

Structures and phases of superconducting alkali-metal doped  $C_{60}$ 

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A simple model for the energetics of solid doped  $A_xC_{60}$  is sufficient to understand the evolution of structures for  $0 \leq x \leq 6$ . The contributions found to be most important are hard-sphere packing constraints, the van der Waals energy, the Madelung energy, and geometric relationships between the atomic arrangements on the surface of the icosahedron and neighboring  $C_{60}$  molecules and dopants. At  $x = 3$  the  $A15$  structure is energetically competitive, despite its larger atomic volume, and is favored for higher values of  $x$  since it has more sites available for dopants. Analysis of the available experimental data and the well-known near instability of the  $A15$  structure suggest that the superconductivity in  $K_xC_{60}$  for  $x$  near 3 is influenced by a connected but poorly ordered metastable matrix with the  $A15$  structure, which may be difficult to detect using conventional crystallographic techniques. The present model explains the large jump in Meissner volume at  $x = 3$ , the negative sign and large magnitude of  $dT_c/dp$ , and the Raman spectrum at  $x = 3$ . Similarities with structures of other exotic materials also follow from the model.

The discovery of superconductivity<sup>1</sup> in  $A_xC_{60}$  ( $A = K, Rb, x \approx 3$ ) has already uncovered a by now familiar collection of anomalous properties. Here we propose a structural model based on lattice instabilities analogous to models already proposed for the layered cuprates, the  $(Ba, K)(Pb, Bi)O_3$  perovskites, and the chalcogenide Chevrel phases. This model provides a unified description of the anomalies and enables us to identify which features of  $A_xC_{60}$  are genuinely distinctive. We believe our model will help to clarify the experimental situation specifically in  $A_xC_{60}$  and more generally in all high-temperature superconductors.

The characteristic feature of high- $T_c$  superconductors<sup>2</sup> is defect enhancement of  $N(E_F)$ , the electronic density of states  $N(E)$  at the Fermi energy  $E_F$ . In general such enhancement by Fermi-energy pinning leads to Jahn-Teller distortions (lattice instabilities<sup>2</sup>) which split the peak in  $N(E)$  at  $E = E_F$  into two components, bonding and antibonding, in a way that drastically reduces  $N(E_F)$ , possibly to zero (metal-insulator transition). The task of a structural model is to provide a mechanism which retains a large  $N(E_F)$  in sufficiently large and connected regions of the sample as to produce macroscopic superconductivity. As experience has shown, the structures of high- $T_c$  superconductors are complex and often metastable, and evidence for a structural model must be gathered from not one but many experiments.

To provide a framework for our discussion we have calculated electrostatic energies for several crystalline models of  $A_xC_{60}$  ( $A = K, Rb$ ) with  $x = 0, 1, 2, 3 - \epsilon$  and  $3 + \epsilon, 4, 5$ , and 6. In the range  $0 \leq x \leq 3$  the  $C_{60}$  sublattice is fcc, while for  $3 < x \leq 6$  it is bcc. Attention is focused on  $x = 3$ , where a recent diffraction study<sup>3</sup> has suggested that the correct structure is fcc  $C_{60}$  with its octahedral and tetrahedral voids filled by  $A^+$  (the  $BiF_3$  structure). We refer to this as the  $(3 - \epsilon)$  structure and compare it to

the  $(3 + \epsilon)$  structure, which is the  $A15$  or  $Nb_3Sn$  structure. We have focused on this alternative structure, which has not been identified by diffraction, for several reasons. The known<sup>4</sup> insulating structure for  $x = 6$  is bcc  $C_{60}$  with  $A$  atoms forming rectangular crosses in the faces of these cubes. Removal of half of the  $A$  atoms in suitable pairs, together with small displacements of the remaining  $A$  atoms, yields the  $A15$  structure, known (because of the linearity of the  $A$  chains)<sup>2</sup> to be favorable for high  $T_c$ . Also removal of one-third of the  $A$  atoms ( $A_4C_{60}$ ) in pairs yields a body-centered tetragonal analogue of the  $A15$  structure.<sup>5</sup> Second, the materials as prepared are not in equilibrium and the alkali concentration must vary locally. When  $x$  locally exceeds 3, the fcc structure becomes energetically unfavorable. Therefore the nominal  $x = 3$  samples are almost certainly biphasic and should be some kind of metastable mixture of the  $(3 - \epsilon)$  ( $BiF_3$ ) and  $(3 + \epsilon)$  ( $Nb_3Sn$ ) phases.

Quantitative support for this picture is provided by our estimates of the total energy of each phase. We believe that this energy is dominated by the electrostatic contribution, because the orientational and van der Waals energies are small ( $< 0.1$  eV per unit cell). The simplest way to calculate the electrostatic energy is to sum the ionic Madelung energy and the electrostatic self-energy of the  $C_{60}^{x-}$ . When a classical point-charge model is used for the self-energy,<sup>6</sup> one finds that the  $x = 1$  (2) phases with octahedral (tetrahedral) void filling are unstable against disproportionation into  $x = 0$  and 3. (The band-structure energy associated with occupying the threefold-degenerate lowest unoccupied molecular orbital<sup>7</sup> of  $C_{60}$  can be simply modeled, using the molecular electron affinity, as a linear function of  $x$ . Within this approximation, the band-structure energy does not affect conclusions about phase stability.) We have used a more realistic self-energy model with the  $(x -)$  charge uni-

formly spread over the  $C_{60}$  sphere. With this model, we find the surprising result shown in Fig. 1, namely, now the  $x=1$  and 2 structures are at best only marginally stable at  $T=0$ , and so far they have not been observed. With a lattice constant chosen to give the same center-to-center  $C_{60}$  spacing, the electrostatic energy is 2% smaller in magnitude for the  $(3+\epsilon)$  structure than the  $(3-\epsilon)$  structure.

We now suppose that near  $x=3$  the structure consists of well-ordered  $(3-\epsilon)$  crystallites embedded in a highly strained but still distinguishably  $(3+\epsilon)$  matrix. The former are responsible for the reported<sup>3</sup> " $x=3$ " diffraction pattern, but their  $T_c$  may be lower than that of the  $3+\epsilon$  matrix, because the softness of the latter, which accounts for its highly strained character, also gives rise to a much larger electron-phonon interaction.

Generally speaking, our two-phase model resolves a number of experimental anomalies. In particular it explains the large jump observed in the Meissner volume fraction<sup>8</sup> in some samples for  $x < 3$  to  $x > 3$ , which is not explicable if the  $BiF_3$  structure has the high  $T_c$ . Second, it explains the very large and negative value  $dT_c/dp = -1$  K/kbar recently reported<sup>9</sup> for both  $A=K$  and  $Rb$ . We believe this effect represents the conversion of the less dense metastable  $(3+\epsilon)$  phase to the more dense  $(3-\epsilon)$  phase under pressure. Several microscopic theories<sup>9</sup> predicted  $dT_c/dp > 0$ , while in the Josephson junction model proposed by one of us<sup>10</sup>  $dT_c/dp < 0$  is

possible if the activation barrier  $\Delta E_a$  across the junctions increases with pressure,  $d\Delta E_a/dp > 0$ . However, under pressure the sign is unambiguous in the two-phase model and the large magnitude is what one would expect for transformation of a metastable phase, with a typical transformation pressure over laboratory times of 20–30 kbar. Raman scattering from some samples shows two overlapping Raman bands, one broad and one narrow, which we assign to the  $x=|3\pm\epsilon|$  phases, respectively, but which later were shown to be due to oxygen contamination.<sup>11</sup>

the temperature and composition dependence of the normal-state electrical resistivity.<sup>12</sup> These show that  $\Delta E_a = 0.2 \text{ eV} + a_{\pm}|x-3|$  with  $a_+$  nearly equal to  $a_-$ . The insulating character of the undoped  $x=0$  and the ionic  $x=6$  phases is easy to understand, but with mixed phases ordinary percolation theory would predict that the resistivity itself, and not  $\Delta E_a$ , would be linear in  $|x-3|$ . We suggest that the randomness of individual resistors assumed by the classical model may not be correct, and instead a graded distribution of  $\Delta E_a$ , centered on the mean  $\Delta E_a$ , is a better assumption. Of course, this would fit the data, and it is physically plausible because  $\Delta E_a$  plays an important role in calculating the electronic polarizability and correlation energy. Another question is the meaning of  $\Delta E_a = 0.2 \text{ eV}$  at  $x=3$ . This cannot be a bulk activation energy, or the samples would not be superconductive. It seems most likely to us that this represents an intergranular energy associated with residual oxygen, for which indications have been observed in high-pressure data.<sup>9</sup> The thickness of the surface oxide layers may also increase with  $|x-3|$ .

Metastable biphasic behavior, as postulated here for the  $(3\pm\epsilon)$  phases, is quite common in solids formed by nucleation and growth which are vicinal to a lattice instability, whether crystalline or glassy. To reduce the strain energy, one phase is usually rigid while the other is much softer (large and small values of  $N_c - N_d$ , where  $N_c$  and  $N_d$  are the numbers of constraints and degrees of freedom per atom, respectively<sup>13</sup>). We list in Table I many such examples.<sup>14–23</sup> In the case of metallic glasses the mixed structure is generally associated with a deep eutectic, obviously favorable for forming a metastable material. Progress in understanding this behavior in the cuprates<sup>2</sup> has been slowed because of their complex crystal structures. In this respect both the Chevrel compounds and  $A_xC_{60}$  are especially instructive examples because of their simpler structures. The generality of the phenomenon, however, is evident from Table I, which shows that it is not restricted to ferroelectric or superconductive perovskite or pseudoperovskite oxides. The general principle underlying all these structures is their two-component character, that is, the rigid elements provide a framework, over which the soft elements are draped.<sup>15</sup>

In the absence of this framework the superconductive soft materials would undergo Jahn-Teller distortions which would greatly reduce  $N(E_F)$  and suppress  $T_c$ .

We conclude by remarking that while not all the elements of our model have been observed directly, this is not surprising, since (for example) the well-ordered  $(3-\epsilon)$  crystallites will always dominate the less-ordered

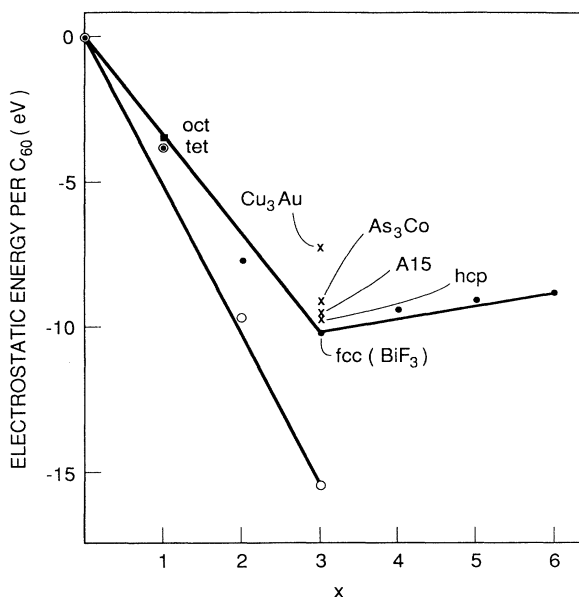


FIG. 1. Our calculation of the electrostatic energy treating  $C_{60}^{x-}$  as a uniformly charged spherical shell (filled circles) rather than as a spherical shell with  $x$  classical point charges in the minimum energy configuration (Ref. 5) (open circles). The structures for  $x=4$  and 5 are obtained from the  $A15$  structure by completing 1 and 2 dopant crosses, respectively. The relative shifts of the electrostatic energy of alternative  $x=3$  phases are shown by the crosses.

TABLE I. Bistructural elements in glasses and marginally stable crystals. In each case rigid and soft elements combined characterize structure and properties.

Property	Material	Rigid	Soft	Ref.
Electrolyte	<i>c</i> -RbAg <sub>4</sub> I <sub>5</sub>	RbI	AgI	14,15
Metallic glass	<i>g</i> -Pd <sub>0.82</sub> Si <sub>0.18</sub>	Pd <sub>3</sub> Si	Pd	14,16
Covalent glass	<i>g</i> -GeSe <sub>4</sub>	GeSe <sub>2</sub>	Se	17
Stable quasicrystal	<i>q</i> -Al <sub>65</sub> Cu <sub>20</sub> Fe <sub>15</sub>	Al <sub>6</sub> Cu <sub>3</sub> Fe	Fe <sub>2</sub> Al <sub>4</sub>	18
Viscous melt	<i>l</i> -GeSe <sub>2</sub>	Ge <sub><i>n</i></sub> Se <sub>2<i>n</i>+2</sub>	Ge <sub>2</sub> Se <sub>6</sub>	17,19
Insulator	<i>c</i> -BaMo <sub>6</sub> S <sub>7.8</sub> O <sub>0.2</sub>	BaO	BaS	10,20,21
Superconductor	<i>c</i> -PbMo <sub>6</sub> S <sub>8-x</sub> O <sub>x</sub>	Mo <sub>6</sub> S <sub>7</sub> O	PbS	10,20,21
Superconductor	<i>c</i> -YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-x</sub>	CuO <sub>2</sub>	CuO <sub>1-x</sub>	2,23
Superconductor	<i>c</i> -YBa <sub>2</sub> (Cu,Zn) <sub>3</sub> O <sub>7-x</sub>	CuO <sub>2</sub>	ZnO	10
Superconductor	A <sub>3</sub> C <sub>60</sub>	A <sub>3-ε</sub> C <sub>60</sub>	A <sub>3+ε</sub> C <sub>60</sub>	

(3+ε) matrix not only in diffraction but also in many other experiments (such as NMR) as well. The absence of diffraction or NMR signatures of the disordered component therefore has no significance because the Meissner volume is measured on the scale of the penetration depth, which is expected to be much larger than the scale of biphasic separation. On the other hand, the ability of the metastable biphasic model to resolve anomalies in homogeneous models of the properties of exotic materials is, as described above, by now very well documented. This suggests that a biphasic model should provide the pre-

ferred description of these materials until it is proved that these anomalies can be resolved with homogeneous models.

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- <sup>1</sup>A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature* **350**, 600 (1991); M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhija, *Phys. Rev. Lett.* **66**, 2830 (1991).
- <sup>2</sup>J. C. Phillips, *Physics of High-T<sub>c</sub> Superconductors* (Academic, Boston, 1989), pp. 2, 31, 42, 70, 78, 81, 172, 174, 201, 221, and 298.
- <sup>3</sup>P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Diedrich and K. Holczer, *Phys. Rev. B* **45**, 543 (1992).
- <sup>4</sup>O. Zhou, J. E. Fischer, N. Constel, S. Kycia, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley, Jr., A. B. Smith III, and D. E. Cox, *Nature* **351**, 462 (1991).
- <sup>5</sup>R. M. Fleming *et al.*, *Nature* **352**, 701 (1991).
- <sup>6</sup>R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, R. M. Fleming, and A. Ramirez, *Phys. Rev. Lett.* **68**, 1912 (1992).
- <sup>7</sup>S. Saito and A. Oshiyama, *Phys. Rev. Lett.* **66**, 2637 (1991).
- <sup>8</sup>K. Holczer, O. Klein, S.-M. Huang, R. B. Kaner, K.-J. Fu, R. L. Whetten, and F. Diedrich, *Science* **252**, 1154 (1991).
- <sup>9</sup>G. Sparr, J. D. Thompson, S. M. Huang, R. B. Kaner, F. Diedrich, R. L. Whetten, G. Gruner, and K. Holczer, *Science* **252**, 1829 (1991).
- <sup>10</sup>J. C. Phillips, *Solid State Commun.* **80**, 517 (1991).
- <sup>11</sup>S. J. Duclos, R. C. Haddon, S. Glarum, A. F. Hebard, and K. B. Lyons, *Science* **254**, 1625 (1991); *Solid State Commun.* **80**, 481 (1991).
- <sup>12</sup>G. P. Kochanski, A. F. Hebard, R. C. Haddon and A. T. Fiory, *Science* **255**, 184 (1992).
- <sup>13</sup>J. C. Phillips and M. F. Thorpe, *Solid State Commun.* **53**, 695 (1985).
- <sup>14</sup>J. C. Phillips, *Comments Solid State Phys.* **10**, 85 (1981).
- <sup>15</sup>J. C. Phillips, *J. Electrochem. Soc.* **123**, 934 (1976).
- <sup>16</sup>R. M. Walser and R. W. Bene, *Appl. Phys. Lett.* **28**, 624 (1976).
- <sup>17</sup>J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979); P. Boolchand, J. Grothaus, and J. C. Phillips, *Solid State Commun.* **45**, 183 (1983).
- <sup>18</sup>J. C. Phillips and K. M. Rabe, *Phys. Rev. Lett.* **66**, 923 (1991).
- <sup>19</sup>I. T. Penfold and P. S. Salmon, *Phys. Rev. Lett.* **67**, 97 (1991).
- <sup>20</sup>R. Bailiff, A. Dunond, J. Müller, and K. Yvon, *Phys. Rev. Lett.* **47**, 672 (1981).
- <sup>21</sup>H. Nohl, W. Klose, and O. K. Andersen, in *Superconductivity in Ternary Compounds I*, edited by O. Fischer and M. B. Maple (Springer-Verlag, Heidelberg, 1982), p. 165.
- <sup>22</sup>D. G. Hinks, J. D. Jorgensen, and H. C. Li, *Phys. Rev. Lett.* **51**, 1911 (1983).
- <sup>23</sup>J. C. Phillips, *Phys. Rev. Lett.* **64**, 1605 (1990).