Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Superconductivity in Doped Fullerites

Michel Lannoo [a]

[a] Institut d'Electronique et de Microélectronique du Nord (UMR CNRS 9929) DépArtement ISEN, 41, boulevard Vauban, 59046, LILLE CEDEX, France

Version of record first published: 23 Oct 2006.

To cite this article: Michel Lannoo (1994): Superconductivity in Doped Fullerites, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 345-351

To link to this article: http://dx.doi.org/10.1080/10587259408051712

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 345–351
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SUPERCONDUCTIVITY IN DOPED FULLERITES

MICHEL LANNOO
Institut d'Electronique et de Microélectronique du Nord (UMR CNRS 9929)
Département ISEN, 41, boulevard Vauban, 59046 LILLE CEDEX, France

Abstract The superconductivity in alkali intercalated C_{60} crystals is analysed on the basis of conventional B.C.S. theory. It is shown that, in the limit of negligible electron phonon coupling between C_{60} molecules, the coupling parameter λ of B.C.S. theory can be rigorously factorized as $\lambda = NV$ where N is the density of states at the Fermi level and V is a pure intraball contribution. We describe several calculations of V (Tight binding, LDA, MNDO) which all lead to a value in the range 50-60 meV. This, together with reasonable values for N (~ $15(eV)^{-1}/C_{60}$) and for the Coulomb pseudopotential μ (~0.2) leads to T_c = 20 K as observed for K_3C_{60}. We show that the dependence of T_c upon lattice parameter strictly reflects that of the density of states and confirms the factorization of λ. We also compare our predictions to available experimental data (phonon self energies, isotope effect ...). We discuss the origin of the difference in T_c between the A_3C_{60} and intercalated graphite. Finally we comment on the validity of the B.C.S. approach showing that different corrections due to the narrow bandwidth tend to compensate each other.

Since the discovery of superconductivity in FCC alkali intercalated A_3C_{60} compounds [1] (A = K, Rb, Cs) various models have been proposed [2-11]. An important question is to know if the relatively high values obtained for T_c (~ 30 K) can be explained using standard B.C.S. theory based on electron-phonon coupling. Our aim here will be to examine this point in detail, essentially on the basis of the results contained in ref. [3, 12, 13]. We shall also compare the predictions of the B.C.S. calculation with experimental data and examine the validity of the approach.

I. - The B.C.S. approach : The best is to consider first the simplest B.C.S. expression, valid only in weak coupling :

$$T_c \sim \frac{\hbar\bar{\omega}}{k_B} \exp\left(-\frac{1}{\lambda - \mu}\right) \qquad (1)$$

This depends on three parameters: an average phonon frequency $\bar{\omega}$, the electron-phonon coupling constant λ which is a measure of the strength of the phonon mediated attraction between electrons, and μ which represents the strength of the electron-electron repulsion. From this a large value of T_c requires large values of $\bar{\omega}$, λ and small values for μ. Although the condition on $\bar{\omega}$ is clearly favorable to C_{60} (strong bonds, light mass) those on λ and μ are not obvious especially if one compares the A_3C_{60} to intercalated graphite which has similar bonding and where $T_c < 1K$. To determine T_c for intermediate and strong λ it is in principle necessary to solve Eliashberg's equations numerically [14]. For the present case we have checked that the analytic form due to Mc Millan [15] gives an excellent approximation for T_c :

$$T_c = \frac{\hbar\omega_{log}}{1\cdot 2k_B}\exp\left(-\frac{1}{\frac{\lambda}{1\cdot 04(1+\lambda)}-\frac{(1+0,62\lambda)}{1\cdot 04(1+\lambda)}\cdot\mu}\right) \qquad (2)$$

This is completely similar to (1) but with renormalized values of λ and μ, which makes it more difficult to get large values for T_c. In this expression ω_{log} is a well defined logarithmic average

$$\ln\omega_{log} = \frac{1}{\lambda}\sum_p \lambda_p \ell n\omega_p \qquad (3)$$

where λ_p is the contribution of the phonon of frequency ω_p to the total $\lambda = \sum_p \lambda_p$. The detailed calculation of λ and ω_{log} requires the knowledge of the electronic properties, the phonon spectrum and the electron-phonon interaction.

II. - Electrons and phonons in A_3C_{60} : As discussed in detail in ref. [3] the atomic structure of f.c.c. C_{60} is such that the closest distance between two C_{60} molecules is 3.1 Å, slightly smaller than the interlayer separation in graphite. Thus interactions between the C_{60} will be small, of the van der Waals type, and a meaningful starting point is the isolated molecule. This one is characterized by σ and π states. The highest occupied (HOMO) state is a fivefold degenerate H_u level while the lowest unoccupied one (LUMO) is a triply degenerate T_{1u}. Both are π derived and their separation is 1-2eV. If one allows for weak coupling between the C_{60} in f.c.c. C_{60} these two molecular levels will broaden into narrow separated bands favoring large values of the

density of states. For A_3C_{60}, we consider that the intercalated atoms simply donate their electrons to the rigid f.c.c. C_{60} band structure. As there are 3 electrons per C_{60} this results in a half filled T_{1u} derived narrow band. Recent calculations (e.g. [16]), have shown that this picture is essentially valid. The phonon spectrum can be discussed in a similar way. It is dominated by intramolecular vibrations which give rise to the main broad band at high frequencies. Other bands at much lower frequencies correspond to alkali optic modes, inter-molecular phonons and libration modes of the individual C_{60}. Among the vibrational modes of particular interest are the Raman active modes of the isolated C_{60} molecule, which are fivefold degenerate with symmetry H_g. There are eight such modes whose frequency increases with their bond stretching character. These play a major role in the calculation of λ.

III. - Electron-phonon interaction for the isolated C_{60} molecule : The isolated C_{60} molecule represents a fairly interesting problem when it is in the charge state C_{60}^{-n} (n = 1, 2, 3) which corresponds to doped systems. In such cases one has to deal with a partially filled degenerate state (n electrons in the triply degenerate T_{1u} level). This will lead to a spontaneous Jahn-Teller distortion of the molecule which we have studied in detail in ref. [12] as a function of the charge state. This distortion is due to the electron-phonon interaction and the total gain in energy can be expressed as a sum over the normal modes p of vibration which, for n = 1, is written as

$$E_1 = \sum_p E_p \tag{4}$$

From symmetry considerations the modes which give rise to electron-phonon coupling are the eight Raman active modes of symmetry H_g as well as the two breathing modes of symmetry A_g. An interesting issue discussed in [12] is the magnitude of the contribution U_d of this distortion energy to the effective electron-electron interaction in C_{60}. This one can be shown [12] to be given by

$$U_d = -2E_1 \tag{5}$$

From the calculations described later U_d is of order - 50 meV which represents a value too small to lead to negative U situations since the electronic contribution is expected to be of order 0.5 eV [17].

IV. - Superconductivity : In the B.C.S. theory of superconductivity the dimensionless electron-phonon coupling constant λ is :

$$\lambda = \frac{2}{N(0)} \sum_{p,\underline{q}} \frac{1}{2K_p(\underline{q})} \sum_{\substack{n,\underline{k} \\ n'\underline{k}'}} \left| I_{n\underline{k},n'\underline{k}'}(p,\underline{q}) \right|^2 \delta(\varepsilon_{n\underline{k}}) \delta(\varepsilon_{n'\underline{k}'}) \tag{6}$$

where $\varepsilon_{n\underline{k}}$ is the energy of the electronic Bloch state of band n with wave vector $\underline{k}$. The delta functions ensure the sum to be restricted to the Fermi surface. $K_p = M\omega_p^2(\underline{q})$ is the force constant of the p^{th} phonon with wave vector $\underline{q}$ and $I_{n\underline{k},n'\underline{k}'}(p,\underline{q})$ is the electron-phonon matrix element, linear in the phonon normal mode amplitudes. N(0) is the density of states at the Fermi level per spin orientation. The calculation of λ involves a complex averaging over the Fermi surface. However, as demonstrated in [12], a remarquably simple result is obtained in the limit where one neglects the contributions of the electron-phonon interaction due to inter-molecular coupling. In this limit λ can be rigorously expressed as

$$\lambda = N(0)V = N(0)\sum_p V_p \tag{7}$$

where the sum is now over the normal modes p of the isolated C_{60} molecule. The quantities V_p are pure intramolecular quantities depending on the strength of the electron-phonon interaction and on the force constants of the phonon modes. It is shown in [12] that they can be related to the distortion energies defined above with, for Hg and Ag modes respectively

$$V_p(H_g) = \frac{5}{3} E_p(H_g) \qquad V_p(A_g) = \frac{2}{3} E_p(A_g) \tag{8}$$

The striking point of the result (7) is that it is the product of a pure intramolecular quantity V by a term N(0) which is fixed by the strength of the electronic intermolecular coupling. This will be reflected in the experimental results discussed later. Calculations of λ have been performed using different techniques : the local density (L.D.A.), the tight binding and the MNDO approximations. Phonon models included two versions of the Keating model [18] and an adaptation of the bond charge model to C_{60} [19]. In tight binding the π-π interactions are assumed to vary with interatomic distance as d^{-n}, the best agreement with the other methods being obtained for n = 2.7. From these numerical results a smaller bound is V = 50 meV. The calculations lead in all cases to an average frequency given by (3) such that $\hbar\omega_{log} \sim 1400K$. This, together with a reasonably estimated value of $N(0) \sim 14/eV.C_{60}$ gives $\lambda = 0.7$. The calculation of T_c from Mc Millan's formula (2) still requires the

knowledge of μ. In ref. [13] we took $\mu = 0.2$ which is already larger than for conventional superconductors. With this set of values we directly get $T_c = 20$ K which is right in the observed range.

V. - Comparison with experiment : The most striking observation is that T_c scales monotonically with the A_3C_{60} lattice constant upon chemical alkali substitution[20]. This is confirmed by measurements under applied hydrostatic pressure [21-23] which fall exactly on the same curve. The variation of T_c versus d strictly reflects the change in density of states N(0) in $\lambda = N(0)V$, V remaining constant. From the tight binding treatment $N(0) \alpha d^n$ with the optimum value $n = 2.7$. This gives a perfect description of the experimental trends. The electron-phonon coupling will also result in a shift and broadening of the phonon lines. This has been shown to occur in Raman [24-26] and neutron scattering [27] studies contrasting the insulating C_{60} and A_6C_{60} phases with the A_3C_{60} metallic phase. Coupling is observed in all cases to both low energy (radial) and high energy (tangential) modes, in general agreement with the predictions of ref. [3,13]. This is even confirmed quantitatively by very precise recent Raman studies [28, 29] which provide an almost direct proof of the importance of the electron-phonon interaction in such systems. However the situation for the isotope shift ($T_c \alpha M^{-\alpha}$) is not so clear. The ideal BCS value is, of course, $\alpha = 0.5$ but there are two sets of experimental values, either in the range 0.25 - 0.4 [30, 31] or larger than 1 [32], this situation being confirmed by the most recent results [29]. Taking into account the fact that μ usually contains a renormalization factor $(1+\ell n(\omega_{e\ell}/\omega_{\log}))^{-1}$ [33] our calculation, with the parameters described above, would lead to $\alpha = 0.29$ for Rb_3C_{60} in good agreement with one set of results. Clearly some more studies are needed to resolve the experimental situation.

With a predicted value of $\lambda = 0.7$ one is not in the strong coupling case of B.C.S. theory. This means that we expect the BCS value $2\Delta \sim 3.5\ k_BT_c$ for the superconducting gap and $\xi_0 \approx 150$ Å for the coherence length. NMR [34] and optical [35] data seem to indicate a B.C.S. gap value, while point contact tunneling [36] yields larger values. Coherence lengths of $\cong$ 150 Å have been inferred from H_{c2} measurements [37] on granular films but much smaller values are typically quoted [29,36]. These experiments do not allow yet to draw firm conclusions about the applicability of B.C.S. However a recent study [38] shows that the variations of the resistivity versus temperature are consistent with electron-phonon coupling with λ in the predicted range. This is also true for the fine structure observed in the low temperature photoemission [39]. Another argument in favor of the electron-phonon coupling is the comparison A_3C_{60} - graphite which is easily interpreted. For graphite

we can also make use of the formula $\lambda = N(0)\ V$. Our calculation shows that V ~ 1eV/atom while N(0) ~ 0.1 to 0.2/eV/atom resulting in $\lambda \sim 0.1$-0.2 and obviously very small T_c. For A_3C_{60} our values are V~ 50 meV/C_{60} (i.e 3 eV/atom) and N(0) = 15/eV/C_{60} (i.e 0.25/eV/atom) resulting in $\lambda = 0.7$ and $T_c \sim 20$ K. The difference is only partly due to a difference in density of states but mostly comes from the much larger value of V. We have been able to show that the physical origin of the increase in V is a coupling of the π electrons with lower frequency modes induced by the finite curvature of C_{60}.

VI. - Discussion and conclusion : Let us discuss the uncertainties and limits of applicability of the BCS calculation with electron-phonon coupling. A first very sensitive parameter is N(0) which we took to be of order 15/eV/C_{60}. This is fully confirmed by recent detailed ab initio calculations [16]. Another serious problem of the theory is the argument of Anderson [40] that, for narrow bands as is the case of the T_{1u} band here, μ should be substantially larger than 0.2 so that BCS theory should not work for T_c. This was only partly confirmed by a detailed calculation [41] concluding that $\mu \sim 0.3$-0.4 (instead of 0.2),which could be easily compensated by slight increases in λ with respect to our calculated $\lambda = 0.7$. Such an increase in λ can be provided by other corrections to the theory described here, due to the fact that the bandwidth becomes comparable to the phonon energies. A first calculation [42] starts from Eliashberg's equations and shows that one can obtain an extension of Mc Millan's formula corresponding to larger values of T_c for the same parameters. Two other studies [43, 44] concentrate on the breakdown of Midgal's theorem which occurs in this limit and show from different arguments that this leads to an effective value of λ which is less severely reduced by renormalization than in Mc Millan's formula. In conclusion, we have shown that the use of B.C.S. theory with electron-phonon interaction yields quite naturally to correct values of T_c for the A_3C_{60} if one accepts that the Coulomb parameter $\mu = 0.2$. The order of magnitude of the electron-phonon interaction is quantitatively confirmed by some experiments. Problems remain for other observations but they are partly of experimental origin. However B.C.S. theory is at its limits of applicability and its success seems to be correlated with the compensation of corrections resulting from the fact that one is dealing with a narrow band.

REFERENCES

1. 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).
2. C.M. Varma, J. Zaanen and K. Raghavachari, Science, 254, 989 (1991).
3. M.A. Schlüter, M. Lannoo, M. Needels, G.A. Baraff and D. Tomanek, Phys. Rev. Lett., 68, 526 (1992).

4. F.C. Zhang, M. Ogato and T.M. Rice, Phys. Rev. Lett., 67, 3452 (1991).
5. S. Charkavarty, M.P. Gelfand and S. Kivelson, Science, 254, 970 (1991).
6. G. Baskaran and E. Tossati, Current Science, 61, 33 (1991).
7. K.H. Johnson, M.E. Mc Henry and D.P. Cloughtery, Physica C (1992), to be published.
8. I.I. Mazin, S.N. Rashkeev, V.P. Antropov, O. Jepsen, A.I. Liechtenstein and O.K. Andersen, Phys. Rev. (1992) submitted.
9. G. Stollhoff, Phys. Rev. B 44, 10, 998 - 11, 000 (1991).
10. L. Pietronero, preprint.
11. J.L. Martins and N. Troullier, preprint.
12. M. Lannoo, G.A. Baraff, M. Schlüter and D. Tomanek, Phys. Rev. B 44, 1210 (1991).
13. M. Schlüter, M. Lannoo, M. Needels, G.A. Baraff and D. Tomanek, J. Phys. Chem. Sol., 53, 1473 (1992).
14. G.M. Eliashberg, JETP, 11, 696 (1960). We thank P.B. Allen for providing us with his Eliashberg code.
15. W.L. Mac Millan, Phys. Rev. 167, 331 (1968).
16. Ming-Zhu Huang, Yong-Nian Xu and W.Y. Ching, Phys. Rev. B 46, 6572 (1992).
17. .O. Gunnarsson, S. Satpathy, O. Jepsen and O.K. Andersen, Phys. Rev. Lett., 67, 3002 (1991).
18. R. Martin, Phys. Rev. B 4, 4005 (1970).
19. G. Onida and G. Benedek, Europhys. Lett., submitted (1992)
20. R.M. Fleming, A.P. Ramirez, M.J. Rosseinsky, D.W. Murphy, R.C. Haddon, S.M. Zahurak and A.V. Makhija, Nature, 352, 787 (1991).
21. J.E. Shirber, D.L. Overmyer, H.H. Wang, J.M. Williams, D.D. Carlson, A.M. Kini, M.J. Pellin, U. Welp and W.K. Kwok, Physica C, 178, 137 (1991).
22. G. Sparn, J.D. Thompson, S.M. Huang, R.B. Kaner, F. Diederich, R.L. Whetten, G. Gruner and K. Holczer, Science, 252, 1829 (1991).
23. O. Zhou, G.B.M. Vaughn, Q. Zhu, J.E. Fischer, P.A. Heiney, N. Coustel, J.P. McCauley and A.B. Smith, preprint.
24. S.J. Duclos, R.C. Haddon, S.H. Glarum, A.F. Hebard and K.B. Lyons, Science, 254, 1625 (1991).
25. M.G. Mitch, S.J. Chase and J.S. Lannin, Phys. Rev. Lett., 68, 883 (1992).
26. P. Zhou, K. Wang, A.M. Rao, P.C. Eklund, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. submitted (1992).
27. K. Prassides, J. Tomkinson, C. Christides, M.J. Rosseinsky, D.W. Murphy and R.C. Haddon, Nature, 354, 462 (1991).
28. M.G. Mitch, S.J. Chase and J.S. Lannin, Phys. Rev. Lett., 68, 883 (1992).
29. Many recent results can be found in the Proceedings of the MRS Fall Meeting, Boston, (1992), to be published.
30. A.P. Ramirez, A.R. Kortan, M.J. Rosseinsky, S.J. Duclos, A.M. Mujsce, R.C. Haddon, D.W. Murphy, A.V. Makhija, S.M. Zahurak and K.B. Lyons, Phys. Rev. Lett., 68, 1058 (1992).
31. C.C. Chen and C.M. Lieber, preprint.
32. T.W. Ebbesen, J.S. Tsai, K. Tanigaki, J. Tabucchi, Y. Shimakawa, Y. Kubo, I. Hirosawa and J. Mizuki, Nature, 355, 620 (1992).
33. P. Morel and P.W. Anderson, Phys. Rev. 125, 1263 (1962).
34. R. Tycko, G. Dabbagh, M.J. Rosseinsky, D.W. Murphy, A.P. Ramirez and R.M. Fleming, preprint.
35. L.D. Rotter, Z. Schlesinger, J.P. McCauley Jr, N. Coustel, J.E. Fisher and A.B. Smith, III, preprint.
36. Z. Zhang, C.C. Chen, S.P. Kelty, H. Dai and C.M. Lieber, Nature, 253, 333 (1991).
37. T.T.M. Palstra, R.C. Haddon, A.F. Hebard and J. Zaanen, Phys. Rev. Lett., 68, 1054 (1992).
38. V.H. Crespi, J.G. Hou, X.D. Xiang, M.L. Cohen and A. Zettl, Phys. Rev. B 46, 12064 (1992).
39. H. Romberg, private communication.
40. P.W. Anderson, unpublished.
41. O. Gunnarsson and G. Zwicknagl, Phys. Rev. Lett., 69, 957 (1992).
42. H. Zheng and K.H. Bennemann, Phys. Rev. B 46, 11993 (1992).
43. L. Pietronero, Europhys. Lett., 17, 365 (1992) and to be published.
44. Y. Asai and Y. Kawaguchi, to be published.