An elusive phase transition in Na_2RbC_{60}

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The ternary Na_2RbC_{60} fulleride is studied by variable-temperature solid-state ^{13}C and ^{23}Na NMR spectroscopies; in addition to the well known orientational order/disorder transition, a phase transformation to a low-symmetry phase which likely contains bonded C_{60}^{3-} moieties is identified at low temperature for the first time.

Intercalation of solid C_{60} with electron donors, like the alkali metals, results in a wealth of intercalated fulleride salts. All salts with stoichiometry $A_2A'C_{60}$ are metallic and display superconductivity (except Li_2CsC_{60})[1] at critical temperatures as high as 33 K at ambient pressure,[2] surpassed only by the high T_c superconducting oxides. All superconducting salts have been classified into two distinct, strictly cubic, families, distinguished through the orientational state adopted by the C_{60}^{3-} ions in the crystal structure. For large alkali metals (A = K, Rb) occupying the tetrahedral interstices, a merohedrally disordered fcc structure in which the C_{60}^{3-} ions are randomly distributed between two orientations related by 90° rotations about the cubic axes is adopted.[3] The second structural family is encountered when Na^+ resides in the tetrahedral interstices and both Na_2RbC_{60}[4] and Na_2CsC_{60}[5] have been shown to adopt a primitive cubic structure in which the majority of the C_{60}^{3-} ions are rotated counterclockwise by *ca.* 98° about the appropriate [111] cube diagonal, with the remaining adopting minor orientations. Near room temperature, these salts also show a transition to an fcc structure, comprising orientationally disordered quasi-spherical C_{60}^{3-} ions.[6] Here, we report the solid-state ^{13}C and ^{23}Na NMR spectra of Na_2RbC_{60} in the temperature range 210–350 K. Our results reveal that in addition to the fcc → primitive cubic phase transition near room temperature, further cooling leads to a very slow phase transformation to a novel unsuspected low-symmetry structural form of Na_2RbC_{60}.

A high-resolution synchrotron X-ray diffraction profile of the Na_2RbC_{60} sample† at 370 K reveals an fcc structure [a = 14.1402(9) Å, space group $Fm\bar{3}m$] comprising quasi-spherical C_{60}^{3-} ions, as expected. Fig. 1 shows the solid-state ^{13}C (MAS, spinning frequency = 6 and 8 kHz) and ^{23}Na (static) NMR spectra‡ of Na_2RbC_{60} at 333, 253 and 213 K. The MAS ^{13}C NMR spectrum at 333 K [Fig. 1(*a*)] displays a single sharp peak at δ 189, consistent with fast rotational motion of the C_{60}^{3-} ions in the fcc phase.[7] On cooling, a second peak appears gradually at δ 186 [Fig. 1(*a*) inset], with its intensity growing at the expense of the δ 189 resonance which becomes less intense until it completely disappears [Fig. 1(*b*)]. It can be assigned to the primitive cubic phase and remains sharp at 253 K, consistent with rapid large-amplitude librational motions of the C_{60}^{3-} ions about their equilibrium orientations.[7] The temperature dependence of the static ^{23}Na NMR spectra mirrors that of ^{13}C NMR with the observation of both orientationally disordered (at 333 K) and ordered (at 253 K) phases, characterised by single resonances at δ 198 and 68 and linewidths at half height, $\nu_{\frac{1}{2}}$, of 1500 and 3300 Hz, respectively [Fig. 1(*d*) and (*e*)]. The increased linewidth in the orientationally ordered phase can arise from increased asymmetry due to two contributing factors: (*i*) the space group $Pa\bar{3}$ allows the displacement of the Na^+ ions (local symmetry C_3) from the ideal tetrahedral $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions along the [111] cube diagonals, and (*ii*) the coordination environment of the Na^+ ions is no longer symmetric, as they lie above the centre of a hexagonal face of one C_{60}^{3-} ion and the midpoints of 6 : 6 bonds of three other neighbouring C_{60}^{3-} ions.[5]

Further cooling to 213 K initially reveals little change in either ^{13}C or ^{23}Na NMR spectra. However, upon standing at 213 K, a continuous decrease in the intensity of the ^{13}C resonance (3 s repetition time, 8 kHz spinning frequency) is observed, until after *ca.* 4 h a plateau is reached at a value of *ca.* 50% of the original intensity. Prolonged time averaging (3700 repetitions)

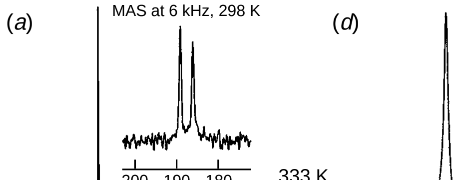

Fig. 1 The solid-state ^{13}C (MAS) and ^{23}Na (static) NMR spectra of Na_2RbC_{60}: (*a*) ^{13}C, fcc phase at T = 333 K; the inset shows the spectrum at 298 K whence the two resonances signify coexistence of the fcc and primitive cubic phases. (*b*) ^{13}C, primitive cubic phase at T = 253 K. (*c*) expanded ^{13}C, coexistence of primitive cubic and orthorhombic phases at 213 K; the vertical bar marks a spinning sideband. (*d*) ^{23}Na, fcc phase at T = 333 K. (*e*) ^{23}Na, primitive cubic phase at T = 253 K. (*f*) ^{23}Na, coexistence of primitive cubic and orthorhombic phases at 213 K; the simulated spectra of the two resonances are also shown.

revealed numerous new features over the chemical shift range δ 0–250 [Fig. 1(*c*)], implying low crystalline symmetry and substantial distortion of the C_{60}^{3-} ions. The shape of the static ^{23}Na NMR spectrum also mirrors this change and evolves with time at 213 K; a new feature appears, saturating again after *ca.* 4 h [Fig. 1(*f*)]. Although the two ^{23}Na resonances partially overlap, they can be separated by judicious choice of the relaxation delay in inversion recovery experiments, as they have very different longitudinal relaxation times, T_1 *ca.* 6 and 60 ms, respectively. Simulations of the complete spectrum are included in Fig. 1(*f*), using values of the NMR shift (arising from the combined effects of the chemical shift and the Knight shift), δ 60 and 208, of the quadrupole coupling constant, (e^2qQ/h) = 2.51 and 4.63 MHz, and of the asymmetry parameter, η = 1.0 and 0.03 for the two resonances, respectively. The two phases exist in almost equal amounts.

The above NMR results are consistent with the presence of two phase transitions for Na_2RbC_{60} in the temperature range 210–350 K. Firstly, the fcc $\longrightarrow$ primitive cubic transformation is essentially complete, before a very slow transition, never going to completion, to a low-symmetry highly distorted structure occurs. Complementary high-resolution synchrotron and neutron diffraction experiments are in good agreement with this picture.[8] The low-symmetry phase at low temperature is identified as orthorhombic (space group *Immm*) with lattice constants at 180 K of a = 9.3819(8), b = 9.943(1) and c = 14.559(1) Å; it co-exists with the remaining fraction of the primitive cubic phase with a = 14.064(1) Å. The structural results for the orthorhombic phase are indicative of C_{60}^{3+}–C_{60}^{3-} bonding in the low-temperature phase, as manifested by the existence of a very short temperature-independent interfullerene separation along a (9.38 Å), analogous to the situation encountered in the polymerised phases of AC_{60} (A = K, Rb, Cs) salts[9] which show partial covalent bonding between strongly deformed C_{60}^{-} ions. The broad ^{13}C NMR spectra of the orthorhombic Na_2RbC_{60} phase are also reminiscent of those measured for polymerised AC_{60}.[10] Work is in progress to search for the resonances associated with the bridging C atoms. An orthorhombic phase with comparable lattice dimensions had been observed at high pressures but it was thought that the application of pressure was essential for the phase transition and the resulting interfullerene bonding to occur.[11]

In conclusion, variable-temperature solid-state NMR measurements on Na_2RbC_{60} establish the following sequence of phase transitions in the 210–350 K temperature range at ambient pressure: orthorhombic $\longrightarrow$ primitive cubic $\longrightarrow$ fcc. The NMR results are consistent with highly restricted C_{60}^{3-} ions, most probably due to the formation of bonds between adjacent C_{60}^{3-}, as is found in the mono-alkali-metal fullerides. The hitherto unsuspected existence of the orthorhombic phase which completely eluded all earlier studies, presumably because of its slow kinetics, should aid rationalisation of many of the puzzling features of the physical properties of Na_2RbC_{60}.[12] In addition, its observation and the associated novel interfullerene bonding should not represent an isolated example, but rather a widespread phenomenon, begging a thorough reinvestigation of sodium (and lithium) fulleride chemistry.

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Footnotes

† The Na_2RbC_{60} sample used in the present work was prepared by reaction of stoichiometric quantities of C_{60}, Na and Rb contained in a sealed tantalum cell inside a sealed glass tube filled with He to 500 Torr at 480 K for 3 h, at 570 K for 12 h and at 620 K for 72 h; after an intermittent regrinding, the sample was annealed at 673 K for 25 days, employing the same experimental setup. Phase purity was confirmed by X-ray diffraction using a Siemens D5000 diffractometer.

‡ Solid-state ^{13}C and ^{23}Na NMR experiments with and without magic angle spinning (MAS) in an applied 9.395 T field were performed in the temperature range 210–350 K on a Bruker DMX-400 spectrometer (89 mm wide-bore magnet) with a 4 mm variable temperature double-bearing probe. The 50 mg sample was packed into a zirconia rotor with Kel-F end caps inside a glovebox and spun with N_2. A 30° excitation pulse was used for the ^{13}C NMR experiments while the ^{23}Na NMR spectra were acquired with a quad-echo pulse sequence.

References

1 I. Hirosawa, K. Prassides, J. Mizuki, K. Tanigaki, M. Gevaert, A. Lappas and J. K. Cockcroft, *Science*, 1994, **264**, 1294.

2 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600; K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo and S. Kuroshima, *Nature*, 1991, **352**, 222.

3 P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S. M. Huang, R. Kaner, F. Deiderich and K. Holczer, *Nature*, 1991, **351**, 632.

4 K. Kniaz, J. E. Fischer, Q. Zhu, M. J. Rosseinsky, O. Zhou and D. W. Murphy, *Solid State Commun.*, 1993, **88**, 47.

5 K. Prassides, C. Christides, I. M. Thomas, J. Mizuki, K. Tanigaki, I. Hirosawa and T. W. Ebbesen, *Science*, 1994, **263**, 950.

6 K. Tanigaki, I. Hirosawa, T. Manako, J. S. Tsai, J. Mizuki and T. W. Ebbesen, *Phys. Rev. B*, 1994, **49**, 12307.

7 C. Christides, K. Prassides, D. A. Neumann, J. R. D. Copley, J. Mizuki, K. Tanigaki, I. Hirosawa and T. W. Ebbesen, *Europhys. Lett.*, 1993, **24**, 755.

8 K. Prassides, K. Vavekis, K. Kordatos, K. Tanigaki, G. M. Bendele and P. W. Stephens, *J. Am. Chem. Soc.*, 1997, **119**, 834.

9 P. W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. Oszlanyi and L. Forro, *Nature*, 1994, **370**, 636; S. Pekker, L. Forro, L. Mihaly and A. Janossy, *Solid State Commun.*, 1994, **90**, 349.

10 T. Kalber, G. Zimmer and M. Mehring, *Z. Phys. B*, 1995, **97**, 1; H. Alloul, V. Brouet, E. Lafontaine, L. Malier and L. Forro, *Phys. Rev. Lett.*, 1996, **76**, 2922.

11 Q. Zhu, *Phys. Rev. B*, 1995, **52**, R723.

12 K. Tanigaki and K. Prassides, *J. Mater. Chem.*, 1995, **5**, 1515; Y. Maniwa, T. Saito, K. Kume, K. Kikuchi, I. Ikemoto, S. Suzuki, Y. Achiba, I. Hirosawa, M. Kosaka and K. Tanigaki, *Phys. Rev. B*, 1995, **52**, R7054.

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