RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 2 1 JULY 1995-II

# Pressure-induced polymerization of ternary fulleride superconductors

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(Received 21 February 1995)

A reversible conversion of the cubic *trianionic* fulleride superconductors $Na_2RbC_{60}$ and $Na_2CsC_{60}$ to orthorhombic structures is observed at modest pressures ($\leq$ 3 kbar) and ambient temperature. Structure refinement based on synchrotron powder x-ray profiles reveals polymer chains with 9.35 Å intermolecular separation, comparable to that in the metastable *monoanionic* dimer and polymer phases of $KC_{60}$ and $RbC_{60}$. In contrast, $K_3C_{60}$, $Rb_3C_{60}$, etc. are stable to much higher pressures due to their larger lattice constants at ambient pressure.

Two striking features of alkali-metal-intercalated $C_{60}$ systems are the occurrence of superconductivity in most of the trianionic cubic compounds, and the (metastable) dimerization or polymerization of the molecules upon rapid cooling of the monoanionic rocksalt phases $KC_{60}$ and $RbC_{60}$. It is shown here that certain of the cubic *trianionic* salts can also be polymerized by applying high pressure; these examples reinforce current ideas about the necessary conditions for fullerene/fulleride intermolecular bonding. Furthermore, published $T_c$ vs $P$ measurements on these compounds suggest that the superconductivity might be retained in the polymeric state, providing yet another avenue for studying the general problem of fulleride superconductivity.

Neutral $C_{60}$ can be photopolymerized at ambient temperature[1] or by the application of high pressure at high temperatures.[2,3] Both processes require a sufficient degree of molecular rotational dynamics for the formation of [2+2] cycloaddition bonds between properly aligned adjacent molecules.[1,4] The monoanionic intercalation compounds $KC_{60}$ and $RbC_{60}$ dimerize or polymerize[5–7] when cooled from their high-temperature rocksalt phases.[8] In these cases, the application of pressure is unnecessary because the cubic lattice constants are unusually small at ambient pressure due to Coulomb attraction and empty tetrahedral sites. Here again, orientational disorder is a prerequisite for dimer or polymer formation.[4,6,9] The ternary superconductors $Na_2MC_{60}$ ($M$=K, Rb, or Cs) are intermediate cases; their ambient pressure cubic lattice constants lie between those of $C_{60}$ and the rocksalt phases, and they exhibit orientational transitions near room temperature.[10] Thus one might expect pressure-induced dimerization/polymerization to occur at pressures well below that necessary to polymerize $C_{60}$ itself. On the other hand, pressure favors orientational ordering[11,12] which in turn competes with [2+2] cycloaddition. Here x-ray studies show that $Na_2RbC_{60}$ and $Na_2CsC_{60}$ undergo a reversible cubic-orthorhombic transformation at 300 K at pressures $\leq$ 3 kbar. The intermolecular spacing in the orthorhombic structure is 9.35 Å, comparable to that found in the monoanionic polymer[13] and dimer[6] states.

Samples were prepared either by reacting NaH, $M_6C_{60}$ ($M$=Rb, Cs), and $C_{60}$,[14] or directly reacting alkali metals with $C_{60}$ in swaged evacuated copper tubes.[15] Superconducting quantum interference device measurements on samples from the same batch revealed superconductivity at onset temperatures close to 3.4 and 11.7 K for $Na_2RbC_{60}$ and $Na_2CsC_{60}$, respectively.[15] Doped powders were then loaded into Merrill-Bassett diamond-anvil cells in a glove box under an Ar atmosphere. Mineral oil or 1:1 pentane/isopentane was used as pressure-transmitting media and either a small amount of $CaF_2$ or a ruby chip was introduced to monitor the pressure. X-ray measurements were carried out at the X7A beamline at the Brookhaven National Synchrotron Light Source using a horizontally-focussing Si(220) monochromator with a beam width of ~ 0.2 mm and a linear position-sensitive detector. The results for $Na_2RbC_{60}$ and $Na_2CsC_{60}$ were similar, and the discussion will concentrate on the former compound, which Kniaź *et al.* showed to be orientationally ordered with a simple cubic structure at low temperature and 1 atm.[16] Further analysis of these data indicates that at 300 K only ~ 10% of the molecules are in the ordered state, the majority being orientationally disordered with a face-centered-cubic structure, consistent with the rather broad differential scanning calorimetry transition observed slightly above room temperature.[10] The 300 K diffraction pattern at 5 kbar, depicted by the dots in Fig. 1, shows a drastic change from cubic symmetry. The threshold pressure is less than the ~ 3 kbar gasket sealing pressure. The pattern is readily indexable as a body-centered orthorhombic phase, with lattice constants similar to those of the $MC_{60}$ orthopolymer structures,[5,13] and a coherence length estimated to be 400 Å from the peak widths.

In the first stage of the analysis the LeBail technique[17] was used, based on the space group of highest possible symmetry, *Immm*. The best fit gave $a$=9.347(3) Å, $b$=9.898(3) Å, and $c$=14.268(4) Å with $R_{wp}$=2.08% and $S^2_{wp}$=2.67. Systematic deviations were noted around the original cubic peak positions, indicative of ~10% untransformed cubic phase. It is tempting to identify the latter as the orientationally-ordered fraction present at 1 atm. It is interesting to note that when the initial parameters are varied, a local minimum is sometimes observed with $a$=9.661(6) Å, $b$=9.813(6) Å, and $c$=14.193(7) Å for which $R_{wp}$=2.45% and $S^2_{wp}$=3.72. This second set of parameters is very similar to the fundamental cell of the temperature-quenched dimer phase of $KC_{60}$.[6]

To satisfy *Immm* symmetry, the $C_{60}$'s must either be orientationally ordered, with three mutually perpendicular mir-

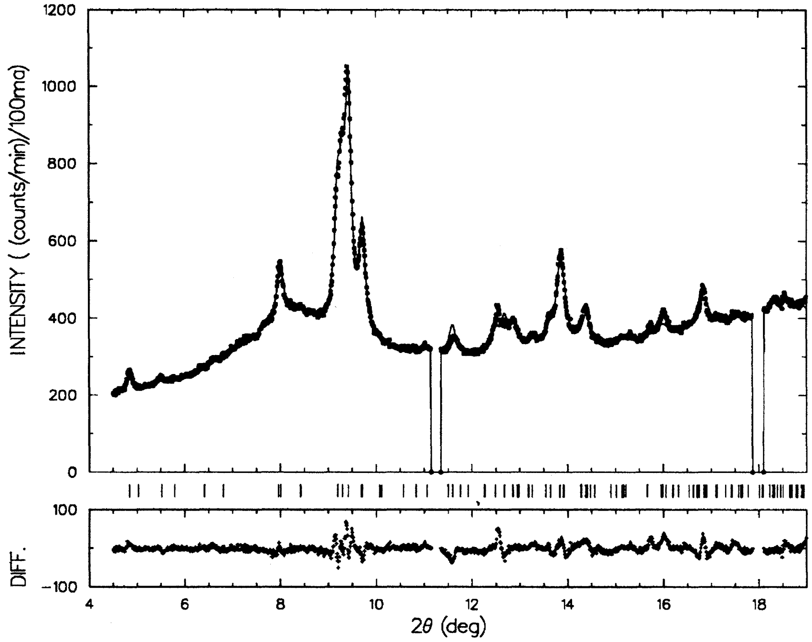

FIG. 1. Synchrotron x-ray powder-diffraction pattern from $Na_2RbC_{60}$ at 5 kbar ($\lambda = 0.6870$ Å). Circles are experimental data and the solid curve is a Rietveld fit based on orthorhombic symmetry *Pmnn* and 45° rotation of $C_{60}$'s. Bragg peak positions are denoted by the markers. Noticeable deviations at the peak positions of the cubic phase are observed, suggesting the presence of a small fraction of undeformed phase. The broad diffuse peak at $2\theta \sim 8°$ was identified as due to an excess of mineral oil and the increasing background at higher scattering angles is from the diamond-anvil cell. Two regions around resolved cubic peaks are excluded.

ror planes normal to the orthorhombic axes in one of the two standard orientations which differ by a 90° rotation, or orientationally disordered as a result of simultaneous rotations of $+\theta$ and $-\theta$ about the polymer chain or *a* axis.[18] The refinement proceeded with the assumption of full orientational order in the primitive space group *Pmnn*, first proposed by Stephens *et al.* for the orthopolymer phases of $MC_{60}$,[13] which allows an arbitrary rotation $\theta$ of the molecule about the *a* axis away from the standard orientations. A subsequent test for orientational disorder was carried out by introducing a similar set of $C_{60}$'s with rotation of $-\theta$ and half overall occupancy. The peak-shape parameters and lattice parameters were held fixed at the values resulting from the LeBail fit, and the initial carbon positions were taken to be those of the undistorted molecule. $Rb^+$ and $Na^+$ ions were initially placed at the high symmetry sites (0,0,1/2) and (0,1/2,1/4), respectively [Fig. 2(b)]. Rotations about *a* at 5° intervals showed an improvement of the fit at $\theta \approx 45°$, as found for the orthopolymer $MC_{60}$ structure.[13] The molecular orientation was then fixed at 45° and the positions of the bridging carbon atom C1 between adjacent $C_{60}$'s [Figs. 2(a) and 2(b)] were refined. A significant improvement was achieved as the distance between neighboring C1 atoms decreased, resulting in a decrease of $R_{wI}$ from 11% to 8%. Carbon atoms connecting C1 [C2 and C3 in Figs. 2(a) and 2(b)] in the $C_{60}$ cage showed similar movements which were judged to be marginally significant, but the refinement was insensitive to the intramolecular C1 distance. Nevertheless, this is a clear indication of bond formation between $C_{60}$ molecules and the distortion of the $C_{60}$ cage as a result of polymerization. The refined bond length (intermolecular C1 spacing) is 1.9(1) Å.

With the $Rb^+$ and $Na^+$ constrained to the high-symmetry sites, large Debye-Waller factors ($B > 10$ Å$^2$) were obtained, indicative of static displacements. Both ions were therefore allowed to relax towards close-packed planes (roughly the $\langle 111 \rangle$ directions in the parent cubic phase), yielding a significant improvement in $R_{wI}$ and a large reduction in $B$ for displacement of octahedral $Rb^+$ to the positions ($\Delta x$, 0, $1/2 + \Delta z$). This can be interpreted as an effect of steric hindrance associated with polymerization, as illustrated in Fig. 2(a). It was not possible to obtain a realistic displacement for the lighter ion $Na^+$ without constraining its Debye-Waller factor, which was set equal to $B(Rb^+)$, due to the strong correlation between the thermal and occupancy factors. Introduction of orientational disorder had no significant effect on the overall quality of the Rietveld fit, indicating the inability of the current data to distinguish $C_{60}$ orientational features. The final refinement yielded $R_I = 5.8\%$, $R_{wI} = 7.0\%$, and $S_{wp}^2 = 4.1$ with the parameters listed in Table I, and the calculated profile is shown as the solid curve in Fig. 1. The projections of the ordered structure are shown in Figs. 2(a) and 2(b).

Similar pressure-induced polymerization was observed in $Na_2CsC_{60}$ and $Na_2C_{60}$, both of which also have orientational transitions near 300 K,[10,19] but with larger ions (Cs) or vacancies in the octahedral sites, respectively. The coherence lengths were considerably shorter than in $Na_2RbC_{60}$ and a full analysis is not yet feasible. The threshold pressures were all less than 3 kbar, while $Na_2CsC_{60}$ transformed somewhat more sluggishly than $Na_2RbC_{60}$. It seems possible that the low-temperature distortion observed in $Na_3C_{60}$ (Ref. 14) may be due to polymerization rather than phase separation.

The formation of dimer and polymer states in quenched $MC_{60}$ is determined not by equilibrium free energies, but by kinetic barriers, in competition with phase separation into $M_3C_{60}$ and the lightly-doped $\alpha$-$C_{60}$ phase.[6] In the present case the competition upon applying pressure is with orientational ordering, in which cubic symmetry is maintained. It is not clear at this point if the trianionic polymer is an equilibrium phase or a kinetically-accessible state. Polymerization of $Na_2RbC_{60}$ occurs quite rapidly (< 3 min) after pressure is applied, and is independent of the two pressure-transmitting media employed. Upon release of the pressure at 300 K, the

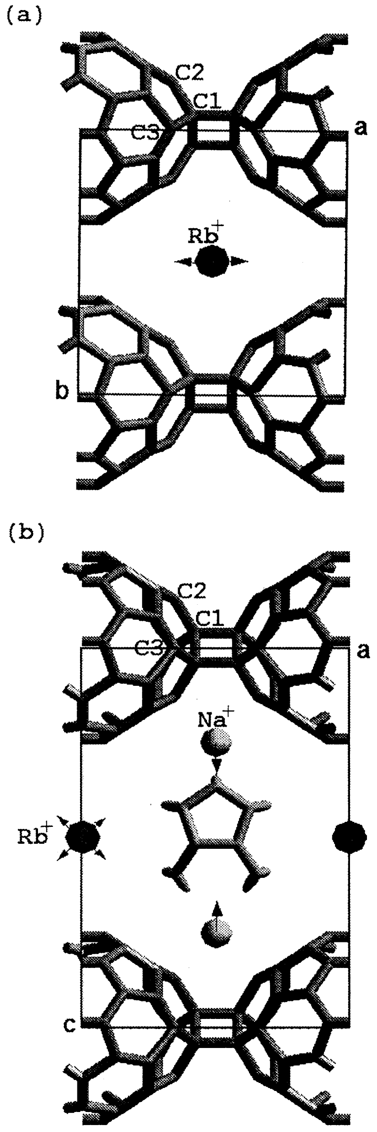

FIG. 2. Schematics of the high-pressure orthopolymer $Na_2RbC_{60}$ structure. (a) (001) and (b) (010) crystallographic planes. In (b), part of the $C_{60}$ molecule at the body center is also drawn to provide a perspective for the crystal packing. Arrows depict major directions of the static displacement of the alkali-metal ions.

original cubic phase with $a=14.08$ Å was almost completely recovered. Both the fast kinetics and the 9.35 Å intramolecular separation are strongly reminiscent of the quenched dimer state of $KC_{60}$.[6] The relatively small displacement required for bonding and the weak intramolecular linkage might be responsible for the fast kinetics.

A critical feature of the formation of this fulleride polymer is the threshold pressure required to induce the transformation, which must be high enough to provide sufficiently close intermolecular contact for bonding, but at the same time low enough not to impede the rotational dynamics required for adjacent molecules to have the proper alignment for [2+2] cycloaddition. It is known from $^{13}C$ NMR that the molecules undergo isotropic rotational diffusion in the precursor monomer states of photopolymerized neutral $C_{60}$ (Ref. 20) and quenched monoanionic rocksalt $MC_{60}$.[21] Neutron inelastic scattering revealed that the high-temperature rotational dynamics of $Na_2MC_{60}$ mimics that of pure $C_{60}$.[22] The same is probably not true for $M_3C_{60}$ at any temperature[23] due to the strong core overlap interaction between tetrahedral $M$ and $C_{60}$ orbitals, which produces deep minima at the two standard orientations.[19] Thus the Coulomb interaction which dominates the orientational potential in compounds with tetrahedral $Na^+$ ions leads to two types of unique behavior relative to the $M_3C_{60}$ phases; orientational order at low temperature, and pressure-induced [2+2] cycloaddition at high temperature.

TABLE I. Refined coordinates of C1, C2, C3, $Rb^+$, and $Na^+$ in the high-pressure polymer phase of $Na_2RbC_{60}$, space group *Pmnn*. The lattice parameters and the peak-shape parameter are fixed at the values resulting from the LeBail fit. The refined parameters are scale factor, C1($x$), C2($x$)[=C3($x$)], $Rb^+$, and $Na^+$ coordinates. The remaining positions are generated based on ideal $C_{60}$ molecular geometry with C-C bond lengths of 1.39 Å and 1.45 Å ($R_I=5.8\%$, $R_{wI}=7.0\%$, and $S^2_{wp}=4.1$).

| | Occupancy | Position ($x,y,z$) |
|---|---|---|
| C1 | 1.0 | 0.40(1), 0.054, 0.037 |
| C2 | 1.0 | 0.34(1), 0.068, 0.129 |
| C3 | 1.0 | 0.34(1), 0.186, 0.002 |
| $Rb^+$ | 0.25 | 0.071(7), 0.000, 0.455(4) |
| $Na^+$ | 0.25 | 0.05(2), ±0.428(7), 0.230(7) |

One may also infer a nonmonotonic dependence on molecular valence of the precursor interball spacing $D$ at which bonding occurs. For *neutral* $C_{60}$, $D=9.62$ Å at the temperature and pressure at which polymerization occurs.[2] The *monoanionic* compound $KC_{60}$ polymerizes from the rocksalt phase at 1 atm near room temperature with $D=9.87$ Å, while for the fcc phase of *trianionic* $Na_2RbC_{60}$ at 300 K, $D=9.95$ Å at ambient pressure. It would be of great interest to search for similar transformations in $MC_{60}$ at high pressure, and in $Na_2MC_{60}$ at high pressure with temperatures both above and below 300 K. $M_3C_{60}$ compounds remain cubic at least up to pressures at which $D=9.76$ Å,[25] no doubt due to the rotational dynamics being frozen out. It would thus be interesting to study $M_3C_{60}$ at high temperature and pressure to extend the study of trianionic polymer formation and its effect on superconductivity.

Mizuki *et al.* have recently reported the pressure dependence of $T_c$ in $Na_2CsC_{60}$.[24] Based on the measured compressibility of $K_3C_{60}$,[25] they deduced a relationship for $T_c$ vs $a$ and claimed that the resulting points fell on a line defined by the 1 atm data for $Na_2CsC_{60}$ and $Na_2RbC_{60}$. It now appears that the lattice parameter they assigned to the end point for the latter compound was underestimated by more than 0.1 Å,[15,26] such that the high-pressure data not only do *not* lie on the above-defined line, but also do not agree with the 1 atm data for the quaternary series $Na_2Rb_xCs_{1-x}C_{60}$.[15] The observation of pressure-induced polymerization in $Na_2MC_{60}$ ($M$=Rb, Cs) emphasizes the need to revisit such pressure studies with careful phase and structural characterizations. One possibility is that Fig. 3 of Ref. 24 depicts $T_c$ of the polymeric state plotted against $a$ of the simple cubic monomer phase. This result now becomes very interesting, since it suggests that superconductivity is retained in the polymeric state (i.e., cubic symmetry is not a prerequisite for fulleride superconductivity). The trianionic polymers thus become prototypes for studies of possible quasi-one-dimensional fulleride superconductivity.[27]

It has been demonstrated that pressure-induced polymerization occurs in the trivalent superconducting compounds $Na_2MC_{60}$. Rietveld refinement reveals the distortion of the $C_{60}$ cage and static displacements of $Rb^+$'s and $Na^+$'s, both consequences of polymerization. The criteria for polymerization to occur are the same for neutral, monovalent, and trivalent $C_{60}$; namely reduced intermolecular spacing and an adequate degree of rotational dynamics, while the barrier apparently decreases with increasing valence. Further investigation of these properties is urgently needed to shed light on the mechanism of fulleride superconductivity.

I am indebted to D. E. Cox and J. E. Fischer for enlightening discussions and a critical reading of the manuscript. I thank M. Rosseinsky, D. Murphy, and T. Yildirim, for providing the samples, and K. Kniaź, T. Yildirim, and A. P. Ramirez for helpful discussions and technical assistance. This work was supported by the U.S. Department of Energy, Division of Materials Sciences under Contract No. DEAC02-76CH00016.

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