## T<sub>c</sub> vs Carrier Concentration in Cubic Fulleride Superconductors

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(Received 27 November 1995)

The effect of carrier concentration on fulleride superconductivity is studied by x ray, Raman, magnetization, and ESR of two new *cubic* families: Na<sub>2</sub>Cs<sub>x</sub>C<sub>60</sub> (0 < x < 1) and  $M_{3-y}$ Ba<sub>y</sub>C<sub>60</sub> (0.2 < y < 2, M = K, Rb, or Cs). These are isostructural with known  $Pa\bar{3}$  and  $Fm\bar{3}m$  trivalent superconductors, respectively, but with variable valence 2 < n < 5.  $T_c$  is peaked at or very near n = 3, decreasing rapidly in either direction to <0.5 K for n = 2.5 and 5. These results underscore the failure of both one-electron and strong correlation models to explain the dependence of  $T_c$  on band filling. [S0031-9007(96)00584-4]

PACS numbers: 74.70.Wz, 74.62.Bf, 74.62.Dh

With rare exceptions, all known fulleride superconductors are either face-centered cubic (fcc) or simple cubic (sc) at  $T_c$ , and contain 3 ions per molecule which singly occupy all the available interstitial sites [1]. Charge transfer is essentially complete, leading to  $C_{60}^{-3}$  trianions according to the frequency of the  $A_g(2)$  Raman mode [2]. Phases which violate one or more of these criteria do not superconduct, and most are not even metallic despite the fact that band structure calculations imply continuous band filling for 0 < n < 6, where *n* is the molecular valence [3]. This has been attributed to on-site electron repulsion comparable to the bandwidth, such that superconductivity occurs in a highly correlated metallic state for some range of *n* while special values of *n* give Mott-Hubbard insulators [4–9].

Experimental tests of these proposals have been frustrated by the lack of an *isostructural* family of compounds in which n can be systematically varied. Thus, for example, the observed nonmetallic behavior of bodycentered tetragonal n = 4 phases could result from a Fermi surface instability [5], but has also been attributed to a small Jahn-Teller gap which closes at modest pressure [10]. The limited solubility of alkali vacancies and interstitials in cubic  $M_3C_{60}$  [11] rules out the tuning of *n* via binary solid solutions (and also explains why many groups using very different synthesis procedures obtain the same  $T_c$ 's). Here we report results from two new cubic fulleride families in which n can be tuned over a wide range. The first,  $Na_2Cs_xC_{60}$  with 0 < x < 1, is derived from our observation that cubic Na2C60 exists and can be *continuously* doped to Na<sub>3</sub>C<sub>60</sub> by inserting Na into octahedral vacancies [12,13], giving access to the range 2 < n < 3 as x varies from 0 to 1. The second,  $M_{3-\nu}Ba_{\nu}C_{60}$ , was motivated by ionic radii (e.g.,  $Ba^{+2} \simeq K^+$ ) which suggested that some combinations

would produce ternary or quaternary phases and/or solid solutions with 3 < n < 5 as y increases from 0 to 2. We find no superconductivity down to 0.5 K in Na<sub>2</sub>Cs<sub>0.5</sub>C<sub>60</sub> (n = 2.5) or  $MBa_2C_{60}$  with M = Rb or Cs (n = 5), or down to 2 K in  $MCsBaC_{60}$  with M = Na or K (n = 4). Furthermore,  $T_c$  in Na<sub>2</sub>Cs<sub>x</sub>C<sub>60</sub> with 0.5 < x < 1 and  $M_{3-y}Ba_yC_{60}$  with  $y \approx 0.3$  is maximum at or very near n = 3, decreasing rapidly as *n* deviates from 3 in either direction. Fulleride superconductivity is thus optimized at or near half filling of the  $t_{1u}$ -derived band, but much more strongly than predicted by band theory.

Gram batches of Na<sub>2</sub>C<sub>60</sub> and Na<sub>2</sub>CsC<sub>60</sub> were first prepared by direct reaction of alkali metals and C<sub>60</sub> in OFHC copper tubes. The x = 0.5 solid solution was obtained by mixing, regrinding, and annealing in pellet form at 550 (1 day), 450 (7 days), and 350 °C (several weeks). This was then mixed with Na<sub>2</sub>C<sub>60</sub> to obtain x = 0.25, etc. In Fig. 1 we show x-ray diffraction profiles of various solid solutions. The peaks are very sharp, indicating good crystallinity and single phase behavior. The crystal structures are very similar to those of  $Na_2C_{60}$  [12,14] and  $Na_2CsC_{60}$ [15,16]. Detailed Rietveld refinements will be presented elsewhere. The basic results are as follows. Na ions fully occupy the tetrahedral sites for all x, while a variable fraction of octahedral sites are occupied by Cs, the refined occupancies being in good agreement with the nominal compositions. At low T the  $C_{60}$ 's are orientationally ordered, space group  $Pa\bar{3}$ , with preferred angles and defect orientations similar to those found in the Na ternaries and quaternaries. The high-T structure is fcc, space group  $Fm\bar{3}m$ , with a first order transition near 300 K for all x. The lattice constant decreases linearly from 14.19 to 14.13 Å as x increases from 0 to 1, confirming solid solution behavior. The lattice contracts upon filling octahedral vacancies with Cs because electrostatic interactions



FIG. 1. X-ray profiles of  $Na_2Cs_xC_{60}$  taken at X7A beam line at Brookhaven National Laboratory with a wavelength of 1.15 Å.

dominate over steric effects. The low- $T Pa\bar{3}$  reflections decrease in intensity as x increases. This we attribute to frustration of the C<sub>60</sub>'s between preferred and defect orientations by octahedral Cs.

Figure 2 shows dc magnetization for samples with x = 1, 0.93, 0.88, and 0.75, indicating that  $T_c$  is very sensitive to *n* near n = 3. We also measured samples with x = 0, 0.25, and 0.5, i.e., n = 2.0, 2.25, and 2.5. For n < 2.5 the magnetization remains near zero down to 0.5 K, indicating that superconductivity is already strongly suppressed relative to n = 3. We emphasize that

these samples all have the same low-T crystal structures and that the (small) increase in lattice constant with decreasing x would drive  $T_c$  in the opposite direction [16]. Thus the dependence of  $T_c$  on n is slightly underestimated in Fig. 2.

One would of course like to know if the nonsuperconducting compositions are metallic. Figure 3 shows the *T*-dependent spin susceptibility and linewidth derived from cw ESR. Solid curves are fits of  $\chi(T)$  with Pauli plus Curie (or Curie-Weiss) terms. For x = 0.75 the Pauli term gives  $N(E_F) \sim 11$  states/eV per molecule (both spins), about 25% less than a similarly obtained value for x = 1. This decreases to  $\sim 7$  and 5 states/eV per molecule at x = 0.50 and 0.25, respectively. The linewidth increases quadratically with *T*, consistent with other metallic fullerides [17]. These results suggest that the system most probably remains metallic down to at least n = 2.25 while superconductivity is lost below n =2.5. Simply scaling the  $N(E_F)$ 's with the BCS formula predicts  $T_c(n = 2.5) = 0.7$  K.

New compounds with n > 3 were prepared by a variety of strategies involving alkali metal or azide, alkaline earth azides, OFHC copper reaction tubes, and pellet pressing. For example, highly crystalline, single-phase RbBa<sub>2</sub>C<sub>60</sub> and CsBa<sub>2</sub>C<sub>60</sub> were prepared by reacting the respective  $MC_{60}$  rock-salt phases [18] with BaN<sub>6</sub>, thus encouraging octahedral occupancy by the alkali metal. These are fcc, space group  $Fm\bar{3}m$ , at high and low *T*, with tetrahedral Ba and octahedral Rb or Cs. The  $A_g(2)$  Raman mode occurs at 1435–1436 cm<sup>-1</sup> indicating n = 5 [2]. Full ionization of Ba is predicted by simple Madelung energy considerations and by a local density approximation (LDA) calculation [19]. dc SQUID and <sup>3</sup>He measurements show that



FIG. 2. Magnetic shielding of  $Na_2Cs_xC_{60}$  measured at 10 G. Sample masses are of order 8 mg so the shielding fractions are of order 90%.



FIG. 3. Spin susceptibility vs T of Na<sub>3</sub>Cs<sub>x</sub>C<sub>60</sub> derived from cw ESR. Bottom right: ESR linewidth vs T.

neither of these compounds superconduct down to 0.5 K. A trivalent  $Fm\bar{3}m$  fulleride with the observed 14.21 Å lattice constant of  $\text{RbBa}_2\text{C}_{60}$  would have  $T_c \sim 17$  K. Neither LDA [19] nor charge contours from x-ray data show any evidence of C-Ba covalent bonding, indicating that the absence of superconductivity is almost certainly due to the deviation of *n* from half filling. A similar procedure ensured octahedral Cs in  $MBaCsC_{60}$  (M = Na or K), except now n = 4, the Raman mode occurs at 1441 cm<sup>-1</sup>, and superconductivity is not observed down to 2 K (<sup>3</sup>He measurements were not performed on this phase). Continuous tuning of n > 3 proved to be more difficult than for n < 3 due to the limited solubility of Ca, Sr, or Ba in  $M_3C_{60}$ , and has yielded only partial success so far. Figure 4 shows representative results for  $M_{3-\delta}Ba_{\delta}C_{60}$  with  $\delta \sim 0.3$ . The magnetization curve (M = K) shows a 5 K depression of  $T_c$  relative to the parent binary (similar data being obtained for M = Rb), while the inset shows the Raman mode at 1444.6 cm<sup>-1</sup> for M = Rb (similar data being obtained for M = K) consistent with an average valence of 3.3-3.4. The reasonable shielding fraction suggests that the depressed  $T_c$  is not a morphology effect but reflects the small deviation from half filling.

Figure 5 summarizes our main point by collecting the results from both families, with the caveat that the n < 3 materials are orientationally ordered ( $Pa\bar{3}$ ) while the mixed alkali–alkaline earth phases with n > 3 are merohedrally disordered ( $Fm\bar{3}m$ ). While it is true that orientational order or disorder affects  $T_c$  quantitatively [16], we believe we are qualitatively correct in concluding that  $T_c$  peaks at or very near n = 3 independent of orientation effects. Further support for this conclusion is the fact that  $M_1C_{60}$  quenched from the  $Fm\bar{3}m$  rock-salt phase does

not superconduct [20]. This result cannot be explained by one-electron band theory or by existing Hubbard models. Band theory predicts neither the sharp decrease of  $T_c$  away from n = 3 nor the lack of superconductivity in RbBa<sub>2</sub>C<sub>60</sub>, Na<sub>2</sub>Cs<sub>0.25</sub>C<sub>60</sub>, etc., since the density of states goes rather smoothly through n = 3 when orientational disorder is accounted for, and increases sharply as n decreases below 3 if orientational order is assumed [19]. It is unlikely that either the phonon spectrum or the electronphonon coupling vary sufficiently drastically with n to explain the results. We can also rule out the effect of chemical disorder, i.e., the fact that the octahedral vacancies are random in the compounds with n < 3 and the partial replacement of Rb by Ba is random in the compound with  $n \approx 3.3$ . Rietveld refinement shows that the n = 5 compound is site ordered, and the  $T_c$  vs lattice constant data for site-disordered alloys such as K<sub>1.5</sub>Rb<sub>1.5</sub>C<sub>60</sub> fall on the same universal curve as their isostructural siteordered relatives, e.g., K<sub>3</sub>C<sub>60</sub>, K<sub>2</sub>RbC<sub>60</sub>, etc. [21].

Calculations based on strong correlations and Hubbard models predict gaps at or near integral values of n, clearly at odds with the data. Lof *et al.* proposed that n = 3 is a Mott-Hubbard insulator, and that superconductivity in " $M_3C_{60}$ " results from accidental vacancies [4]. This is inconsistent with our finding that  $T_c$  is strongly depressed as n deviates from 3 in either direction. Lu suggested that superconductivity is possible at x = 3 for some range of Hubbard parameters [6]. A similar calculation by Gunnarsson, Koch, and Martin suggests that the degeneracy of the half-filled  $t_{1u}$  band ensures metallic behavior at n = 3, whereas n = 1 and 5 lie in the Mott-Hubbard regime [22]. Chakravarty *et al.* proposed a theory in which correlation



FIG. 4. Magnetic shielding of  $K_{2.75}Ba_{0.25}C_{60}$  at H = 10 G. Sample mass ~5 mg, so the shielding fraction is of order 70%. Inset shows the  $A_g(2)$  Raman mode of  $Rb_{2.7}Ba_{0.3}C_{60}$  at 1446.6 cm<sup>-1</sup>, consistent with  $n \approx 3.3$  (dashed curve typifies n = 3).



FIG. 5.  $T_c/T_c^{\text{max}}$  vs conduction electron concentration *n* in fulleride superconductors. Here we scale  $T_c$  vs *n* by the  $T_c$ 's of the end members Na<sub>2</sub>CsC<sub>60</sub> and K<sub>3</sub>C<sub>60</sub>. The heavy line connecting the points is a guide for the eye and indicates upper bounds on the uncertainties in  $T_c$  and *n*.

effects within single molecules play a central role. They predicted that  $T_c$  should peak when there are (approximately) an odd number of electrons per molecule [7], which disagrees with the observed absence of superconductivity in pentavalent RbBa2C60. Finally, Sarker obtained a Hartree-Fock phase diagram for a Hubbard model on the fcc lattice and predicted that  $T_c$  reaches a minimum slightly above 3 electrons/molecule but increases very rapidly on either side of the minimum [8], again in disagreement with our experimental findings. Our results strongly suggest that a correct theory should predict a  $T_c$ which decreases rapidly as the  $C_{60}$  valence deviates from half filling in either direction. Suzuki and Nakao introduced a very general model in which spin fluctuations and dynamic effects introduce a sharp Kondo-type density-ofstates peak at  $E_F$  for  $M_3C_{60}$  [9], in agreement with our finding for n near 3. However, their theory also predicts a sharp peak for n = 1 and 5, in disagreement with our findings for  $MBa_2C_{60}$ .

The usual McMillan formalism has been very successful in explaining many aspects of fulleride superconductivity: isotope effect [23], phonon-mediated coupling [1],  $T_c$  vs lattice constant in orientationally disordered phases [21], and the much steeper  $T_c$  vs *a* behavior in ordered materials [16]. A fuller understanding of variations in  $N(E_F)$  from compound to compound are needed (since the coupling strength and phonon frequencies are believed to be about the same in all fulleride superconductors). For example, a recent NMR study of Na<sub>2</sub>MC<sub>60</sub> [24] confirms our finding that the steep  $T_c$  vs a for  $Pa\bar{3}$  phases results from a steeper dependence of  $N(E_F)$  on a relative to  $Fm\bar{3}m$  phases [16]. Similar experiments [which probe  $N(E_F)$  directly] on the new materials reported here would be of great interest. A correct theory of fulleride superconductivity should predict  $N(E_F)$  decreasing rapidly as the molecular valence deviates from half filling in either direction, possibly due to a unique combination of electron-phonon and electron-electron interactions.

We acknowledge helpful discussions with P.W. Stephens and G. Bendele. This research was supported by the Department of Energy, DEFC02-86ER45254, and benefited from central facility support provided by the National Science Foundation MRL Program under Grant No. DMR91-20668. Carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

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