Rb-, and Cs-intercalated C_{60} , with emphasis on the concentration range $x \sim 1$. These show that the site-ordered rocksalt phase of MC_{60} is stable at high rather than low T , whereas the low- T ground state exhibits a small distortion from cubic symmetry. A third distinct structure is observed at intermediate T but only for $M = K$ and $x \geq 1.4$. This is another fcc phase, but with random tetrahedral and octahedral occupancy. A preliminary report of the x-ray results for RbC_{60} was given previously.¹¹

Samples were prepared by the McCauley *et al.* method.¹² Final annealing was carried out for two weeks at 773–823 K to ensure equilibrium. X-ray powder diffraction was performed at the X10B and X7B beamlines at the Brookhaven National Synchrotron Light Source ($300 < T < 473$ K) and in-house using an INEL diffractometer equipped with a linear detector ($240 < T < 723$ K). DSC traces from 10-mg samples of $K_{1.4}C_{60}$, $Rb_{1.3}C_{60}$, and CsC_{60} hermetically sealed in Al pans are shown in Fig. 1. All three samples exhibit broad endothermic peaks on heating, with onset temperatures close to 333 K. $K_{1.4}C_{60}$ exhibits a second distinct peak with onset at 423 K. The individual heats of transition are ~ 2.4 and 9.4 J/g for $K_{1.4}C_{60}$, comparable to the total heats of ~ 12 J/g for $Rb_{1.3}C_{60}$ and ~ 15 J/g for CsC_{60} . Heating up to 873 K showed no additional transitions. A sample of KC_{60} exhibited a DSC trace very similar to that of $K_{1.4}C_{60}$; in both cases the upper endotherm coincides with the onset of motional narrowing of the ^{13}C

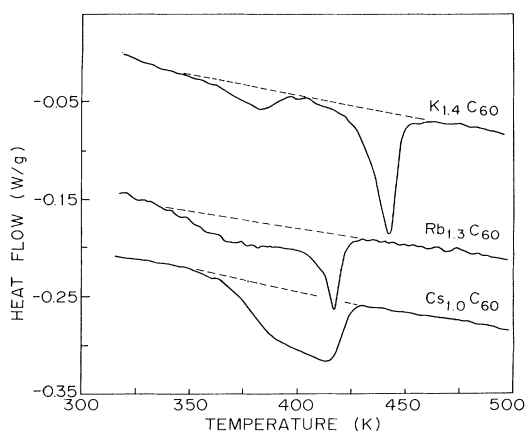


FIG. 1. Differential scanning calorimetry of the indicated compounds. Heating rate $10^{\circ}\text{C}/\text{min}$.

NMR line.¹³ Similar scans of phase-pure K_3C_{60} and Rb_3C_{60} gave flat baselines.

Figure 2 shows x-ray profiles of $K_{1.4}C_{60}$ (dots) and Rietveld refinements (solid curves, discussed below) taken at 300, 393 (just between the two DSC peaks), and 473 K (above the second peak). The dominant phases in both high- T profiles index well as fcc but the relative intensities are systematically different, indicating two distinct phases. As shown below, these phases differ in that only

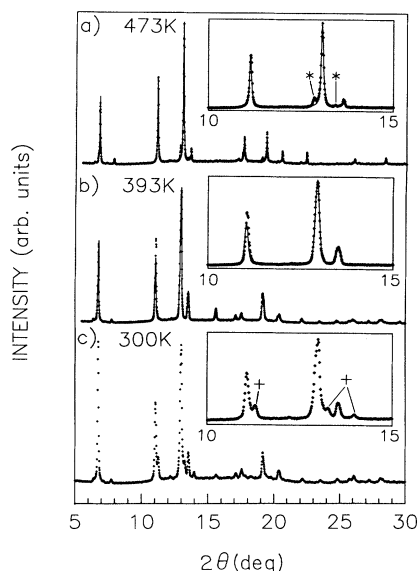


FIG. 2. Synchrotron x-ray powder diffraction profiles of $K_{1.4}C_{60}$ at the indicated temperatures ($\lambda = 0.9698 \text{ \AA}$). Dots are experimental data and solid curves are Rietveld refinements described in the text. (a) 473 K: majority-phase fcc with only octahedral sites occupied, $a = 14.07 \text{ \AA}$, plus minority-phase fcc K_3C_{60} reflections denoted by (*); (b) 393 K: pure-phase fcc with random occupancy of tetrahedral and octahedral sites, a expanded to 14.27 \AA ; (c) 300 K: dominated by the intermediate phase (b), plus weak and broad peaks which may be approximately indexed as rhombohedral (+). No reflections from K_3C_{60} are evident.

octahedral sites are occupied at high T , whereas both octahedral and tetrahedral sites are randomly occupied in the intermediate fcc phase. Since there is only one octahedral site per C_{60} , it is not surprising that for $K_{1.4}C_{60}$, weak reflections which are clearly identifiable as K_3C_{60} from their positions and relative intensities [denoted by (*) in Fig. 2(a)] are observed. These are first visible at 433 K, the temperature of the second DSC onset. A profile taken at 723 K shows the same phase mixture. In contrast, no second phases are detectable in the 393-K profile, Fig. 2(b), since now all three sites are available. $K_{1.4}C_{60}$ thus evolves from a nonstoichiometric single-phase region below 433 K to a mixture of $x = 1$ and ≈ 3 above 433 K, while KC_{60} shows two-phase behavior below the transition and an essentially single-phase rocksalt profile above it. We conclude that the intermediate structure has a stability range which extends at least up to $x = 1.4$ but not as low as $x = 1$, while the high- T octahedral site-ordered phase is restricted to $x \leq 1$.

NMR suggests that the onset of quasifree rotations is implicated in the transition to the high- T site-ordered phase.¹³ In pure C_{60} , orientational melting is accompanied by a 0.3% lattice dilation.¹⁴ This is apparently overwhelmed in KC_{60} by electrostatic effects since the lattice constant of the high- T rocksalt component is significantly smaller than that of the intermediate phase in the $K_{1.4}C_{60}$ sample. With tetrahedral sites vacant at high T , the octahedral site contracts by $\sim 2\%$ relative to C_{60} at the same T .

The 300-K profile of $K_{1.4}C_{60}$, Fig. 2(c), shows sharp reflections from the intermediate fcc phase as well as broader peaks which can be approximately indexed as rhombohedral with $\sim 2^{\circ}$ distortion from cubic symmetry. Many rhombohedral peaks coincide with fcc reflections; two of the uniquely rhombohedral positions are labeled by (+) in the inset to Fig. 2(c). Since the rhombohedral reflections are considerably broader than the fcc ones, and due to the overlapping of peaks from the two phases, the peak intensity of the sharp reflections gives an incorrect impression of the relative amounts of the two phases. A similar phase mixture was observed at 260 K, suggesting that the boundary between rhombohedral and intermediate fcc phases lies below 260 K, or that the latter is quenched in from higher T . There is no evidence of K_3C_{60} reflections.

Figures 3 and 4 show similar results for $Rb_{0.9}C_{60}$ and CsC_{60} , respectively. Both 473-K profiles, Figs. 3(a) and 4(a), show only reflections from the site-ordered rocksalt phase, again consistent with a limiting $x = 1$ composition for this phase. For these samples, and for $Rb_{1.3}C_{60}$, profiles taken at 10–20-K increments did not reveal an intermediate phase analogous to Fig. 2(b) for $K_{1.4}C_{60}$. We did not observe $x = 3$ reflections at any T for several Rb-doped samples with various x values < 1 , another indication that RbC_{60} exists as a distinct phase. Figure 3(b) shows an example for $x = 0.9$ at 300 K. On the other hand, profiles of $Rb_{1.3}C_{60}$ exhibit mixtures of $x = 1$ and 3 at both high and low T , the $x = 3$ peaks being much sharper than the rhombohedral ones at 300 K, Fig. 3(c). The 300-K profiles of $Rb_{0.9}C_{60}$, $Rb_{1.3}C_{60}$, and CsC_{60} [the latter shown in Fig. 4(b)] are dominated by rhombohedral

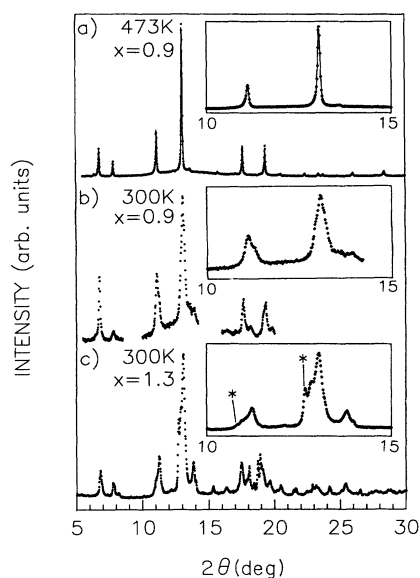


FIG. 3. X-ray profiles of Rb-intercalated C_{60} . (a) $Rb_{0.9}C_{60}$ at 473 K; pure-phase fcc, octahedral occupancy only, $a=14.08$ Å; (b) $Rb_{0.9}C_{60}$ at 300 K: rhombohedral, no Rb_3C_{60} ; (c) $Rb_{1.3}C_{60}$ at 300 K: rhombohedral plus fcc Rb_3C_{60} (*).

reflections, but they all show evidence for small fractions of quenched high- T phase.

These data suggest a common, well-ordered high- T structure for all the heavy alkali metals MC_{60} (coherence length ~ 1500 Å, excellent fcc indexing with $R \leq 0.001$). Rietveld refinements of all three high- T profiles converged on perfect rocksalt ordering (ions in ideal octahedral sites, tetrahedral sites vacant) and orientationally disordered C_{60} 's (consistent with NMR). Weighted intensity R factors were 12% for $K_{1.4}C_{60}$, 7% for $Rb_{0.9}C_{60}$, and 12% for CsC_{60} . The large value for $K_{1.4}C_{60}$ is no doubt due to the presence of weak K_3C_{60} reflections. These fits are shown as the solid curves in Figs. 2(a), 3(a), and 4(a), respectively. Models with partially or fully ordered C_{60} 's gave poorer fits and unphysically large carbon Debye-Waller factors. Constraining M to the high-symmetry octahedral site (1/2, 1/2, 1/2) resulted in a large isotropic thermal factor, $B \sim 12$, as observed in refinements of M_3C_{60} at 300 K.² Equally good fits were obtained by allowing small M displacements along the eight equivalent (111) directions with the constraint $B = 2$ and assuming equal occupation of the eight inequivalent positions within the octahedral site. This model is reminiscent of the $Na_{11}C_{60}$ structure,⁹ and would imply that the alkali ions exhibit small-amplitude jumps within the octahedral volume. Refined 473-K lattice constants are 14.07, 14.08, and 14.12 Å for the $x \approx 1$ component of $K_{1.4}C_{60}$, $Rb_{0.9}C_{60}$, and CsC_{60} , respectively. These are all substantially smaller than $a = 14.23$ Å of pristine C_{60} at 473 K. Optimized occupancy factors yield compositions in the range $0.85 < x < 0.96$. Similar refinements of $Rb_{0.3}C_{60}$ and $Rb_{0.7}C_{60}$ show continuous filling of only the octahedral sites at $T > 343$ K, consistent with solid solution behavior in the range $0 < x < 1$ in the high- T limit.

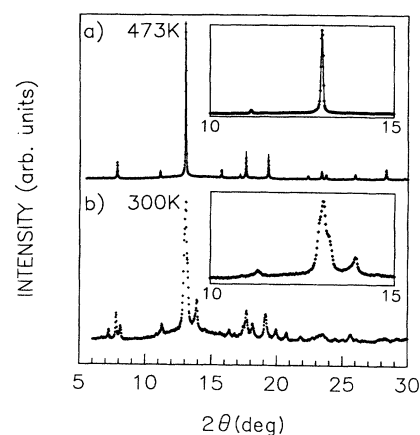


FIG. 4. X-ray profiles of CsC_{60} . (a) 473 K: pure-phase fcc, octahedral occupancy only, $a=14.13$ Å; (b) 300 K: nearly pure-phase rhombohedral.

Intermediate phases distinct from the high- T rocksalt structure were searched for by taking profiles at 10–20-K increments in the range 323–463 K. $K_{1.4}C_{60}$ alone gave evidence for such a phase in the range $353 < T < 423$ K. Figure 2(b) shows a 393-K profile which is single-phase fcc in contrast to the 473-K profile, Fig. 2(a). The coherence length is only ~ 500 Å. Rietveld refinement ($R = 14\%$) gives $a = 14.27$ Å, comparable to that of K_3C_{60} at 300 K, with random occupancy of both octahedral and tetrahedral sites (essentially equal occupation factors) and a refined composition $x = 1.6$. Since no K_3C_{60} was detected, we identify this intermediate phase with solid solution behavior for $x > 1.4$ and $T < 433$ K.

The progression of $K_{1.4}C_{60}$ from a site-disordered lattice gas to a site-ordered structure with increasing T is counterintuitive in the context of Ising-like stage-ordering transitions in other intercalation families.^{8,15} Furthermore, the lattice constant contracts from 14.27 to 14.07 Å upon heating through the transition at ~ 433 K. We attribute this “inverse Ising” behavior to the entropy provided by the C_{60} orientational disorder¹³ and/or the random distribution of K among symmetry-equivalent positions within the octahedral site. The lattice contraction implies a reduction in the octahedral volume at high T , which in turn implies a qualitative change in the C_{60} and/or M dynamics at ~ 433 K.

The intermediate- T structure of $K_{1.4}C_{60}$ can be viewed as that of K_3C_{60} with random vacancies. The fact that similar phases are not observed with Rb or Cs is most likely an ionic size effect; large-amplitude thermal displacements of tetrahedral Rb or Cs would impose large dilations of the octahedral site if cubic symmetry were to be maintained, evidently resulting in an octahedral volume which is too large even for thermally disordered Rb or Cs. This constraint is removed in the high- T $x \leq 1$ rocksalt phases; with the tetrahedral sites empty, the octahedral volume is free to contract and adapt itself to the effective diameter of the thermally disordered ions. Following the same argument, M_3C_{60} is also marginally stable as a cubic ionic compound, as reflected by the very

large Debye-Waller factor of the octahedral ions;² the large size difference between octahedral and tetrahedral sites could in fact be partially alleviated by a symmetry-lowering distortion. Results on the Na_xC_{60} family clearly show that the thermal stability of doped fcc structures may also be enhanced by increasing the octahedral site occupancy.^{7,9} This is most likely the result of a concentration-dependent "chemical pressure" balance between octahedral and tetrahedral ions, similar to the proposed explanation for the nonexistence of fcc Cs_3C_{60} .¹⁰

It is now evident from a number of experiments that MC_{60} represents an additional definite compound in the family of intercalated fullerenes. Our x-ray results are consistent with x-ray photoelectron spectroscopy¹⁶ (XPS) in showing the unusual selective occupancy of octahedral sites at high T , but can be reconciled with 300-K XPS, Raman scattering,¹⁷ and NMR (Ref. 18) only by invoking the presence of nanocrystalline K_3C_{60} which escapes x-ray detection. Band-structure calculations indicate that

rocksalt MC_{60} is metallic independent of M ,¹⁹ similar to fcc M_3C_{60} (Refs. 6 and 16) and Raman spectra¹⁷ clearly show that the C_{60} 's carry a net negative charge. NMR results suggest that the lattice-gas phase *might* be metallic.¹³ For Cs_xC_{60} , the temperature-independent part of the total susceptibility peaks near $x = 1$ implying metallic behavior, although it is not clear which of the $x = 1$ phases are present.²⁰ Further work is needed to fully elucidate the interplay between chemical pressure effects, molecular orientational order, and alkali site order.

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