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Synthesis and properties of mixed alkali-metal–alkaline-earth fullerides

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A new class of fullerides, \( \text{MBa}_2 \text{C}_{60} \) (\( M = \text{K}, \text{Rb}, \text{or Cs} \)) and \( \text{MBaCsC}_{60} \), allows us to study the effect of molecular valence on electronic structure while maintaining the crystal structure of \( \text{M}_3 \text{C}_{60} \) superconductors. X-ray diffraction and Raman scattering show that these are face-centered cubic with pentavalent and quadrivalent \( \text{C}_{60} \)’s, respectively. We find no evidence for superconductivity down to 0.5 K, while electron spin resonance indicates weakly metallic behavior. \(^{13}\)C NMR indicates strong dynamical disorder above room temperature, which may be related to the anisotropic crystal field induced by cations of different valence.

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An important unresolved problem in fulleride superconductivity is elucidating the structural, chemical, and electronic criteria which distinguish these materials from their nonsuperconducting or non-metallic counterparts.\(^1\)–\(^6\) While the cubic trivalent \( \text{M}_3 \text{C}_{60} \)’s are the best understood,\(^1\) there are many other conducting and superconducting phases: \( \text{M}_1 \text{C}_{60} \) polymers,\(^5\) alkaline earth fullerides,\(^6\) and ammonia-alkali metal compounds.\(^7\) These all differ from \( \text{M}_3 \text{C}_{60} \) in important ways (crystal structure, degree of hybridization, molecular valence, solvation effects, filling of higher bands), so that the reasons for the presence or absence of superconductivity cannot be compared between the different materials. Here we report the synthesis and properties of mixed alkali–alkaline-earth fullerides which allows us to manipulate the charge per molecule without changing the basic structure.

Empirical evidence suggests that alkali metal fullerides superconduct only if the lattice is fcc and the average molecular valence \( n = 3 \).\(^8\),\(^9\) There is no definite theoretical understanding of either of these criteria. The search for compounds with \( n 
eq 3 \) is also motivated by predictions of higher \( T_c \)’s,\(^10\),\(^11\) which has not been the case for the alkaline earth binaries, all of which exhibit relatively low \( T_c \)’s. We thus set out to design mixed alkali–alkaline-earth fullerides with three ions but >3 donated electrons per molecule, while remaining isostructural to the fcc alkali fullerides. The ionic radius of \( \text{Ba}^{2+} \) is approximately equal to that of \( \text{K}^+ \), and so we expect Ba to occupy the tetrahedral site with strong preference if the alkali metal is Rb or Cs.

Direct synthesis of alkali–alkaline-earth fullerides by vapor transport is impractical due to extremely large differences in the vapor pressures. This can be avoided by using the azides \( \text{BaN}_3 \) and \( \text{MN}_3 \) instead of pure metals;\(^12\) these were prepared by neutralizing the corresponding hydroxides with 3\% hydrazoic acid \( \text{HN}_3 \). Direct reactions with two azides were unsuccessful, yielding complicated mixed phases including the very stable \( \text{A}_15 \) phase \( \text{Ba}_3 \text{C}_{60} \).\(^13\) This suggested a strategy avoiding all contact between Ba and unreacted \( \text{C}_{60} \). The key was to react Ba with \( \text{MC}_{60} \), which at high temperature has a rocksalt structure with octahedral sites occupied by \( \text{M}^5 \) (K, Rb, or Cs) and the tetrahedral sites vacant.\(^14\) This was done by first reacting \( \text{MN}_3 \) with \( \text{C}_{60} \) powder in evacuated swaged OFHC copper tubes rather than decomposing the azide under dynamic vacuum, with the advantage that there is no risk of losing either powdered material during azide decomposition (in which copious \( \text{N}_2 \) gas evolves). Rapid cooling from this first
step inhibited formation of the polymeric state and ensured that the metastable product was primarily in the rocksalt structure. This was then mixed with $\text{BaN}_6$ powder, reground, and loaded into a OFHC copper foil capsule and compressed into a pellet. The pellet was then heated to 550 °C under dynamic vacuum for 1–2 h until the azide completely decomposed. This second intermediate product was reground and pressed into a new pellet and annealed at 350 °C for several days. This worked well for all three compounds, $M_{2}\text{BaC}_60$ with $M = \text{K}, \text{Rb}, \text{or Cs}$, which have relative proportions consistent with $\text{Ba}^{12}$ and $M^{11}$ (see below).

Conversely, we were unable to obtain $M_{2}\text{BaC}_60$, our initial target for $n = 4$, perhaps because the same $M$ ion must now occupy both octahedral and tetrahedral sites. An obvious solution was to exploit size selectivity, viz., $M\text{BaCsC}_60$ where $M$ is a small alkali metal, Na or K. Again we started from CsC$_60$ ensuring octahedral Cs, and then added $\text{BaN}_6$ and $MN_3$ together in the second step. This yielded single-phase products for $M = \text{Na}$ or K, while phase separation occurred for $M = \text{Rb}$ or Cs.

Figure 1 shows room temperature synchrotron powder x-ray profiles of $M\text{Ba}_{2}\text{C}_60$ ($M = \text{K}, \text{Rb}, \text{and Cs}$) and $K\text{BaCsC}_60$ along with Rietveld refinements and difference curves. Bragg peaks are observed up to very high angles, indicating excellent crystallinity. All patterns can be indexed as fcc. Lattice constants listed in Fig. 1 are all smaller than $K_3\text{C}_60 (14.24 \text{Å})$, while $R(\text{Ba}^{+2}) = 0.02 \text{Å}$ larger than that of K$^+$. We attribute this to the larger Coulomb attraction associated with Ba$^{+2}$. The Rietveld refinements give the expected site occupations listed above, with the caveat that x-rays cannot distinguish Ba$^{2+}$ from Cs$^+$. The observed metal vacancy concentrations are approximately the same as found in $M_3\text{C}_60$.

Rietveld refinements performed both in space group $Fm\bar{3}m$ and $Fm\bar{3}$ [the former describing the merohedral disorder of the $\text{C}_60$ molecules found in $M_3\text{C}_60$ (Ref. 17)] were unable to distinguish between these two cases. A recent neutron diffraction study of Cs$\text{Ba}_{2}\text{C}_60$ finds space group $Fm\bar{3}$ with 87% of the fullerenes in one of the standard orientations and 13% orientational defects in the other. This apparent difference between the merohedrally disordered alkali fullerenes and the present $\text{partial}$ order of the fullerenes is not expected to create the difference in superconducting properties found here.

We turn now to the issue of molecular valence. While there is little doubt that alkali metals are completely ionized,

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FIG. 1. X-ray profiles (dotted) and refinements (solid) of $M\text{Ba}_{2}\text{C}_60$ ($M = \text{K}, \text{Rb}, \text{Cs}$) and $K\text{BaCsC}_60$. $P_I$ is the refined occupancy and $U_I$ is the thermal factor (in Å$^2$) of alkali or alkaline-earth ion $I$. Data collected at National Synchrotron Light Source beamline X3B1 with $\lambda = 0.7 \text{Å}$.

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FIG. 2. Raman spectrum of $M\text{Ba}_{2}\text{C}_60$ and $K\text{BaCsC}_60$. Top panel shows the $A_g(2)$ mode energy vs $\text{C}_60$ valence (Ref. 20); the best linear fit yields $n = 5.0$ and $\sim 4.3$ for nominally pentavalent and quadrivalent fullerenes, respectively.
local density approximation (LDA) calculations for RbBa$_2$C$_60$ and CsBa$_2$C$_60$ measured on superconductors C$_60$ and MBCsC$_60$ and MBa$_2$C$_60$, respectively. This is supported by LDA charge density contours and by resonant photoemission studies of Ba$_x$C$_60$ which indicate no hybridization for x = 3. If the Ba were covalently bonded to C, we would expect it to show up in the Rietveld refinements, either as a lowering of the symmetry from fcc, 5 as positional disorder reflected in large Ba thermal parameters. The best proof that we have indeed realized the desired valence states comes from Raman scattering. Figure 2 shows the A$_g$ modes, measured on the same four samples. These occur at 1435 cm$^{-1}$ and 1441 cm$^{-1}$ for MBa$_2$C$_60$ and KBaCsC$_60$, respectively, indicating pentavalent and quadrivalent C$_60$, according to ~6.3 cm$^{-1}$ redshift per electron relative to neutral C$_60$ (Ref. 20) (shown in the top panel of Fig. 2).

The synthesis of this new family of materials puts us in a position to discuss variations of electronic properties with respect to molecular valence in isostructural compounds. We first searched for superconducting in all four compounds down to 2 K using dc superconducting quantum interference device (SQUID) magnetometry and found no sign of a diamagnetic transition. These were supplemented with ac susceptibility measurements on RbBa$_2$C$_60$ and CsBa$_2$C$_60$ using a $^3$He dilution refrigerator, and again we found no evidence for superconductivity down to 0.5 K. Hence we can report the absence of superconductivity in these new compounds. The Pauli contribution to χ(T) is essentially zero in Na$_2$C$_60$ and K$_4$C$_60$, 25 suggesting that these mixed alkali–alkaline-earth compounds are weakly metallic. At higher temperatures χ increases with $T$ up to 300 K and then slowly decreases, similar to the behavior observed in Na$_2$C$_60$ and K$_4$C$_60$. Differential scanning calorimetry does not show any evidence for a phase transition in MBa$_2$C$_60$ or MBCsC$_60$.

Local fields at the carbon positions are addressed by $^{13}$C NMR. Magic-angle-spinning NMR results for CsBa$_2$C$_60$ are shown in Fig. 4 and are typical of all the mixed alkali–alkaline-earth fullerenes. The 380 K spectrum shows two isotropic motionally narrowed lines with shifts of 157.6 ppm and 177.3 ppm. Fitting with Lorentzian curves for RbBa$_2$C$_60$ and CsBa$_2$C$_60$ shows in Fig. 3 are qualitatively similar to those of Na$_2$C$_60$ and K$_4$C$_60$. From 10 K to 200 K, the product $\chi T$ increases monotonically and continuously with temperature, suggesting a Pauli contribution. Fitting the CsBa$_2$C$_60$ data to Pauli + Curie terms yields $N(E_F) = 2$ states/eV/molecule (both spins) [about one-tenth that of an ESR-derived value 22 states/eV per molecule (both spins) for K$_3$C$_60$ (Ref. 26)] and ~0.01 defects (of spin-1/2) per molecule. Figure 3 suggests that $N(E_F)$ in RbBa$_2$C$_60$ is a further order of magnitude smaller. Within the context of BCS theory, these low values are consistent with the absence of superconductivity. The Pauli contribution to $\chi(T)$ is essentially zero in Na$_2$C$_60$ and K$_4$C$_60$, 25 suggesting that these mixed alkali–alkaline-earth compounds are weakly metallic. At higher temperatures χ increases with $T$ up to 300 K and then slowly decreases, similar to the behavior observed in Na$_2$C$_60$ and K$_4$C$_60$. Differential scanning calorimetry does not show any evidence for a phase transition in MBa$_2$C$_60$ or MBCsC$_60$.

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and so it is plausible to see two resonances with the observed intensity ratio 12/48. Furthermore the latter carbons (C\textsubscript{1} in Ref. 17) are farther from the tetrahedral site and are thus expected to have the smaller shift relative to neutral C\textsubscript{60}, again as observed.

The narrow isotropic lines indicate substantial reorientational dynamics at 380 K, as observed in K\textsubscript{3}C\textsubscript{60}.\textsuperscript{27,28} On the other hand, the observation of two distinct resonances suggests that the two species of carbon atoms, C\textsubscript{1} and C\textsubscript{2}+C\textsubscript{3}, remain distinct in the reorientations. This implies that the reorientational jumps are 90\degree rotations about the cube axes, instead of the smaller rotations observed in K\textsubscript{3}C\textsubscript{60}.\textsuperscript{27} At 300 K each line broadens and/or splits because the more subtle anisotropy of each site becomes visible with reduced orientational averaging. The static spectrum at 300 K (not shown) resembles the MAS spectrum, consistent with a mechanism other than magnetic dipole coupling as the source of the observed broadening.

The observation of the two $^{13}$C NMR lines implies that the crystal field splitting of C\textsubscript{60} states is significantly stronger in MBA\textsubscript{2}C\textsubscript{60} than in M\textsubscript{3}C\textsubscript{60}. This point may be relevant to the absence of superconductivity in the mixed alkali–alkaline-earth fullerides.

The data presented here underscore the fact that we are still far from a complete understanding of fulleride superconductors. The preparation of the new alkali–alkaline-earth-doped phases was motivated by the intention to isolate the role of C\textsubscript{60} valence in fulleride superconductivity. Experiments which probe the metallic state in these new phases, such as NMR $T_1$ vs $T$ and transport measurements, will be of great interest. Clearly, further work is needed to determine if the difference in superconductivity between these materials and the trivalent fullerides is solely due to the change in the charge state of the fullerene.

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16. Traces of a minority phase give rise to weak broad peaks near 2\theta$–10\degree$ in all the MBA\textsubscript{2}C\textsubscript{60}’s. The most likely candidate is a poorly crystalline decomposition product of Ba\textsubscript{3}N\textsubscript{2}; N.E. Brese and M. O’Keeffe, in *Structure and Bonding*, edited by M.J. Clarke *et al.* (Springer, 1992), Vol. 79, pp. 306–378.