

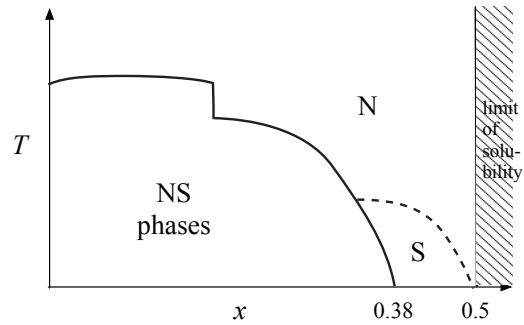
## Non-cuprate exotics I: BKBO, MgB<sub>2</sub>, alkali fullerenes

BKBO (Ba<sub>1-x</sub>K<sub>x</sub>BiO<sub>3</sub>)\*: discovered to be superconducting in 1988, with a  $T_c$  which (eventually) reaches 34 K, which would have been spectacular news a few years earlier. Structure of BaBiO<sub>3</sub> is cubic perovskite (ABO<sub>3</sub>), with Ba at the center and Bi in the ‘corner’ positions. K goes in Ba sites: lattice parameter is 4.27 – 4.29 Å depending on K components. Pure BaBiO<sub>3</sub> is not superconducting.†  $T_c$  is a strong function of  $x$ , with max of  $\approx 39$  K at  $x = 0.375$ .

Normal-state properties: symmetry is cubic (obviously!): d.c. resistivity  $\rho$  is sometimes metallic, but also in some samples semi-conducting, probably due to mixture of phases:  $\rho(T_c+) \approx 15$  mΩ cm (roughly comparable to cuprate ab-plane value). Band structure calculation indicates conduction band is hybridized Bi(6s)-O(2p), and nearly parabolic.

In the superconducting state material is quite strongly type-II, with  $H_{c1} \approx 42$  mT at  $T = 0$  and  $H_{c2}$  reported in the range 10–30 T; this would correspond to a  $T = 0$  penetration depth  $\lambda_0 \approx 3350$  Å and a  $T = 0$  coherence length  $\xi_0 \approx 30 - 60$  Å (both comparable to cuprate ab-plane properties). The highest  $J_c$  measured (in films) is  $> 3 \times 10^6$  A/cm<sup>2</sup>.

Diagnostics: tunneling experiments yield fairly ‘clean’ gap (i.e. little DOS at energies  $< \Delta$ ) with  $2\Delta/k_B T_c \approx 3.7 - 4.0$  (BCS: 3.5). Substitute of O<sup>17</sup> gives isotope effect with  $\alpha = 0.41 \pm 0.03 \Rightarrow$  BCS, phonon mechanism, s-wave pairing. (Historical anomaly only).



### MgB<sub>2</sub>††

Discovery of superconductivity: 2001 (*almost* discovered in 1957!); most standard experiments already done by early 2003. (though mostly on polycrystalline samples).

Structure: honeycomb lattice of B atoms interleaved with hexagonal lattice of Mg atoms, thus 3 atoms per hexagonal unit cell. Conventional notation: ab-axes in plane, c-axis perpendicular. *Normal state* properties pretty much textbook:  $\rho(300\text{K}) \sim 10 \mu\Omega$  cm,  $\rho(40\text{K}) \sim 0.4 \mu\Omega$  cm (comparable to Cu): since  $v_F \sim 5 \times 10^7$  cm/sec  $\Rightarrow l \sim 600$  Å. (but these are isotropic averages).

*Superconducting state*:  $T_c \approx 40$  K (highest intermetallic  $T_c$  to date: Nb<sub>3</sub>Sn is 23 K).  $H_{c2}$  strongly anisotropic:  $H_{c2\parallel}$  (i.e. for  $\mathbf{H} \parallel \mathbf{c}$ )  $\sim 2.5$  T,  $H_{c2\perp}$  ( $\mathbf{H}$  in ab-plane)  $\sim 16$  T  $\Rightarrow \gamma \equiv H_{c2\perp}/H_{c2\parallel} \sim 6 - 7$ . Value of  $H_{c2\parallel} \Rightarrow \xi_0 \sim 50$  Å ( $\ll l$  so in clean limit). (However, there is a complication, see below).  $\lambda(T = 0) = 1400$  Å  $\Rightarrow$  strongly type-II,  $J_c \sim$  a few  $\times 10^6$  A/cm<sup>2</sup>. (lower than Nb<sub>3</sub>Sn at a few K, but still not bad).

\*Ref.: B.A. Baumert, J. Sup. **8**, 175 (1995). [original paper: R.J. Cava et al., Nature **332**, 814 (1986)]

†but BaPbBiO<sub>3</sub> known to be superconducting with 13 K.

††The most accessible review is Canfield and Crabtree, Phys. Today March 03. The whole of volume **385** (2003) of Physica is devoted to MgB<sub>2</sub>.

*Electronic structure:* Mg donates one each of its two valence electrons to the two B atoms, which thereby become electronically like C ( $1s^2 2s^2 2p^2$ ). Since the B lattice is honeycomb, very similar to graphene (see below): 3  $sp^2$  bands in plane, 1  $p$ -state ( $p_z$ ) out of plane. In contrast to graphene or fullerenes, where the  $sp^2$  bands are fully covalent and only the  $p_z$ -states can form metallic states, in MgB<sub>2</sub> *both  $sp^2$  and  $p_z$  states form partially occupied bands*. Thus we have a  $\sigma$  band (formed from  $sp^2$  states) which is very strongly 2D, and a  $\pi$  band (formed from the  $p_z$  states) which is much more 3D.

*Evidence for two gaps:* both electronic specific heat and tunneling data support the idea that to a first approximation Cooper pairs form independently in the  $\sigma$  and  $\pi$  bands, with only fairly weak interband contact: the corresponding gaps are quite different in magnitude ( $\Delta_\sigma \sim 7\text{meV}$ ,  $\Delta_\pi \sim 2.4\text{meV}$ ).

*Mechanism:* pronounced B isotope effect (substitution of <sup>11</sup>B for <sup>10</sup>B depresses  $T_c$  by  $\sim 1\text{K} \Rightarrow \alpha_B \approx 0.25$ ). No observable Mg isotope effect. Principal phonon involved in superconductivity believed to be an in-plane optical ' $E_{2g}$ ' mode of the B atoms with  $\omega \sim 570\text{meV}$  ( $\sim 5000\text{K}$ !). High value of  $T_c$  attributed to this large prefactor *plus* strong electron-phonon coupling matrix element ( $N(0)$  is *not* anomalously large).

*The bottom line:* everything seems consistent with hypothesis that MgB<sub>2</sub> (like BKBO) is essentially 'classical' BCS superconductor, its qualitatively anomalous properties being due mainly to the 2D crystal structure and the resulting unusual electronic band structure.

(What if superconductivity of MgB<sub>2</sub> had been discovered in 1957?)

### Alkali fullerenes.<sup>§</sup>

The buckminsterfullerenes (fullerenes, 'buckyballs') were originally identified in 1985, and in 1990 it was shown how to produce them in large enough quantities to form a respectable crystal. In 1991, it was discovered that when doped with suitable amounts of alkali atoms those crystals become superconducting; the highest  $T_c$ , achieved for this system is  $\sim 40\text{K}$ , which was until 2008 the highest  $T_c$  for any non-cuprate material.

### The pure fullerenes.

#### (a) The fullerene molecule C<sub>60</sub>

Being the most abundant element in the galaxy which is solid at RT, carbon is of great interest to astrophysics, and the two great advances in fullerene physics arose directly out of attempts to replicate astrophysical conditions in the lab. Originally, Kroto et al. were looking for long-chain forms of C, but they eventually realized that their data were most easily understood if the C rather formed almost spherical molecules ('Buckyballs'). It is known that bulk solid C, as well as the diamond form, can occur as graphite, consisting of covalently-bonded sheets<sup>†</sup> with weak Van der Waals intersheet bonds; the buckyball

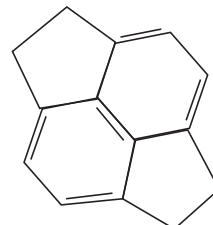
<sup>§</sup>Ref: M.P. Gelfand, Superconducting Review **1**, 103 (1994) (+A.P. Ramirez, *ibid.*, **1**, 1): T. Yildirim et al., in *The Physics of Fullerene-based and Fullerene-related Materials*, (W. Andreoni ed.) Kluwer Academic 2000, ch.3: O. Gunnarsson, Rev. Mod. Phys. (1997)

<sup>†</sup>Since 2004 individual sheets ('graphene') have been obtained experimentally.

molecules are essentially a single graphite sheet rolled up into (nearly) a sphere. Various forms of buckyball have been found (C<sub>60</sub>, C<sub>70</sub>, C<sub>84</sub>, ...) but C<sub>60</sub> is by far the most studied.

The C<sub>60</sub> molecule has the familiar ‘soccer-ball’ pattern, with alternating hexagons (20) and pentagons (12); bonds separating 2 hexagons are double and of length 1.39Å, those separating a hexagon + a pentagon single and = 1.46Å.

The whole molecule has icosahedral symmetry. A consequence is that we can choose the orientation so that each Cartesian axis  $x, y, z$  corresponds to a 2-fold rotation axis (‘standard orientation’), but there are 2 inequivalent choices, related by  $\pi/2$  rotation around a Cartesian axis (or by a rotation of 44.48° around any [111] axis): see Yildirim et al., op. cit, ch 2, fig 3. This is important when we consider the crystal.



Electronic states can be classified by their parity ( $g, u$ ) and by their behavior under the operations of the icosahedral group: irreducible representations are labeled  $a$  (non degenerate),  $t$  (3 fold),  $g$  (4 fold) and  $h$  (5 fold). The C atom has 6 electrons, which in free space take the configuration  $1s^2 2s^2 2p^2$ , but in a molecule or solid, the  $2s$  and  $2p$  states tend to hybridize to form  $4sp^2$  states. By inspection of the ‘surface’ bonding diagram we see that 3 electrons per atom are used up in it, so this leaves 1 electron per atom or 60 in total occupying an  $sp^2$ -like orbital (mostly  $2p_z$ ) which ‘sticks out’ of the plane, and it is linear combinations of such atomic states which form the occupied molecular orbitals. It is believed that they occupy successively  $a_g, t_{1u}, h_g, t_{2u}, g_u, g_g + h_g, h_u$  orbitals ( $2 \times (1 + 3 + 5 + 3 + 4 + 9 + 5) = 60$  states). The highest occupied molecular orbital (‘HOMO’) is therefore  $h_u$  and 5-fold degenerate. The next lowest orbital (lowest unoccupied molecular orbital, ‘LUMO’) is believed to be of  $t_{1u}$  symmetry, hence 3-fold orbitally degenerate: its properties are crucial for the alkali-doped fullerenes.<sup>¶</sup>

The single-molecule HOMO-LUMO splitting is believed to be  $\sim 0.6$ eV (result of TB band-structure calculation with  $t_{ij} = 2.7$ eV for n.n., ignoring difference between single- and double- bonded nearest neighbors), while the splitting between the LUMO orbital  $t_{1u}$  and the next one up ( $t_{1g}$ ) is  $\sim 0.35$ eV. The LUMO orbital has a complicated pattern (see e.g., Gelfand Fig. 2) but usually changes sign along a double bond.

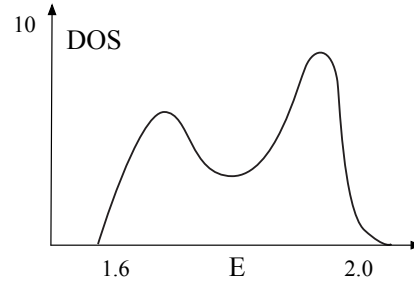
### (b) Pure fullerene crystals

Pure C<sub>60</sub> condenses at  $\sim 300$ K into fcc crystal with (cubic) lattice parameter 14.2Å, corresponding to close packing of 10Å diameter ‘spheres’ (approximately the C<sub>60</sub> molecule). The question of orientational disorder of the molecules is quite complicated: in pure C<sub>60</sub> the molecule appear to be freely rotating at RT, but to undergo a first-order transition to a simple cubic orientationally ordered state at  $\sim 250 - 260$ K. This is also the case for some mixed A<sub>3</sub>C<sub>60</sub>’s, e.g. Na<sub>2</sub>Rb<sub>x</sub>Cs<sub>1-x</sub>C<sub>60</sub>. At low temperatures in most of the A<sub>3</sub>C<sub>60</sub> compounds, by contrast, the orientational state appears to be one of so-called ‘merohe-

<sup>¶</sup>The definitive discussion is by R.C. Haddon et al, Chem. Phys. Lett. **125**, 459 (1986).

dral disorder' in which the two nonequilibrium orientations are populated at random. The compressibility is high, comparable to that of graphite in the direction  $\perp$  to the planes ( $-d \ln a/dp = 2.3 \times 10^{-12} \text{cm}^2/\text{dyn}$ ), indicating that the intermolecular bonding is of VdW type (for comparison, diamond has  $0.18 \times 10^{-12} \text{cm}^2/\text{dyn}$ ).

For orientationally ordered pure C<sub>60</sub>, the band which evolves from the LUMO ( $t_{1u}$ ) orbital is calculated to be roughly of the form shown (where  $E$  is measured in eV relative to the top of the HOMO band and the DOS is in units of states/eV·spin·C<sub>60</sub>). Merohedral disorder is predicted to wash out most of the structure. The above diagram is for  $a = 14.24 \text{\AA}$ : for  $a = 14.44 \text{\AA}$  the DOS in the middle of the band is believed to be increased by  $\sim 15 - 25\%$ , an effect which is important in interpreting the data on superconductivity (see below).



Experimentally, pure solid C<sub>60</sub> is a wide-gap semiconductor, with a band gap of  $\sim 1 \text{eV}$  as seen e.g. in photoemission, in reasonable though not perfect agreement with the band structure calculations.

An important observation concerning the fcc structure of pure C<sub>60</sub> is that it has 12 quite large 'voids' (sites) per cubic unit cell, i.e. 3 per C<sub>60</sub> molecule, one with octahedral (O) symmetry and 2 with tetrahedral (T) symmetry. The effective site radii are  $1.12 \text{\AA}$  for the T sites and  $2.06$  for the O ones.

Those sites<sup>||</sup> can then accommodate one or sometimes more intercalated atoms, in particular the (small) alkali atoms, and so one gets inter alia the possibility of compounds of the form  $A_x\text{C}_{60}$ , where  $x$  should at first sight range from 0 to 3. Actually, it turns out that even for the heavier alkalis, the compounds  $A_4\text{C}_{60}$  and  $A_6\text{C}_{60}$  can occur, by distorting the lattice to a bcc or bct structure: and in the case of doping with Na, up to 11 Na atoms per C<sub>60</sub> can be tolerated (because of multiple occupancies of the O and T sites by the (small,  $r \sim 0.95 \text{\AA}$ ), Na ions). However, superconductivity seems to occur only very close to  $x = 3$  (where the structure remains fcc)\*\*, so let us concentrate on that case.

[Note: In recent years other intercalations besides alkali have been tried: in particular some NH<sub>3</sub>-expanded fullerenes such as  $(\text{NH}_3) \cdot \text{Na}_2\text{K}_6\text{C}_{60}$  show superconductivity, with quite high  $T_c$  ( $\sim 17 \text{K}$ ). Also superconducting are  $A_{3-x}\text{Ba}_x\text{C}_{60}$  (structure similar to  $A_3\text{C}_{60}$ ),  $\text{Ca}_x\text{C}_{60}$  ( $x \sim 5$ ) and some others: see Gunnarsson op. cit.]

### Alkali fullerenes

Will usually consider 'pure' alkali fullerenes with  $x = 3$ , e.g.,  $\text{K}_3\text{C}_{60}$  or  $\text{Rb}_3\text{C}_{60}$  or  $\text{Cs}_3\text{C}_{60}$ ; however, can also get e.g.  $\text{NaRbCsC}_{60}$  ( $T_c \sim 10 \text{K}$ ). As mentioned, except in the case of

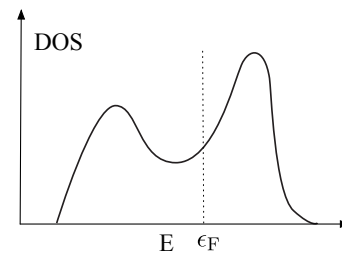
<sup>||</sup>The O sites are situated in the middle of the edges of the cubic unit cell (3 per c.u.c.) plus one in the 'middle': the T sites are at the vertices of an internal 'cube'. See Yildirim et al Fig. 3.

\*\*Except for  $\text{Cs}_3\text{C}_{60}$  which appears to form a mixture of bct and A15 structures.

Cs<sub>3</sub>C<sub>60</sub> the fcc structure is preserved and the merohedral disorder characteristic of pure C<sub>60</sub> is (probably) also preserved.

A very simple view of the electronic behavior is obtained if we assume that the only role of the alkalis (apart from changing the lattice constant slightly) is to act as donors of their valence electrons into the LUMO ( $t_{1u}$ ) band of the pure C<sub>60</sub> host. (There is no hybridization, because the  $ns$  alkali groundstate lies well above the top of the LUMO band). This picture is confirmed by the fact that the shift of Raman lines attributed to phonon lines of the pure C<sub>60</sub> crystal shift appreciably with alkali doping, the shift being approximately proportional to  $x$ .

If this picture is correct, we would expect to be able to represent the normal state of the A<sub>3</sub>C<sub>60</sub> system to a first approximation in terms of a more or less free-electron like model of the LUMO band, with occupation 1/2. If we ignore for the moment the possible effects of merohedral disorder, the Fermi energy should lie roughly as indicated and the DOS  $N(0)$  is calculated to be in the range 6–10 states/eV·spin·C<sub>60</sub> for  $a = 14.24\text{\AA}$  (K<sub>3</sub>C<sub>60</sub>) and around 15–25% higher for  $a = 14.44\text{\AA}$  (Rb<sub>3</sub>C<sub>60</sub>). The Fermi velocity (averaged over the Fermi surface) should be  $\sim 1.8 \times 10^7$  cm/sec and the plasma frequency  $\omega_p \approx 1.2\text{eV}$ .



This picture seems at least roughly consistent with the existing experimental data on the normal phase of A<sub>3</sub>C<sub>60</sub>. The ‘Pauli’ DOS (i.e. that derived from the Knight shift assuming a known Fermi-liquid (Stoner) enhancement) is  $\sim 11 \pm 3$  in the above units, and estimates based on the bulk  $\chi$  with a plausible subtraction of the Landau diamagnetism and an estimated Stoner factor  $\sim 1.5–1.6$  gives results consistent with this. Estimates of  $N(0)$  based on the nuclear spin relaxation time  $T_1$  appear also in reasonable agreement, and in particular the  $a$ -dependence of  $N(0)$  (which can be more reliably extracted from  $T_1$  measurements than the absolute value) appears consistent with the Rb/K ratio of 1.15–1.25 predicted. The infrared reflectivity can be interpreted in terms of a Drude model with  $\omega_p \sim 1.56\text{eV}$ , rather larger than the predicted 1.2eV.

One quantity which is quite surprising is the dc resistivity, which increases\* with temperature roughly as  $a + bT^2$ ; the natural interpretation is that the  $T^2$  term is due to electron-electron Umklapp scattering and the constant due to static disorder. However, the constant is typically of order  $2\text{m}\Omega\text{ cm}$ , which would correspond to a mean free path  $< 10\text{\AA}$ , i.e., less than the (cubic) unit cell size and about equal to the C<sub>60</sub> molecular radius. The most natural interpretation is in terms of the merohedral disorder.

There is a problem in interpreting the photoemission data in terms of this simple picture, however, since the ‘width’ of the occupied region of the conduction band deduced from this by a naive analysis is at least 0.7eV, compared with a calculated value of something more like 0.18eV (see Gelfand Fig 4a). It is not clear whether this is due to surface effects, phonons, electron-electron interactions or something else.

Another anomaly is the behavior of the ‘plasmon peak’ (?) seen in EELS experiments:

\*As a function of  $x$ ,  $\rho$  goes through a minimum at  $x \approx 3$ .

for all wave vectors in the range  $0.1\text{\AA}^{-1} < q < 0.5\text{\AA}^{-1}$ , it seems to occur at around 0.55eV, with negligible dispersion, contrary to what simple theory would predict. [see Knupfer et al, in Andreoni, ed., op. cit.]. There is a second, smaller bump in the EELS spectrum at  $\sim 1.3\text{eV}$ , again with no noticeable dispersion. (In some sense this would appear to indicate that each C<sub>60</sub> molecule is effectively a ‘point site’ - though cf. refs cited by Knupfer).

*In summary:* apart from the photoemission which is difficult to interpret, most normal state data on the A<sub>3</sub>C<sub>60</sub> compounds are consistent with a simple free-electron-like ‘textbook’ model with a DOS at the FS which is quite strongly dependent on the lattice constant  $a$  (as we should expect).

### Superconductivity of A<sub>3</sub>C<sub>60</sub>

Some alkali-intercalated graphite compounds show superconductivity, but only at  $\sim 1\text{K}$  (e.g., KC<sub>8</sub>). It is therefore remarkable that superconductivity is observed in the alkali fullerenes up to  $\sim 40\text{K}$  (Cs<sub>3</sub>C<sub>60</sub> under pressure). As a function of  $x$ , superconductivity appears to occur only close to  $x = 3$  (i.e. half-filled  $t_{1u}$  band), with  $T_c$  peaking at very close to  $x = 3$ .

A very interesting feature is that  $T_c$  increases with increasing lattice spacing (verified both from pressure-dependence and from comparison of K<sub>3</sub>C<sub>60</sub>) ( $a \sim 14.24\text{\AA}$  at zero  $P$ ) with Rb<sub>3</sub>C<sub>60</sub> ( $a \sim 14.44\text{\AA}$ ). The increase is approximately linear, with a slope of  $\sim 33\text{K}/\text{\AA}$  in the merohedrally disordered system (like the above ones) and much steeper in orientationally ordered cases such as Na<sub>2</sub>Rb <sub>$x$</sub> Cs <sub>$1-x$</sub> C<sub>60</sub> (where  $a$  depends on  $x$ )<sup>†</sup> This behavior can be understood qualitatively if we assume that  $T_c$  is as in BCS theory proportional to  $\exp -1/N(0)V_0$  and that the effective coupling constant  $V_0$  comes mainly from intramolecular effects and is therefore almost independent of  $a$ , while  $N(0)$  depends on  $a$  as found experimentally; then the quantity  $N(0)V_0$  increases with  $a$ , and the behavior of  $T_c(a)$  is therefore consistent. More quantitatively, the observed behavior can be well fitted to the McMillan formula if we assume  $\mu^* = \text{const}$  and  $\lambda \propto N(0)$ .

The superconducting A<sub>3</sub>C<sub>60</sub>’s are strongly type-II, with  $H_{c1} \sim 60-130\text{G}$ ,  $H_{c2} \sim 50\text{T}$ , implying an extrapolated GL coherence length  $\xi(0) \sim 26\text{\AA}$  ( $< 2$  lattice spacings!). The zero- $T$  penetration depth  $\lambda_0$  is in the range 2400-4800 $\text{\AA}$ ; a quantity which is better known is the ratio of  $\lambda_0$  for Rb<sub>3</sub>C<sub>60</sub> and K<sub>3</sub>C<sub>60</sub>, which can be estimated quite accurately from the broadening of the C<sup>13</sup> NMR line, and is then 0.77. This is incompatible with the clean-limit expression (since  $a$  is greater for Rb<sub>3</sub>C<sub>60</sub>,  $n$  should be less and hence  $\lambda_0$  greater), but in fairly good agreement with the dirty-limit one ( $\lambda_0 \sim (l/\xi_0)^{-1/2} \propto T_c^{-1/2}$ ) since the zero pressure  $T_c$ ’s of K<sub>3</sub>C<sub>60</sub> and Rb<sub>3</sub>C<sub>60</sub> are 19.3K and 29K respectively.

Now let’s discuss the pairing state. Both  $T_1$  and infrared-reflectivity measurements indicate that the quasiparticle density of states is very small below a gap  $\Delta$  which is approximately equal to the BCS values  $1.76k_B T_c$ . (but up to 2.1 in some measurements). A HS peak is seen just below  $T_c$  in the  $\mu\text{SR}$ , though apparently not in the <sup>13</sup>C NMR.

<sup>†</sup>This suggests that ‘merohedrally annealed’ Rb<sub>3</sub>C<sub>60</sub> might have a  $T_c > 40\text{K}$ . (though cf. Yildirim et al Fig. 30).

(later measurements do show it). These pieces of evidence strongly suggest simple *s*-wave pairing as in the classic superconductors, and there seems no compelling evidence against this hypothesis.<sup>§</sup>

What about the mechanism? An isotope effect is seen (for <sup>12</sup>C → <sup>13</sup>C) with a magnitude 0.4 which is close to the BCS value of 0.5. Also, as already mentioned, the experimental *T<sub>c</sub>*'s seem to fit the McMillan formula reasonably well if we make the natural assumption that the only relevant variation with *a* is of the DOS *N*(0). Note that even if the phonon mechanism is dominant A<sub>3</sub>C<sub>60</sub> would differ from traditional BCS superconductivity in that the ratio  $\omega_D/\epsilon_F$  is 0.3 – 0.6 rather than  $\mathcal{O}(10^{-2})$ . Alternative explanations based on a purely electronic mechanism have been proposed (an effective attraction within a single C<sub>60</sub> molecule is generated if the energy needed to put two electrons on one molecule is less than that needed to put them on different molecules, as may conceivably be the case), and are claimed to accommodate the above data. However, at present, there seems no compelling evidence against the 'default' hypothesis, namely that the alkali fullerene superconductors are well described by standard BCS theory but manage, probably because of their strongly molecular structure, to avoid the traditional upper limit on *T<sub>c</sub>*.

---

<sup>§</sup>However,  $\mu$ SR seems to be fitted by  $\lambda(T) = \lambda(0)(1 - (T/T_c)^\alpha)$ ,  $\alpha \sim 3.2$ . (Uemura et al, Nature **352**, 605 (1998)).