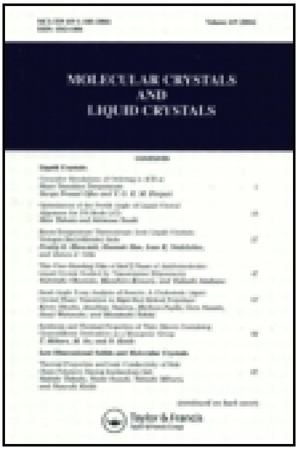

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Disorder IN C_{60} Intercalation Compounds and Implications for Superconductivity

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Version of record first published: 23 Oct 2006.

To cite this article: J. E. Fischer (1994): Disorder IN C_{60} Intercalation Compounds and Implications for Superconductivity, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 261-270

To link to this article: http://dx.doi.org/10.1080/10587259408051699

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 261–270
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Printed in the United States of America

DISORDER IN C_{60} INTERCALATION COMPOUNDS AND IMPLICATIONS FOR SUPERCONDUCTIVITY

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INTRODUCTION

Alkali metal intercalation compounds of C_{60} have attracted a great deal of interest, due primarily to the existence of superconductivity in some members of the family but also to the richness of the binary phase equilibria versus metal concentration, temperature and hydrostatic pressure. The C_{60} host lattice itself exhibits novel structural and dynamical properties, many of which are associated with orientational ordering of the molecules [1]. The extent to which disorder of all kinds plays a role in phase equilibria and superconductivity of the doped phases is just beginning to be appreciated. Here I review briefly what is currently known.

In principle, disorder in fullerene intercalation compounds can be divided into four main categories. Most obvious is the degree of orientational order, or lack thereof. The saturated heavy alkali compounds M_6C_{60}, M = K, Rb or Cs, are body-centered cubic with a high degree of orientational order; molecular 2-fold axes are aligned with cubic Cartesian axes identically for all molecules [2], and the ordered phase remains stable up to at least 700 K. The superconducting M_3C_{60} binary compounds (M = K, Rb) are face-centered cubic, and the molecules exhibit "merohedral disorder" at 300 K in which they adopt one of two standard orientations A or B at random, with equal probabilities [3]. The standard orientations consist again of aligning 2-fold molecular axes with the cube edges; A differs from B by a 90 degree rotation about the 2-fold axis, but both present hexagon faces to the tetrahedral site so the site volume is maximized independent of orientational correlations. Classical x-ray and neutron diffraction are unable to say if there are short-range correlations between A and B. This is an important question since the superconducting coherence length is about the same as the second-neighbor C_{60}–C_{60} distance. Furthermore, it is not known in detail if the situation changes below T_c.

A second kind of disorder occurs in nonstoichiometric fcc phases, e.g. heavy alkali compounds M_xC_{60} with $x < 3$. We refer to this as "site disorder", meaning that M's can either randomly occupy tetrahedral (T) and octahedral (O) sites with probabilities determined by the global stoichiometry, or they can preferentially occupy T and/or O sites (the latter being about twice as large) driven by differences in ionic radii. For example, one would expect the M's in an $x = 1$ compound to preferentially occupy O sites at low temperature (one site per molecule) in order to minimize mixing entropy; one might even envision an order-disorder transition to a high-temperature "lattice gas" phase with random site occupancy, by analogy to staging transtions in layer intercalates [4]. It would not be surprising to find that molecular orientational disorder and site order/disorder could be coupled in some cases.

A third class is chemical disorder in ternary phases of the form $[M_yM'_{1-y}]_3C_{60}$ with $0 < y < 1$ and M, M′ = Li, Na, K, Rb or Cs. The optimum size match occurs for Na_2CsC_{60}, which indeed is reported to exhibit a high degree of chemical order [5]. Finally for completeness we mention the possibility of planar defects such as hcp-type stacking faults, which are known to occur in pure C_{60} [6] and have been inferred to be present in Rb_3C_{60} [7]. Such defects would obviously play a role in the superconducting properties. For example, if the size of a defect-free region is comparable to the London penetration depth, then the diamagnetic shielding fraction will be reduced [8]. Stacking faults can also be important flux pinning centers and therefore may control the critical current density. Electron microscopy studies on the alkali-doped phases are crucially needed, but their extreme air-sensitivity makes this problematic.

M_1C_{60}: AN INVERTED ISING-LIKE TRANSITION

X-ray diffraction and differential scanning calorimetry of M_xC_{60}, with x ~ 1 and M = K, Rb or Cs, reveal an unusual T-dependent phase sequence [9]. A low-symmetry ground state is found, while the high-T limit is an ordered rocksalt structure in which only O sites are occupied. This conclusion is based on Rietveld refinement of T-dependent synchrotron x-ray powder diffraction profiles, an example of which is shown in Figure 1. These show that the site-ordered rocksalt phase of M_1C_{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 temperatures but only for M = K and $x \geq 1.4$. This is another fcc phase, but with random T and O occupancy, which is therefore isostructural with the superconducting M_3C_{60} phase suggesting the possibility of off-stoichiometry superconductivity [10].

Figure 1 shows x-ray profiles of $K_{1.4}C_{60}$ (dots) and Rietveld refinements (solid curves) taken at 300 K, 393 K and 473 K. The dominant phases in both high-T profiles index well as fcc but the relative intensities are systematically different, indicating two distinct structures. Since there is only one octahedral site per C_{60}, the high-T limit *must* phase-separate into rocksalt K_1C_{60} plus a trace of K_3C_{60}, reflections from the latter denoted by (*). In contrast, no second phases are detectable in the 393 K profile, since now all 3 sites are available. The 300 K profile shows sharp reflections from the intermediate fcc phase as well as broader peaks which can be approximately indexed as rhombohedral. Many rhombohedral peaks coincide with fcc reflections; two of the uniquely rhombohedral positions are labelled by (+) in the inset. 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.

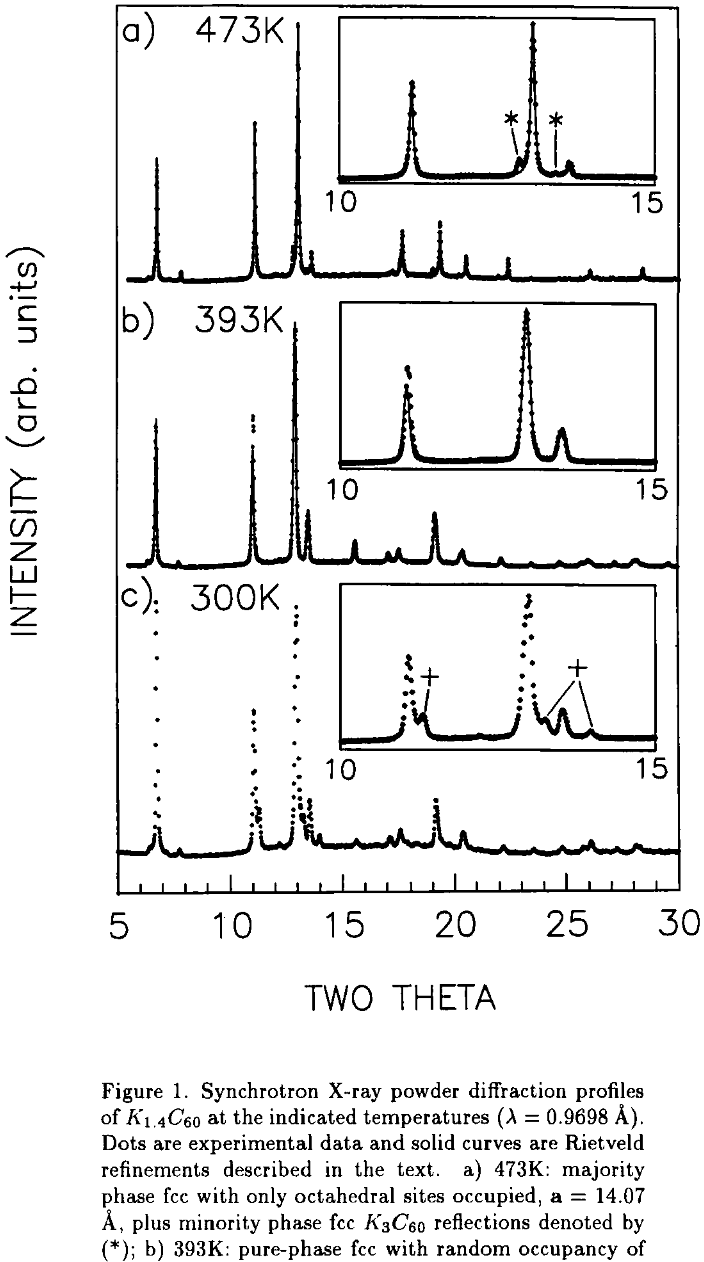

Figure 1. Synchrotron X-ray powder diffraction profiles of $K_{1.4}C_{60}$ at the indicated temperatures ($\lambda = 0.9698$ Å). Dots are experimental data and solid curves are Rietveld refinements described in the text. a) 473K: majority phase fcc with only octahedral sites occupied, **a** = 14.07 Å, plus minority phase fcc K_3C_{60} reflections denoted by (*); b) 393K: pure-phase fcc with random occupancy of tetrahedral and octahedral sites, **a** *expanded* to 14.27 Å; c) 300K: 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.

NMR suggests that the onset of quasi-free rotations is implicated in the transition to the high-temperature site-ordered phase [11]. This is borne out by the 473 K Rietveld refinement (Figure 1), which converged on perfect rocksalt ordering and orientationally-disordered C_{60}'s, with a weighted intensity R-factor 12%. In pure C_{60}, orientational melting is accompanied by a 0.3% lattice dilation. This is apparently overwhelmed in K_1C_{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 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. Furthermore, the lattice constant *contracts* from 14.27 Å to 14.07 Å upon heating through the transition at $\sim$ 433K. We attribute this "inverted Ising" behavior to the entropy provided by the C_{60} orientational disorder and/or the random distribution of K among symmetry-equivalent positions within the O site. It appears that K prefers to occupy the large O site at high temperature because its effective thermal radius (either from random fluctuations or static displacements) is too large for the T site.

Band structure calculations indicate that rocksalt M_1C_{60} is metallic independent of M [12], similar to fcc M_3C_{60}. NMR results suggest that either the lattice-gas or the rhombohedral phase *might* be metallic [11].

AN ORIENTATIONALLY-ORDERED SUPERCONDUCTOR

A nice, monotonic empirical correlation between T_c and 300 K lattice constant **a** has been found for most of the superconducting binary and ternary fcc phases with x = 3 [13, 14]. The weakly parabolic dependence with positive curvature is even consistent with LDA calculations based on BCS theory [15]. However, there exist a few compounds with M or M′ = Na which appear to be isostructural from 300 K x-ray data but with anomalously low T_c's [16, 5]. The general problem arises because, in the fcc structure, the O site (1 per C_{60}) is twice as large as the T site (2 per C_{60}), the closest to optimum size matching being obtained with Na_2CsC_{60} for which the T_c and **a** values indeed lie on the universal curve. We have used hydrostatic pressure, ac susceptibility and low-temperature x-ray diffraction to find out if the anomalous compounds exhibit instabilities of any kind [17]. The results allow us to rule out all but one of the anomalous compounds; the only remaining mystery, Na_2RbC_{60}, calls into question the importance of molecular order in superconducting fullerene phases.

X-ray diffraction and scanning calorimetry clearly show that Na_3C_{60} either phase-separates or distorts away from cubic symmetry below 260 K, so the absence of superconductivity in this material is no surprise [16]. Na_2KC_{60} is reported to exhibit a small shielding fraction at 1 atm. with $T_c \sim 2K$ [5], whereas its 300 K lattice constant would imply a T_c more like 10 K. We applied 5 kbar He pressure to a sample of this material at 300 K, then cooled to 4.2 K without detecting any superconductivity. We then warmed up to about 60 K and reduced the pressure to 1.5 kbar, whereupon we found a clear signature of superconductivity at 19 K, suggestive of phase separation into something plus K_3C_{60}. An extended series of (P,T) cycles indicated that superconductivity can *only* be formed by application of ≥ 5 kbar at 300 K (3.7 kbar is insufficient). Essentially identical (P,T) cycling of Na_2RbC_{60} failed to reveal any superconductivity above 4.2K under any circumstances. In sharp contrast, T_c of Rb_2CsC_{60} responded to (P,T) cycling in the same normal manner as the K and Rb binaries.

Instabilities in the ternary phases were probed by high-resolution, high-pressure x-ray diffraction at 300 K. For Na_2KC_{60} we found already at 1 atm. a mixture of two fcc phases with **a**'s of 14.08 and 14.18 Å, whereas low resolution data implied a single phase [5]. The splitting became more obvious with increasing pressure. So this "anomalous" compound can also be eliminated from further consideration. In contrast, Na_2RbC_{60} remained well-ordered and single phase up to 6 kbar, above which the peaks abruptly broadened and could no longer be indexed as cubic. The kinetics of this distortion were extremely rapid; small pressure excursions about 6 kbar caused essentially instantaneous and reversible transformations (recorded with a linear detector) between the fcc and distorted phases. Finally, Rb_2CsC_{60} remained pure phase fcc up to 44 kbar, **a** decreasing sub-linearly with increasing pressure.

At this point it would appear that Na_2RbC_{60} is the only truly anomalous compound. The instability above 6 kbar, 300 K observed by x-rays may lie just beyond the range accessible with rf impedance. We therefore performed high-resolution diffraction at low temperature and 1 atm. to see if a similar instability might occur. Profiles taken at 300 K and 27 K both show well-ordered single-phase behavior, with lattice constants 14.084 and 14.021 Å respectively, consistent with the average thermal expansion coefficients of the K and Rb binaries. The big surprise was that both profiles contain observable Bragg intensities at positions which are only allowed by simple cubic indexing, and these peaks are stronger at low temperature. This is clear evidence for a high degree of orientational order in this putative superconductor, unlike the usual merohedral disorder typically found in fullerene superconductors. The 27 K profile and refinement are shown in Figure 2, in which the uniquely simple cubic peaks are labelled by (*).

A refinement in Fm3m space group yielded a poor fit, R_p = 18%. For the Pa3 refinement we first constrained all molecules to have the same orientation, specified by rotation about molecular threefold axes which are aligned with $< 111 >$ directions, as in pure C_{60}. By varying the rotation angle, we found global and broad local minima in R_p at 24-26° (R_p=13.8%) and 75-86° (R_p=16%) respectively, very similar to what occurs in pure C_{60} [18, 19]. The final optimized refinement (R_p=12.8%) consists of a two-phase mixture with an 80:20 ratio of the two orientations, essentially the same as occurs in pure C_{60} below 90 K. The refinement also reveals a high degree of chemical ordering, T-Na and O-Rb, as expected.

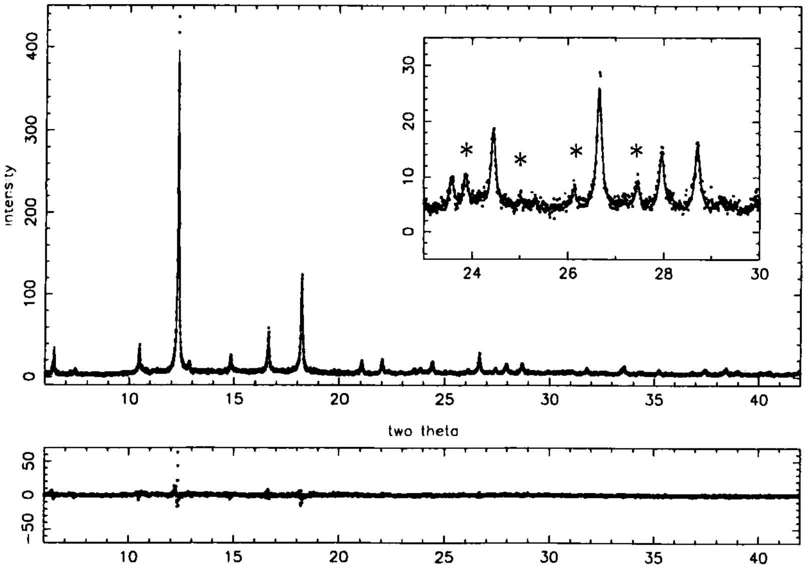

Figure 2. 27 K x-ray profile (dots) and Rietveld refinement in space group Pa3 (solid curve) for Na_2RbC_{60}. Asterisks on the inset denote uniquely simple cubic reflections.

This result is in sharp contrast to a recent claim that the anomalously low T_c in Na_2RbC_{60} results from a *higher* degree of orientational disorder than its otherwise isostructural relatives [20]. This contrary result is again based on moderate resolution x-ray profiles. If it were true, one would expect modest hydrostatic pressure to drive the fullerenes into an orientationally-ordered state, as in pure C_{60} [21], whereas applying pressure at 300 K resulted in a T_c which is still less than 4.5 K. It is unclear why Na_2RbC_{60} is the only example thus far of an orientationally-ordered superconductor. What is clear is that the anomalously low T_c is not a consequence of orientational disorder.

In a recent experiment, Kiefl *et al.* observed a Hebel-Slichter (coherence) peak in the T-dependent muon relaxation rate of Rb_3C_{60} [22]. The peak is much broader and weaker than in traditional superconductors, an effect that may result from the interplay between merohedral disorder and the multiband nature of the Fermi surface [23]. If so, it would be very interesting to find out if our only remaining mystery compound Na_2Rb_{60} exhibits a stronger coherence peak. The anomalously low T_c of this otherwise well-behaved compound remains a mystery for further study.

ACKNOWLEDGMENTS

The work summarized here is largely drawn from the efforts of my students Qing Zhu and Krzysztof Kniaź, and collaborations with J. Schirber (Sandia) and D. Murphy (AT&T Bell Labs), and was supported by DOE Grants DE-FC02-86ER45254 and DE-FG05-90ER75596 and by the NSF MRL Program, DMR91-20668.

REFERENCES

1. Comprehensive reviews have appeared in Account of Chemical Research 25 (March 1992) and J. Phys. Chem. Solids 53 (November 1992)
2. O. Zhou, J.E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A.R. Mc Ghie, W.J. Romanow, J.P. Mc Cauley Jr, A.B. Smith III and D.E. Cow, Nature 351, 462 (1991)
3. P.W. Stephens, L. Mihaly, P.L. Lee, R.L. Whetten, S.M. Huang, R.B. Kaner, F. Diederich and K. Holczer, Nature 351, 632 (1991)
4. J.E. Fischer, in Chemical Physics of Intercalation, ed. by A.P. Legrand and S. Flandrois, 59 (Plenum, NY 1987)
5. K. Tanigaki, I. Hirosawa, T.W. Ebbesen, J. Mizuki, Y. Shimakawa, Y. Kubo, J.S. Tsai and S. Kuroshima, Nature 356, 419 (1992)
6. D.E. Luzzi, J.E. Fischer, X.Q. Wang, D.A. Ricketts-Foot, A.R. Mc Ghie and W.J. Romanow, J. Mat. Research 7, 335 (1992)
7. Q. Zhu, O. Zhou, N. Coustel, G. Vaughan, J.P. Mc Cauley Jr, W.J. Romanow, J.E. Fischer and A.B. Smith III, Science 254, 545 (1991)
8. M. Baenitz, E. Straube, S. Gartner, H. Werner, R. Schlogl and K. Luders, in Springer Series in Solid State Sciences, to be published
9. Q. Zhu, O. Zhou, N. Bykovetz, J.E. Fischer, A.R. Mc Ghie, W.J. Romanow, C.L. Lin, R.M. Strongin, M.A. Cichy and A.B. Smith III, Phys. Rev. B (May 15, 1993)
10. R.W. Lof, M.A. Van Veenendaal, B. Koopmans, H.T. Jonkman and G.A. Sawatzky, Phys. Rev. Lett. 68, 3924 (1992)
11. R. Tycko, G. Dabbagh, D.W. Murphy, Q. Zhu and J.E. Fischer, Phys. Rev. B (in press)
12. S.C. Erwin, private communication
13. R.M. Fleming, A.P. Ramirez, M.J. Rossiensky, D.W. Murphy, R.C. Haddon, S.M. Zahurak and A.V. Makhija, Nature 352, 787 (1991)
14. O. Zhou, G.B.M. Vaughan, Q. Zhu, J.E. Fischer, P.A. Heiney, N. Coustel, J.P. Mc Cauley Jr and A.B. Smith III, Science 255, 833 (1992)
15. A. Oshiyama and S. Saito, Solid State Comm. 82, 41 (1992)
16. M.J. Rosseinsky, D.W. Murphy, R.M. Fleming, R. Tycko, A.P. Ramirez, T. Siegrist, G. Dabbagh and S.E. Barrett, Nature 356, 416 (1992)
17. J.E. Schirber, D.L. Overmyer, W.R. Bayless, M.J. Rosseinsky, O. Zhou, D.W. Murphy, Q. Zhu, K. Kniaz and J.E. Fischer, J. Phys. Chem. Solids (in press)
18. W.I.F. David, R.M. Ibberson, T.J.S. Dennis, J.P. Hare and K. Prassides, Europhys. Lett. 18, 219 (1992)
19. R. Moret, P.A. Albouy, V. Agafonov, R. Geolin, D. André, A. Dworkin, H. Swarc, C. Fabre, A. Rassat, A. Zahab and P. Bernier, J. Phys. I France 2, 511 (1992)
20. I. Hirosawa, J. Mizuki, K. Tanigaki, T.W. Ebbesen, J.S. Tsai and S. Kuroshima, preprint (1993)
21. G. Kriza, J.C. Ameline, J. Jerome, A. Dworkin, H. Szwarc, C. Fabre, D. Schutz, A. Rassat and P. Bernier, J. Phys. I France 1, 1361 (1991)
22. R.F. Kiefl, A. Mc Farlane, K. Chow, S. Dunsiger, T.L. Duty, T.M.S. Johnston, J.W. Schnieider, J. Sonier, L. Brard, R.M. Strongin, J.E. Fischer and A.B. Smith III, Phys. Rev. Letters 70, 3987 (1993)
23. E.J. Mele and S.C. Erwin, Phys. Rev. B 47, 2948 (1993)