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Orientational Phase Transition in Na_xC_{60} ($1 < x < 3$)

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X-ray diffraction and calorimetry data on cubic Na_xC_{60} ($1 < x < 3$) reveal orientational ordering transitions at T_m above that of pure C_{60} , e.g., $T_m(x = 1.3) = 325$ K. The ordered phases are the same as in pure C_{60} : simple cubic, space group $Pa\bar{3}$, but the orientations in the disordered phase are more restricted. We explain how Na stabilizes the ordered phase to rather high T , while K and Rb do not, in terms of Coulomb interactions between C_{60} molecules and Na ions which we calculate from the local density approximation charge density of C_{60} .

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Undoped solid C_{60} transforms at $T_m = 260$ K from an orientationally disordered (space group $Fm\bar{3}m$) to an ordered phase ($Pa\bar{3}$) [1–5]. Analogous ordered structures are not observed in the alkali-intercalated $M_3\text{C}_{60}$ superconductors ($M = \text{K}, \text{Rb}$) due to strong short-range repulsive interactions between tetrahedral ions and C_{60} molecules [6]. This effect should be much weaker for smaller ions such as Na, suggesting unique and interesting ordering phenomena in Na-intercalated C_{60} , which are the subject of this Letter.

Two unique features of Na_xC_{60} are already apparent. First, Na_3C_{60} does not superconduct, despite the fact that its 300 K fcc lattice constant implies a $T_c > 10$ K [7,8]. Second, the small ionic radius permits intercalation of clusters of up to 8–9 Na ions into the octahedral sites [7,9], yielding compounds with x up to ~ 10 –11 which preserve the fcc structure of the host lattice. In the present work, we find that for $0 < x < 1$ the system phase separates into essentially pure C_{60} and NaC_{60} at 300 K, while for $1 < x < 3$ we find solid solution behavior. At 300 K, all compounds with $1 < x < 3$ are simple cubic, implying orientational order. Differential scanning calorimetry (DSC) shows first order phase transitions as in undoped C_{60} , but with higher T_m and lower enthalpy changes ΔH . Both T_m and ΔH are maximum at $x = 1$, 329 K and ~ 5 J/g, respectively, as compared to 260 K and ~ 9 J/g for pure C_{60} . As x approaches 3, both T_m and ΔH decrease; for $x = 2.8$ we do not observe any transition at all. The phase diagram study is reported in detail elsewhere [10]; here we focus on the nature of the ordered and disordered states by presenting x-ray and DSC data from a sample with $x = 1.3$ and interpreting it in terms of Coulomb interactions between C_{60} and Na ions calculated from first principles.

The $x = 1.3$ sample was prepared by diluting Na_9C_{60}

with C_{60} . The estimated error in x is about 0.1. Details have been presented elsewhere [9]. DSC measurements showed no sign of unreacted C_{60} , and a transition at 325 K with $\Delta H \approx 4$ J/g, as compared to 260 K and 8.8 J/g for the starting C_{60} . Powder diffraction was carried out on samples loaded into evacuated quartz capillaries at the National Synchrotron Light Source beamline X3B1 [wavelength 1.15 Å, flat Si(111) monochromator and Ge(111) analyzer]. The 300 K profile shown in Fig. 1 can be indexed on a simple cubic lattice with $a = 14.184$ Å. The final refinement will be discussed later.

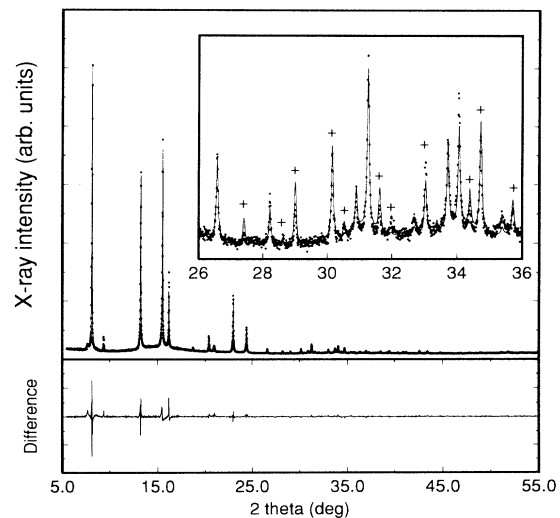


FIG. 1. X-ray powder diffraction pattern (dots) of $\text{Na}_{1.3}\text{C}_{60}$ at 300 K, a Rietveld profile refinement in space group $Pa\bar{3}$ (solid curve), and a difference plot (bottom). All simple cubic peaks are denoted by (+) in the inset.

First we enumerate all possible space groups subject to the condition that there are four inequivalent molecules per conventional cubic cell, as required by the indexing. If we assume inversion symmetry, there are only three possibilities [11], $Pm\bar{3}$ (T_h^1 , No. 200), $Pn\bar{3}$ (T_h^2 , No. 201), and $Pa\bar{3}$ (T_h^3 , No. 205) [12]. In $Pm\bar{3}$ the C_{60} orientations are fixed by symmetry, so that there are two types of octahedral sites, one at $(1/2, 1/2, 1/2)$ and the others at $(1/2, 0, 0)$. The space groups $Pn\bar{3}$ and $Pa\bar{3}$ allow rotations of the four molecules per cube through the same arbitrary setting angle ϕ but about different [111] axes [11], and there is only one type of octahedral site. For $Pa\bar{3}$ there is one type of tetrahedral site, whereas $Pn\bar{3}$ has two types of tetrahedral sites. (Strictly speaking, these sites do not actually have tetrahedral and octahedral symmetry any longer, due to the C_{60} orientations.) For the intercalated phases, three additional space groups are compatible with different fractional occupancies of the two tetrahedral sites per molecule which breaks inversion symmetry. These are $P2_13$ (T^4 , No. 198) and two choices of $P23$ (T^1 , No. 195). $P2_13$ is like $Pa\bar{3}$ but lacks inversion symmetry. The two choices of $P23$ are similar to $Pm\bar{3}$ and $Pn\bar{3}$ but without inversion symmetry.

Rietveld refinements were performed to test all these possibilities. Models lacking inversion all gave worse R factors than those with inversion, so we eliminate $P2_13$ and $P23$. The R factor obtained with $Pm\bar{3}$ is about 2% worse than obtained with $Pa\bar{3}$ or $Pn\bar{3}$. We examined the latter two with many different setting angles and found that $Pn\bar{3}$ predicts a few strong peaks which are not observed while $Pa\bar{3}$ does not (similar to pure C_{60} [11]). Furthermore, we observe the (610) simple cubic peak which is forbidden by $Pn\bar{3}$ symmetry. Hence we will restrict our attention to the space group $Pa\bar{3}$.

In Fig. 2 we show the variation of the weighted R factor with setting angle ϕ in $Pa\bar{3}$. For reference, $\phi = 0$ and $\phi = 2\phi_0 = 44.48^\circ$, where $\cos \phi_0 = (3\sqrt{2} + \sqrt{10})/8$, corre-

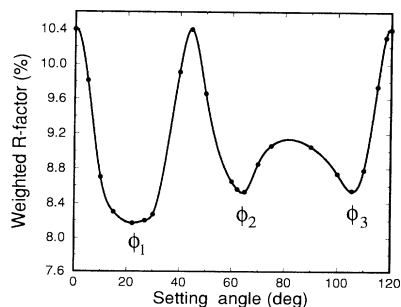


FIG. 2. Weighted R factor as a function of setting angle of the $Pa\bar{3}$ structure for $Na_{1.3}C_{60}$ at 300 K. The dots show the actual points and the solid line is a cubic spline. The global minimum is at $\phi_1 \approx 22^\circ$ and the two local minima are at $\phi_2 \approx 65^\circ$ and $\phi_3 \approx 105^\circ$. The refinement shown in Fig. 1 optimizes the fractional occupancies of the setting angles ϕ_1 , ϕ_2 , and ϕ_3 (see text).

spond to the two standard orientations in merohedrally disordered M_3C_{60} [13]. If all molecules adopted either of these setting angles, the symmetry would be $Fm\bar{3}$ which does not reproduce the observed simple cubic reflections and therefore these angles give the worst R factors. The global minimum occurs near 22° , as in pure C_{60} [2,14,15], indicating the importance of C_{60} - C_{60} interactions in Na-intercalated compounds. In addition, we find two local minima at 65° and 105° , in contrast to pure C_{60} which exhibits only one local minimum at 82° . Our final refinement (solid curve in Fig. 1) allows probabilities p for occupying the global minimum and $(1-p)/2$ for each of the two local minima. Optimizing p reduces the R factor from 8.2% with $p = 1$ to 7.6% with $p = 0.62$ at 300 K, a highly significant improvement at this level [16]. The tetrahedral sites are generated from the site (y, y, y) , and y refines to $= 0.25$, the value required by $Fm\bar{3}m$ symmetry in the disordered phase. The tetrahedral and octahedral occupancies are 0.59 and 0.08, respectively, yielding $x = 1.26$ in excellent agreement with the nominal value $x = 1.3$. Refined (isotropic) mean thermal displacements are 0.026 and 0.1 Å for tetrahedral and octahedral Na, respectively, and 0.056 Å for carbon.

The defect orientations in the above model represent fluctuations about an ordered ground state, so this model is inappropriate to describe the system close to and above T_m when long-range orientational order is weak or nonexistent. We therefore introduce a second simple model, again based on $Pa\bar{3}$ symmetry, for which each sublattice has a molecule having the correct orientation (for that sublattice) with probability $(1 + 3\sigma)/4$, and having one of three "wrong" orientations each with probability $(1 - \sigma)/4$ [17]. Refining the 372 K data (Fig. 3) yields σ

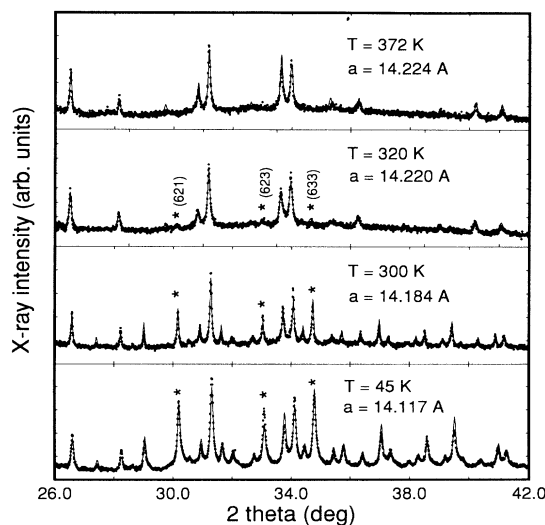


FIG. 3. High- Q region of the x-ray powder pattern of $Na_{1.3}C_{60}$ at various temperatures, as in Fig. 1. Peaks denoted by (*) are the three strongest simple cubic peaks which first appear as T is reduced through T_m .

$= 0$, signifying complete orientational disorder and corresponding to an increase in symmetry to $Fm\bar{3}m$ [17] as evidenced by the absence of simple cubic reflections. Indeed at this temperature, representing each molecule by a spherical shell gives about the same R factor. The tetrahedral and octahedral occupancies are 0.58 and 0.14, respectively, indicating that most of the Na's remain confined to tetrahedral sites. Cooling to 320 K (second panel in Fig. 3), we observe three weak simple cubic peaks, denoted by (*). Refining the order parameter σ gives the small value, $\sigma = 0.19$. The simple cubic peaks grow in intensity with decreasing T , as shown in the bottom two panels in Fig. 3. For the fits to $T = 300$ and $T = 45$ K data, we take $\sigma = 1$ and account for thermal disorder by using the previous model. The 45 K refinement shows that p increases to 0.86 from its 300 K value of 0.62, again similar to observations on pure C_{60} [4,15,16]. Within the experimental resolution, we do not observe any peak broadening or splitting at 45 K, indicating that for $x = 1.3$ a single-phase cubic structure is the ground state, in contrast to Na_3C_{60} [7].

The reason that Na stabilizes the $Pa\bar{3}$ structure while K and Rb do not can be understood as follows. Large tetrahedral ions (such as K or Rb) lock the C_{60} 's at random into one of two standard orientations [6,13]. The ionic radius of Na^+ is 0.98 Å, substantially smaller than the average tetrahedral site radius 1.16 Å, so the short-range repulsive force between Na^+ and C_{60} is smaller than for K^+ or Rb^+ , and the Na- C_{60} Coulomb interaction arising from charge transfer dominates. We calculated the Coulomb potential between a C_{60} molecule and its 8 near-neighbor tetrahedral Na^+ 's as a function of C_{60} rotation angle about one of its threefold axes, as shown in the inset to Fig. 4. For simplicity we assumed that all sites are occupied, corresponding to $x = 2$; for $x < 2$ the potential will be approximately rescaled by the fractional occupancy without changing shape. Higher-neighbor interactions may safely be neglected because the Coulomb interaction falls off as $1/r^7$ due to the icosahedral symmetry of C_{60} [18]. We assumed point charges for Na^+ and used the local density approximation charge density of C_{60} [18], neglecting in the latter the 2 transferred electrons as compared to the distribution of 240 valence electrons [19]. The result is shown in Fig. 4 [20], which quite remarkably predicts global and local minima at essentially the same angles inferred from the x-ray refinement; Fig. 2. Since the Na- C_{60} and the C_{60} - C_{60} interactions are both minimized near $\phi \approx 22^\circ$, there is almost no frustration. Thus the resulting structure is $Pa\bar{3}$ with a transition temperature increased by the Na- C_{60} interaction.

Whereas the Na- C_{60} Coulomb interactions are clearly important, we emphasize that these interactions alone cannot stabilize the $Pa\bar{3}$ structure because they do not distinguish between the four $Pa\bar{3}$ orientations corresponding to the global minima in Fig. 4. Thus, this interaction confines the orientational fluctuations predom-

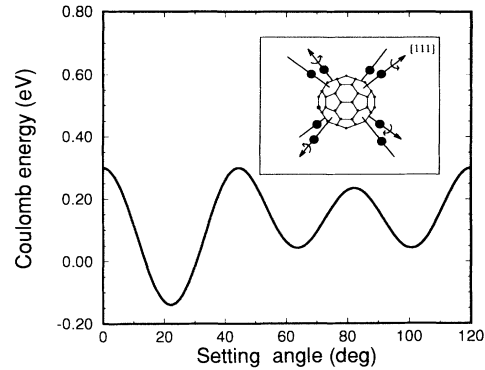


FIG. 4. The orientation-dependent part of the Coulomb potential $V(\phi)$ between a C_{60} molecule and its eight nearest-neighbor Na^+ ions as the C_{60} is rotated about a [111] axis [$V(\phi + 120^\circ) = V(\phi)$] (see inset, where Na^+ ions are represented by filled circles and the molecule is shown in the standard orientation corresponding to $\phi = 0^\circ$). The global minimum is at $\phi = \phi_0 = 22.24^\circ$. For $\phi = \phi_0$ (see Ref. [17]) there are four such distinct global minima corresponding to rotating the C_{60} molecule about any of the four possible choices of [111] directions.

inantly into the four global minima, while the C_{60} - C_{60} interaction determines which of the four minima each molecule must choose in order to form the $Pa\bar{3}$ structure. Since orientational fluctuations are confined to be among the four minima, the transition temperature goes up relative to pure C_{60} with essentially random fluctuations. This situation has an analogy in magnetic ordering. The transition temperature for a spin system described by the Hamiltonian $-\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i K S_{iz}^2$ is greater for $K \neq 0$ than for $K = 0$ because the (anisotropy) term in K reduces the fluctuations along the x and y directions even though such a term by itself cannot cause spin correlations. Our model also enables us to understand why Na intercalation reduces the enthalpy change accompanying the transition. The entropy associated with orientational fluctuations among four minima just above T_m is much less than that associated with the quasifree rotations in pure C_{60} , yielding a smaller ΔH as measured by DSC.

The results presented here are typical throughout the range $1 < x < 2$, over which a increases while T_m decreases with increasing x . This is qualitatively consistent with the behavior of T_m as a function of pressure in pure C_{60} [21]. Also, the depth of the global minima in the Coulomb potential increases with increasing x , further confining the orientational fluctuations and thus reducing the entropy and enthalpy change through the transition [10]. For x larger than 2, the situation becomes more complicated because of both the recontraction of the lattice constant and the tendency of octahedral Na towards (y, y, y) positions, causing frustration for the orientations of C_{60} molecules. Further work on $Na_x C_{60}$ with x close to 3 is in progress.

It is now clear that the competition between C_{60} - C_{60}

and M^+ - C_{60} interactions implies a rich variety of structural and dynamical phenomena in fullerene intercalation compounds. The choice of M plays two roles: it directly or indirectly controls the strength of C_{60} - C_{60} interactions via the lattice constant, and it limits the orientational degrees of freedom to a varying degree depending on the relative strengths of two competing M^+ - C_{60} interactions. The first of these is the short-range repulsion due to charge overlap, which is smaller for smaller M 's since the M^+ - C_{60} spacing is fixed by the C_{60} - C_{60} spacing. This repulsion is minimized if the C_{60} molecules occupy either of the two standard orientations. The second is the long-range Coulomb interaction between M ions and C_{60} , which is minimized by having C_{60} molecules in the orientations of the $Pa\bar{3}$ structure with setting angle $\phi = 22.24^\circ$, as discussed above. For $M=Rb$ we accept the usual picture according to which the short-range repulsion is dominant. In this Letter we give evidence that for Na doping the Coulomb interactions are dominant. For $M=K$ it is possible that although the short-range interactions are stronger, they may not completely dominate the Coulomb interactions, in which case there would be some probability of having $Pa\bar{3}$ orientations in addition to randomly occupying the two standard orientations. Indeed, new 2D NMR data on the molecular dynamics of K_3C_{60} are more consistent with 44.48° jump rotations about [111] among the $Pa\bar{3}$ orientations, as opposed to the 90° jumps about [100] implied by meroheral disorder [22]. Similarly, since the Na in Na_2MC_{60} ternary compounds is essentially confined to tetrahedral sites [8], we would expect these compounds to adopt the $Pa\bar{3}$ structure (assuming that the octahedral M plays a minor role). This appears to be true in the one case for which high-resolution x-ray data are available ($M = Rb$) [23,24]. One is tempted to speculate that the anomalously low T_c in these ternaries may be due to the additional degrees of orientational freedom associated with the $Pa\bar{3}$ minima.

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