decrease with increasing alkanoate chain length; however, $k_{cat}/K_M$ maximizes at $n = 14$. These parameters are consistent with effective binding of substrate to catalyst and efficient catalysis of hydrolysis ($t_{1/2}$ for **1** ($n = 14$) is 15 s at [cat.] = $1.0 \times 10^{-5}$ M). The factors that control substrate selectivity in **4** are believed to be those responsible for enzyme specificity.[16]

The performance of **4** as a *p*-nitrophenyl esterase was compared with those of cholesterol esterase ($k_{cat}/K_M = 125 \times 10^4$ M$^{-1}$ s$^{-1}$)[28] and chymotrypsin ($k_{cat}/K_M = 7.6 \times 10^4$ M$^{-1}$ s$^{-1}$).[29] The enzymic reactions are only moderately faster and show optimum activity with substrates of shorter chain length (**1**, $n = 6$, for cholesterol esterase and **1**, $n = 7$, for chymotrypsin). An important distinction between **4** and the enzymes is that the latter utilize bifunctional catalysis with histidine imidazole and serine hydroxyl as key participants.[16,28]

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**Supplementary Material Available:** Plot of $1/V$ vs $1/[S]$ for **1** ($n = 14$) in the presence of **4** and tables that list Michaelis–Menten parameters for hydrolysis of **1** ($n = 12, 14, 16$) in the presence of **4** and compare **4** with cholesterol esterase, chymotrypsin, and active synthetic catalysts as a *p*-nitrophenyl esterase (4 pages). Ordering information is given on any current masthead page.

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# Synthesis, Structure, and Superconducting Properties of Single-Phase $Rb_3C_{60}$. A New, Convenient Method for the Preparation of $M_3C_{60}$ Superconductors

John P. McCauley, Jr.,[†] Qing Zhu,[†] Nicole Coustel,[†]
Otto Zhou,[†] Gavin Vaughan,[†] Stefan H. J. Idziak,[†]
John E. Fischer,[*,†] S. W. Tozer,[‡] David M. Groski,[‡]
Nicholas Bykovetz,[†,§] C. L. Lin,[∥] Andrew R. McGhie,[†]
Brent H. Allen,[†] William J. Romanow,[†]
Arnold M. Denenstein,[†] and Amos B. Smith, III[*,†]

*Departments of Chemistry, Physics, and Materials Science*
*Laboratory for Research on the Structure of Matter*
*University of Pennsylvania*
*Philadelphia, Pennsylvania 19104*
*Central Research and Development Department*
*E. I. du Pont de Nemours & Co., Inc.*
*Experimental Station, Wilmington, Delaware 19880*
*Department of Physics, Temple University*
*Philadelphia, Pennsylvania 19122*

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Several synthetic procedures have been developed to produce alkali metal intercalated fullerite superconductors ($M_xC_{60}$, $x = 3$). The UCLA version[1] of the original AT&T method[2] (vapor-phase reaction of stoichiometric amounts of M = K or Rb and $C_{60}$) is thus far the only protocol demonstrated to yield phase-pure material (i.e., $K_3C_{60}$).[3] A significant drawback of this method is the limited accuracy of stoichiometric control when only modest quantities of $C_{60}$ are used (e.g., 3 mg of K + 20 mg of $C_{60}$). Moreover, we have been unable to completely reproduce the UCLA results using our $C_{60}$ powder (ca. 1500 Å crystallite size, which according to the described doping model[1] may be an important processing variable). Solution techniques[4] promise greater versatility but also present problems of stoichiometric control. The difficulty of accurately weighing small amounts of reactive metals was reportedly overcome by treating $C_{60}$ with alkali/heavy metal amalgams. Exploiting this approach, Kelty et al.[5] claim that the heavy metal acts merely as a spectator. However, Kraus et al.[6] find from weight uptake measurement that the heavy metal Tl is co-intercalated from the KTl (1.5) amalgam; the latter depresses the $T_c$ value to 17.6 K from 19.3 K for the $K_3C_{60}$ binary compound.[3] In all of these methods, the final product of desired stoichiometry ($x$) may be thermodynamically or kinetically limited by miscibility gaps in the binary phase diagram.

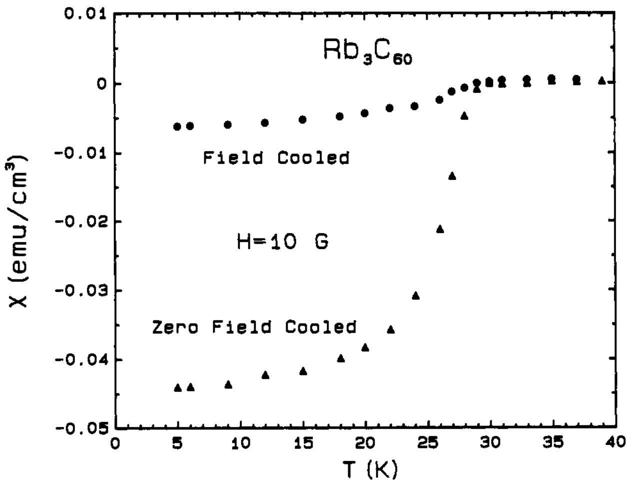

Figure 1. Diamagnetic susceptibility of $Rb_3C_{60}$ (uncompacted powder, 3.5 mg). Circles: field cooled. Triangles: zero field cooled.

We describe here a new vapor-transport technique for producing $M_xC_{60}$. Stoichiometric control of small batches is markedly improved by reacting pristine $C_{60}$ with the saturation-doped product,[7] which simply requires weighing two aliquots of $C_{60}$[8] outside the drybox. A weighed amount of $C_{60}$ is treated with a large excess of alkali metal at 225 °C under vacuum. A small temperature gradient during cooldown prevents condensation of excess metal onto the powdered product. The crystallographic composition is $M_6C_{60}$, whereas repeated weight uptake measurements (K, Rb, or Cs) give $x$ in the range 6.4–6.7.[7,9] This air-sensitive material is then diluted with $C_{60}$ in the drybox to give a desired $x$. The two powders are ground together, sealed under vacuum, heated for 24 h at 250 °C, and then further annealed for 24 h at 350 °C, followed in some cases by 1 h at 400 °C or longer periods at 350 °C. Annealing is crucial to the process since the initial treatment usually yields a multiphase mixture. Extended annealing

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[†] Departments of Chemistry, Physics, and Materials Science, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104.

[‡] Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc., Experimental Station, Wilmington, DE 19880.

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(9) Further analysis of the X-ray data is underway to determine if this "excess" metal exists in defect sites in the bcc structure.

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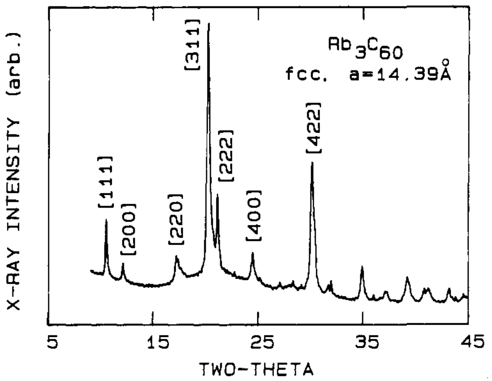

**Figure 2.** X-ray powder profile of $Rb_3C_{60}$, taken on beam line X10A at the National Synchrotron Light Source, Brookhaven National Laboratory; wavelength 1.5289 Å.

was also found necessary by the UCLA group to obtain large diamagnetic shielding fractions at nominal $x = 3$.[1]

We have successfully prepared single-phase $K_3C_{60}$ and $Rb_3C_{60}$ using this technique, the latter apparently for the first time.[10] Figure 1 shows SQUID (superconducting quantum interference device) magnetometer results for a typical $Rb_3C_{60}$ sample [3.5 mg, crystallographic density 2.17 g/cm$^3$ (vide infra)]. The shielding diamagnetism (zero field cooled) is 60% of the ideal value ($1/4\pi$), and the transition onset ($T_c = 29.8$ K) is quite sharp. Previous susceptibility data for $Rb_xC_{60}$ superconductors gave only 1% shielding and a broad transition,[11] or 7% shielding.[1] The limited Meissner fraction (field-cooled signal, 8% of ideal value) that we observe here would no doubt be improved by measurements on a compacted pellet.[12] Typical results for $K_3C_{60}$ prepared via our dilution protocol are 38% shielding fraction and $T_c = 19.6$ K.

For $Rb_3C_{60}$, synchrotron X-ray powder diffraction reveals a structure analogous to that of $K_3C_{60}$.[3] Detailed analysis will be described elsewhere. Figure 2 shows the experimental profile. The face-centered-cubic lattice constant is 14.39 Å, slightly larger than the 14.24 Å found (and confirmed by us) for $K_3C_{60}$.[3] This would appear to support the conjecture that the higher $T_c$ obtained with Rb doping is due to reduced molecular overlap relative to $K_3C_{60}$.[4] On the other hand, preliminary analysis of integrated intensities is equally consistent with complete molecular orientational disorder (as in pristine $C_{60}$[13]), or with a statistical distribution between two fixed orientations.[3] This leaves open the possibility that there may be important differences in the dynamics of $K_3C_{60}$ and $Rb_3C_{60}$ which could also contribute to different superconducting properties.

The dilution technique described here also permits the systematic preparation of varied, accurate stoichiometries other than $x = 3$, thus providing a convenient method to explore the phase boundaries between undoped and $x = 3$ fcc phases, and between $x = 3$ fcc and $x = 6$ body-centered cubic,[7] without sacrificing large amounts of $C_{60}$. The utility of this approach has already been demonstrated in the process of optimizing the synthesis of $Rb_3C_{60}$. For example, some of the reflections in Figure 2 exhibit high-$Q$ shoulders which we attribute to the presence of a small amount of a dilute fcc phase resulting from a small error in stoichiometry (i.e., for this sample the actual $x = 3 - \epsilon$). The shoulder is particularly notable on the 220 reflection near $2\theta = 17°$; a similar shoulder is apparent in the $K_3C_{60}$ data in ref 3. The implication is that the miscibility gap, implied by photoemission results,[14,15] does not cover the entire range $0 < x < 3$. Furthermore, these shoulders are absent in a slightly "overdoped" sample ($x = 3 + \epsilon$), which instead shows reflections of a second phase of symmetry lower than cubic. Increasing the design stoichiometry to $x = 4$ allowed us to isolate this new, body-centered-tetragonal, nonsuperconducting phase, which will be described in detail elsewhere.[10b] Extension of this new approach to the preparation of ternary compounds[16] will be straightforward.

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## Direct Yb–Fe Interaction in an Organometallic "Ladder Polymer": Synthesis and Structure of $\{[(CH_3CN)_3YbFe(CO)_4]_2{\cdot}CH_3CN\}_\infty$

Haibin Deng and Sheldon G. Shore*

*Department of Chemistry, The Ohio State University*
*Columbus, Ohio 43210*

*Received March 25, 1991*

Metal–metal interactions involving lanthanides and transition metals are rare in organometallic chemistry.[1-3] Although such interactions have been reported by several authors on the basis of infrared and $^1$H NMR spectroscopic data,[2] confirmation through diffraction studies is scarce.[3] A direct $Lu^{3+}$ to Ru bond of 2.955 (2) Å in $[Cp_2(THF)LuRu(CO)_2Cp]$ determined by an X-ray analysis was recently reported;[3a] however, neither an ORTEP drawing nor structural details were given. Divalent lanthanide to transition metal bonds have not been structurally characterized. Since divalent lanthanides are softer Lewis acids than trivalent lanthanides, they are expected to form more stable metal–metal bonds with low-valent transition metals that are soft bases.[4]

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