

Loss of Cubic Symmetry in Low-Temperature $\text{Na}_2\text{RbC}_{60}$

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A_3C_{60} alkali fullerides exhibit superconductivity with T_c 's as high as 33 K.¹ For large cations (K^+ , Rb^+) occupying the tetrahedral interstices, the structures are face-centered cubic (fcc), incorporating merohedrally disordered C_{60}^{3-} .² For the smaller Na^+ , $\text{Na}_2\text{A}'\text{C}_{60}$ are fcc at high temperatures, displaying on cooling a transition to a primitive cubic (pc) phase.³ Structural work at elevated pressures⁴ has identified for $\text{Na}_2\text{-RbC}_{60}$ an orthorhombic phase with short $\text{C}_{60}^{3-}\text{-C}_{60}^{3-}$ distances (~ 9.35 Å), reminiscent of polymerized $\text{A}'\text{C}_{60}$ salts (~ 9.11 Å).⁵ As $\text{Na}_2\text{RbC}_{60}$ has an anomalously low T_c (~ 3.5 K)⁶ and many measurements⁷ are incompatible with a cubic phase, we have paid particular attention to heating and cooling protocols. Here, we report that at ambient pressure and low temperatures the ground state of $\text{Na}_2\text{RbC}_{60}$ is not the $Pa\bar{3}$ phase believed up to now; instead slow cooling stabilizes an orthorhombic phase with a short interball distance of 9.38 Å. The metastable cubic phase survives upon rapid cooling, in analogy with $\text{A}'\text{C}_{60}$.⁸ These results provide an unexpected dimension to the behavior of fullerides, implying a richer abundance of bridged fullerene structures than hitherto appreciated and should help to rationalize puzzling features associated with sodium (and lithium) C_{60} salts.

The synchrotron X-ray diffraction (XRD) profile of $\text{Na}_2\text{-RbC}_{60}$ ⁹ revealed at 370 K a structure ($a = 14.1406(8)$ Å, $Fm\bar{3}m$) comprising orientationally disordered C_{60}^{3-} ions.³ At 299 K, the sample is predominantly pc ($a = 14.0951(3)$ Å, $Pa\bar{3}$) with

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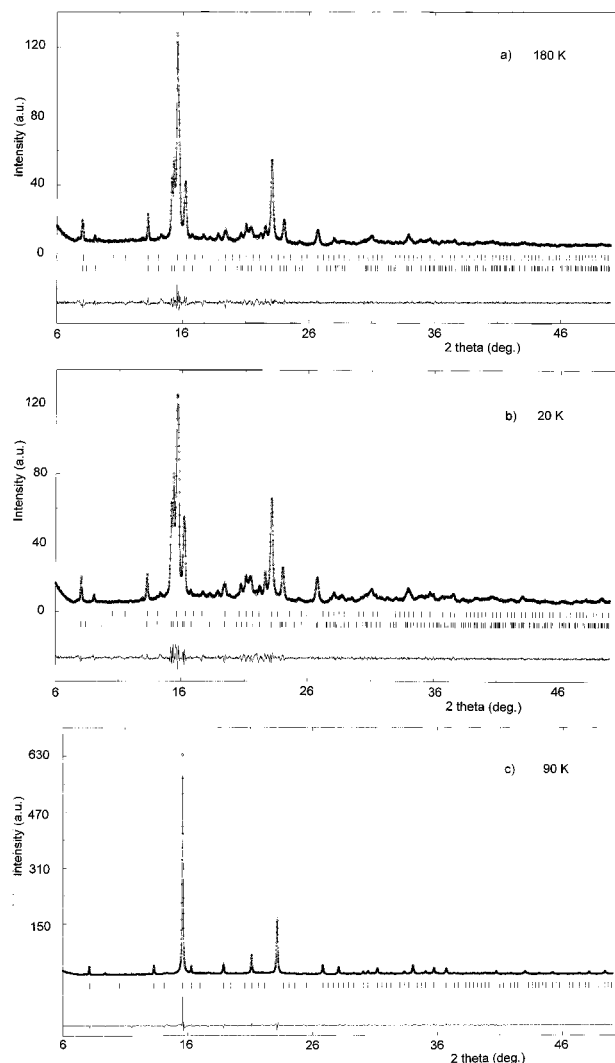


Figure 1. Observed (O), calculated (—), and difference (lower panel) plots for the LeBail pattern decomposition refinements of the synchrotron powder XRD ($\lambda = 1.14956$ Å) data of $\text{Na}_2\text{RbC}_{60}$; (a) slow cooling, $T = 180$ K, (b) slow cooling, $T = 20$ K, and (c) rapid cooling, $T = 90$ K. Reflection positions are shown as tick marks.

a coexisting fcc component. Slow cooling to 180 K over ~ 2 h resulted in the appearance of a new phase (Figure 1a) which was found to be orthorhombic using standard techniques. Two data sets were collected over a period of 12 h, and intensity differences confirmed that the transition is extremely slow and incomplete. Cooling to 20 K leads to a diminution of the intensity of the cubic peaks but not to their disappearance (Figure 1b); analysis with the LeBail pattern decomposition technique¹⁰ gave lattice constants $a = 9.3809(6)$ Å, $b = 9.940(1)$ Å, and $c = 14.492(1)$ Å for the low-temperature $o\text{-Na}_2\text{-}$

(9) $\text{Na}_2\text{RbC}_{60}$ was prepared by reaction of stoichiometric quantities of C_{60} , Na, and Rb contained in a sealed Ta 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 intermediate regrinding, the sample was annealed at 673 K for 25 days. Phase purity was confirmed by XRD using a Siemens D5000 diffractometer. For the neutron diffraction measurements, the sample was placed in a cylindrical 6-mm diameter vanadium sample holder and was press sealed with In wire. Data were collected on heating between 1.5 and 349 K (at 0.33 K/min) with the high-intensity medium-resolution D1b powder diffractometer ($\lambda = 2.5242$ Å, $2\theta = 10\text{--}90^\circ$) at the ILL, Grenoble. High-resolution XRD data on a sample sealed in a 0.5-mm glass capillary were collected on the X3B1 beamline ($\lambda = 1.14956$ Å, $2\theta = 6\text{--}50^\circ$) at the NSLS between 20 and 300 K. A diffraction profile was also recorded at 370 K at the SRS Station 9.1, Daresbury Laboratory ($\lambda = 0.87236$ Å, $2\theta = 5\text{--}40^\circ$). Data analysis was performed with the FULLPROF suite of powder diffraction programs. SQUID measurements to 2 K were performed on a 50-mg sample with a Quantum Design MPMS7 magnetometer.

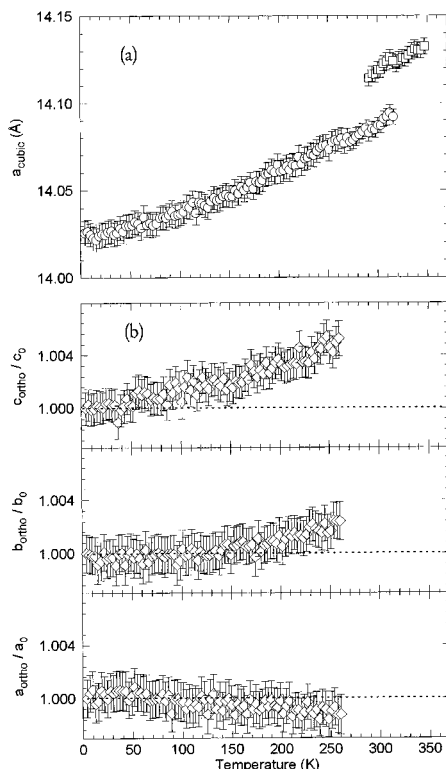


Figure 2. Temperature dependence of (a) the lattice constant in *c*-Na₂RbC₆₀ and (b) the normalized (to the 1.5 K values) lattice constants in *o*-Na₂RbC₆₀, extracted from the neutron diffraction data.

RbC₆₀ (*Immm*) and $a = 14.024(1)$ Å for *c*-Na₂RbC₆₀ (*Pa* $\bar{3}$) ($R_{wp} = 5.7\%$, $\chi^2 = 3.4\%$). This scheme is also successful in describing the neutron diffraction data. Figure 2 shows the evolution of the lattice constants of both *c*- and *o*-Na₂RbC₆₀. The *ortho* phase is essentially absent above 280 K, while at ~ 290 K the *pc* \rightarrow *fcc* transition occurs, accompanied by a discontinuous jump of ~ 0.035 Å in a . Solid state NMR experiments¹¹ also confirmed the occurrence of a phase transformation, unrelated to the *fcc* \rightarrow *pc* one, in the vicinity of 200 K. Finally, in order to make contact with the earlier results of Kniaz *et al.*,^{3a} we recorded the synchrotron XRD profile of Na₂RbC₆₀ at 90 K (Figure 1c) after rapid cooling in liquid N₂—quenched Na₂RbC₆₀ is *pc* ($a = 14.0309(2)$ Å).

Several points arising from the present results are of interest. *o*-Na₂RbC₆₀ is strongly anisotropic with close contacts between the C₆₀³⁻ (9.38 Å) and negligible thermal expansivity along a (Figure 2). This is reminiscent of polymerized A'C₆₀⁵ in which there are two bridging C—C bonds between deformed C₆₀⁻ ions, thereby implying the existence of covalently bonded, deformed C₆₀³⁻ ions in *o*-Na₂RbC₆₀. However, the observed interfullerene separation is larger than that in A'C₆₀ (~ 9.11 Å). Zhu⁴ analyzed the high-pressure *o*-Na₂RbC₆₀ results with the same model; the observed elongation might then reflect the stronger repulsive forces associated with C₆₀³⁻. However, this model cannot be unambiguously established, because of the coexisting *c*-Na₂RbC₆₀. Interestingly, the interfullerene separation in *o*-Na₂RbC₆₀ is identical to that in (C₆₀)₂²⁻¹² and (C₅₉N)₂¹³ in which the fullerenes are bridged by single C—C bonds. Finally, the question arises whether similar polymerization reactions occur on cooling in other C₆₀³⁻ salts: synchrotron XRD experiments on Na₂CsC₆₀ reveal no evidence of an *ortho* phase on slow cooling to low temperatures ($a = 14.0556(4)$ Å at 50 K).

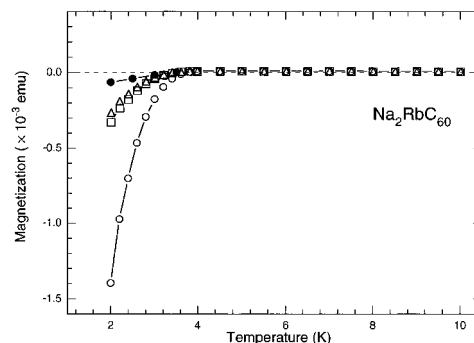


Figure 3. Magnetization (dc) measurements on Na₂RbC₆₀ at 50 Oe: (O) rapid cooling, ZFC conditions, (●) rapid cooling, FC conditions, (□) sample temperature kept at 180 K for 10 h before cooling to 2 K, ZFC conditions, and (Δ) sample heated back to 180 K and remained there for an additional 10 h, ZFC conditions.

Finally, one would like to know whether *c*-Na₂RbC₆₀ and/or *o*-Na₂RbC₆₀ are superconducting. Figure 3 shows the dc magnetization for a rapidly cooled sample: bulk superconductivity is observed with $T_c = 3.8$ K. However, if the sample is kept at 180 K for ~ 10 h to ensure conversion to *o*-Na₂RbC₆₀ before further cooling to 2 K, we observe little change in T_c (~ 3.6 K) but a drastic decrease in the superconducting fraction (to $\sim 25\%$ of the original value), consistent with two coexisting fractions: one superconducting (*c*-Na₂RbC₆₀) and one non-superconducting (*o*-Na₂RbC₆₀). Similar experiments on Na₂CsC₆₀ ($T_c = 12$ K) reveal no dependence of the magnetization on thermal history, in agreement with the nonappearance of *o*-Na₂CsC₆₀ in the diffraction experiments. Zhu⁴ has suggested that pressure-polymerized Na₂A'C₆₀ may be superconducting, on the basis of the observation of superconductivity in pressurized Na₂CsC₆₀.¹⁴ Our observation that superconductivity in Na₂RbC₆₀ and Na₂CsC₆₀ is only confined to the isotropic 3D phases makes that unlikely. The connection of the suppressed value of T_c in quenched Na₂RbC₆₀ with the presence of the *ortho* phase, for instance, since non-superconducting small size polymer domains can be present in the quenched monomer phase is an intriguing possibility and is currently under investigation.

In conclusion, slow cooling of Na₂RbC₆₀ at ambient pressure leads to a transition to a non-superconducting orthorhombic phase whose properties are consistent with covalently bonded C₆₀³⁻. The orientationally ordered *pc* phase is obtained only on rapid cooling through the cubic \rightarrow orthorhombic transition. The existence of non-superconducting *o*-Na₂RbC₆₀ and the thermal history dependence of the properties can now rationalize the wide differences from Na₂CsC₆₀. In addition, the present results bear direct relevance to the properties of all other known sodium (Na₂A'C₆₀, Na₂A'₂C₆₀, Na₂Rb_{1-x}Cs_xC₆₀) and lithium (Li₂C₆₀, Li₂A'C₆₀) salts, since it is unlikely that *o*-Na₂RbC₆₀ is an isolated example in C₆₀³⁻ chemistry. As a consequence, the properties of these systems merit thorough reinvestigation.

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