Superconductivity in C_{60}

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Abstract

Recently, a superconducting transition temperature of 117 K has been reported for lattice expanded hole-doped C_{60} single crystals, and evidence suggests that C_{60} compounds could soon overtake the cuprates as the highest temperature superconducting materials [1]. In this paper, I will review the history of investigations of the superconductivity of C_{60}, overviewing experimental observations and attempts as theoretical explanations of this phenomena, as well as summarizing some of the open questions.

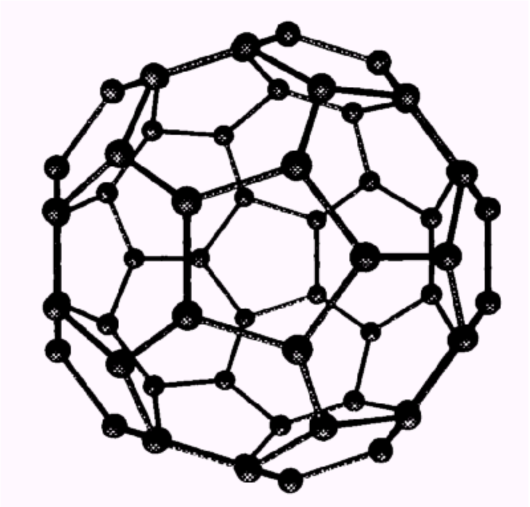

Figure 1: The C_{60} molecule.

1 Introduction

In 1985 fullerenes such as C_{60} were discovered, and by 1991, purification and crystallization techniques had advanced to the point where the superconducting properties of alkali-doped C_{60} crystals could be observed. See Figure 1 on the title page for a graphic representation of this molecule. The lengthy review article by O. Gunnarsson provides nearly 300 references to the important discoveries related to the superconductivity of C_{60} to 1997, as well as a useful overview of the state of this field to that date [2]. Most of the references included in that article have not been reproduced in this essay, and all figures and numerical values are taken from that article except where otherwise noted. Over 150 journal articles cite Gunnarsson's review, and references to the ones that seem the most important have been included here.

In 2001, J. H. Schön, Ch. Kloc, and B. Batlogg reported a transition temperature of 117 K in lattice expanded hole-doped C_{60} [1]. These results were not surprising in light of theoretical evaluations and previous experimental work; the authors suggest that values of T_c exceeding 150 K should be achievable. The supremacy of the cuprates in the high-T_c world is being challenged.

First we consider some background information on C_{60}. Then in Section 3 we examine the experimental observations of superconducting C_{60}, including the significant effects of the lattice spacing and charge carrier density on T_c. Other properties such as the superconductivity gap and the isotope effect are also reviewed. Section 4 overviews the current theoretical attempts at understanding this phenomena. Conclusions and open questions come in Section 5.

2 Background

In 1985 the soccerball-shaped molecules of 60 carbon atoms each, known as buckminsterfullerene or buckyballs, were discovered rather serendipitously by H. W. Kroto, *et al.* [3] in an attempt to understand carbon nucleation in red giant stars as a possible source of long carbon chain molecules in interstellar dust clouds. Kroto's 1991 article reviews the early history of our knowledge of this molecule [4]. The following paragraph provides a brief summary.

The experiment consisted of laser vaporization of graphite and an analysis of the resulting molecules. It was found that under certain conditions, the mass peak of C_{60} dominated the mass spectrum. Fifteen years earlier, E. Osawa had hypothesized the existence of a molecule of 60 carbon atoms, located at the vertices of a truncated icosahedron. Initially, however, there was not conclusive evidence that these observed molecules of 60 carbon atoms had any special configuration. Many experiments were carried out, and it became clear that C_{60}, and to lesser extent C_{70}, could be preferentially formed, while no other similarly sized carbon molecules could be made to dominate the spectrum. This strengthened the argument that the C_{60} molecules formed were in the highly symmetric configuration hypothesized. Then it was shown that all 60 atoms were chemically identical, consistent with the buckyball hypothesis. Solid proof finally came in 1990 when enough C_{60} could be made and purified to crystallize it and study its bulk properties. Electron diffraction clearly showed arrays of 7 Å spheroidal molecules separated by a distance of 3.1 Å. As no other form of C_{60} is known to exist, the label C_{60} is exclusively used here to refer to the structure shown in Figure 1.

C_{60} molecules form weakly bound crystals. There are several relevant length and energy scales. Within each molecule, adjacent atoms are separated by about 1.4 Å, and the energy scale is on the order of 30 eV; nearest-neighbor separation of atoms on adjacent molecules is about 3.1 Å, with an energy scale of about 0.5 eV. The band structure of a single molecule has been calculated — see reference [2] for a diagram. The lowest energy valence band is located at about 1.5 eV and holds 6 electrons; the conduction band holds 10 electrons at about -0.5 eV. These energies are measured relative to the Fermi energy, and both bands have a width of about 0.5 eV. It is believed that the band structure is not qualitatively modified in the crystallized form due to the weak interactions between the molecules, but the bands are broadened, and the amount of broadening is affected by the separation of the molecules, which can be adjusted in several ways, as discussed in Section 3.1.

There are various phonon modes to be considered in a C_{60} crystal. The lowest frequency modes are librations, or the rotations of the C_{60} molecule, with energies of 4-5 meV. Intermolecular phonon modes and vibrations involving atoms or molecules doped into the crystal are more energetic, ranging up to 17 meV for pure C_{60}. The highest frequency modes involve intramolecular vibrations, with the radial modes being less energetic than the tangential modes. For undoped C_{60}, the intramolecular energies range from 0.034 to 0.195 eV. Figure 2 shows a schematic representation of the phonon modes for A_3C_{60}, where A is potassium or rubidium. There has been controversy over which phonons are involved in the electron-phonon coupling believed by many to mediate the superconductivity.

3 Experimental Results

The first reports of the superconductivity of C_{60} appeared in early 1991; see reference [2] for a list of references. It soon became apparent that the lattice spacing of the molecules and the charge carrier density have significant effects on the transition temperature. These and other factors are discussed below. Many other properties have also been measured to assist in the theoretical understanding of the mechanism of superconductivity in C_{60}.

3.1 Effects of Lattice Spacing on T_c

Figure 3 displays the effect of lattice spacing on the transition temperature of superconducting C_{60} compounds. These are the relevant results up to 1997. All

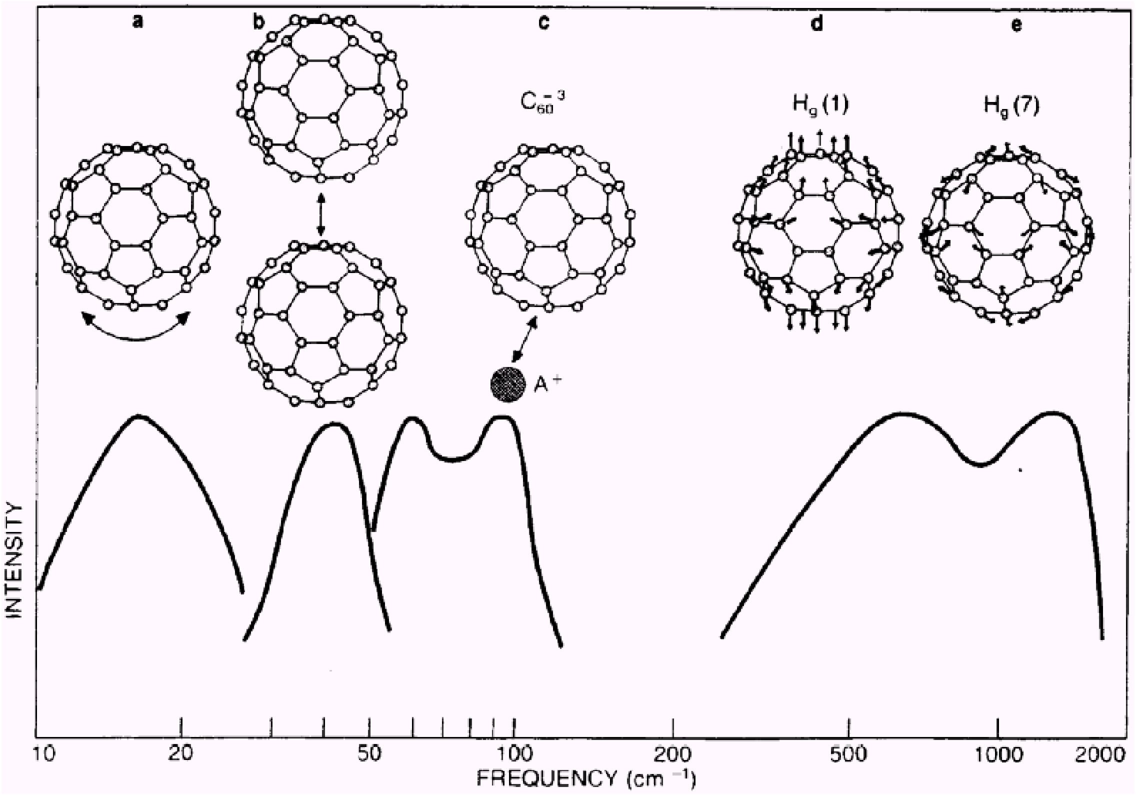

Figure 2: Phonon modes of A_3C_{60}, for A = K or Rb.

of these compounds are C_{60} crystals intercalated with alkali atoms between the C_{60} molecules. Two methods have been used to adjust the lattice spacing: chemical doping and pressure. Larger atoms such as rubidium and cesium expand the lattice more, while the application of pressure decreases the lattice constant. It is interesting to note that no lithium compounds are listed in Figure 3; while Li_2AC_{60} is not superconducting for A representing any of the stable alkali atoms, in 1999 it was found that Li_3CsC_{60} and Li_4CsC_{60} are superconducting [5].

Alkali atoms were used in part because they donate electrons to the crystal; see Section 3.2 for a brief discussion. But more recently the neutral molecules $CHCl_3$ and $CHBr_3$ have also been used to increase the lattice spacing, and the search is on for other molecules or methods to expand the lattice even further, given the positive correlation between lattice parameter and transition temperature [1]. There has been, however, at least one report of a negative correlation between lattice parameter and T_c under certain conditions [6].

It should also be noted that the crystal structure depends on what atoms or molecules are intercalated between the C_{60} molecules. Both face-centered cubic and body-centered cubic configurations can be achieved with the smaller alkali atoms, larger atoms introduce an orthorhombic distortion to the cubic lattice, and the addition of the neutral molecules mentioned above results in a hexagonal structure.

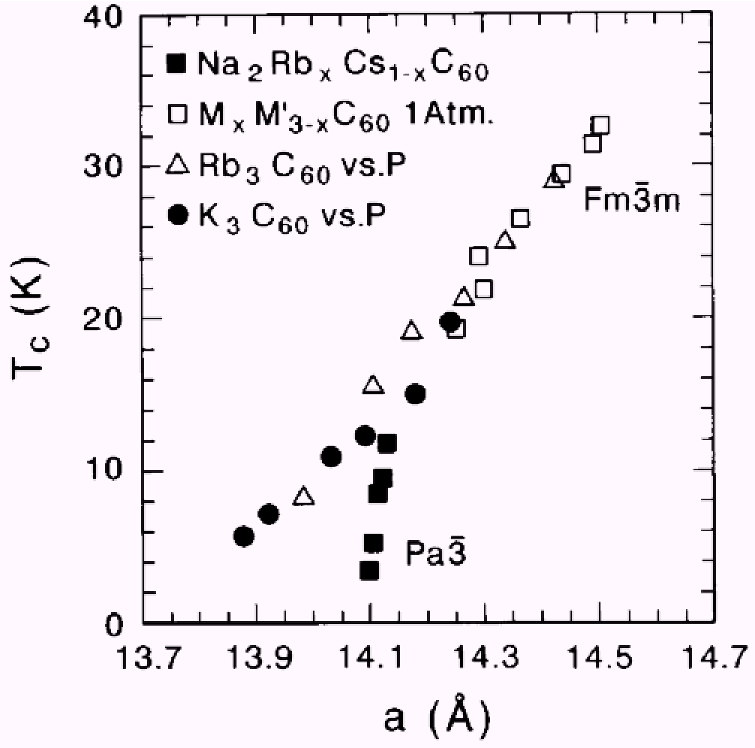

Figure 3: Effect of lattice spacing, a, on T_c for various compounds. M and M′ represent K, Rb, and Cs.

The orientation of the C_{60} molecules on their lattice sites is somewhat disordered, and this has an effect on some of the electronic properties, but has generally been ignored in calculations.

3.2 Effects of Charge Carrier Concentration on T_c

The first superconductivity experiments involved compounds with three charge carriers per C_{60} molecule. This was easily achievable and seemed to work best — electron concentrations of 0.1 less or 0.25 more than 3 per molecule show significant decreases in T_c for the alkali compounds. Rare earth elements have also been used to produce superconducting C_{60}, with estimated concentrations of 5.5 electrons per molecule and T_c's in the single digits

In 2000, Schön, *et al.*, published reports of superconductivity in pure C_{60} crystals with the charge carriers introduced via a field-effect device. See references [1] and [7]. A schematic of the setup is shown in Figure 4. Figure 5 shows the effect of various carrier concentrations on T_c, for both electrons and holes. There was no success in doping the crystals with holes by chemical means, but this field-effect setup allows fine tuning of both negative and positive charge carrier concentrations.

Figure 5 indicates that electron-doped crystals only exhibit superconductivity

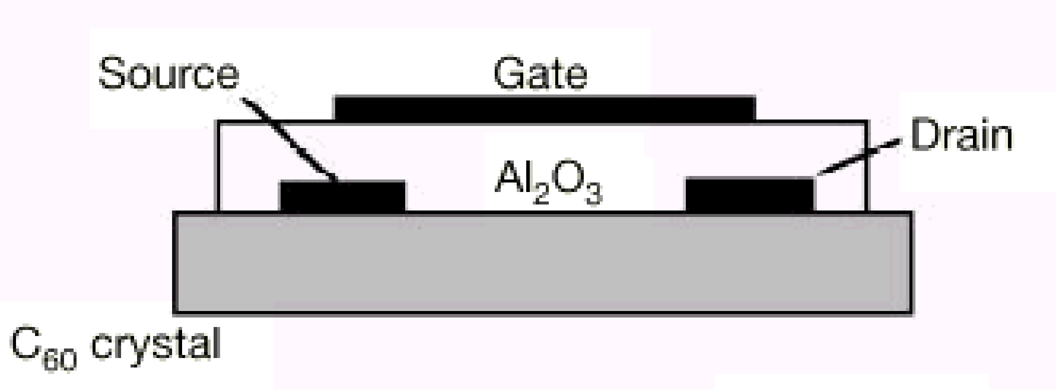

Figure 4: Field-effect setup for inducing charge in C_{60}. This diagram is taken from reference [7].

when they have between 2.5 and 3.5 electrons per C_{60} molecule. This is consistent with measurements done on samples doped with electrons by chemical means. Three electrons half fill the valence band, and this fact is often used as an explanation of the peak T_c being at that concentration. For holes, a much wider range of carrier concentrations exhibits superconductivity; the upper limit was not measured due to a breakdown of the oxide layer between the crystal and the gate. The peak transition temperature is between 3 and 3.5 holes per C_{60} molecule, which does not represent a half-filled conduction band. At least one explanation has been offered for the shape of these curves [8].

3.3 Superconductivity Gap, Isotope Effect, and Other Properties

The superconductivity gap, Δ, is important in determining electron-phonon coupling strength. Early measurements yielded some values for the reduced gap, $2\Delta/T_c$, that were significantly higher than the BCS weak coupling value of 3.53; various measurement methods gave results ranging from 2.0 to 5.4. For Rb_3C_{60}, the consensus seems to have settled on 4.2 ± 0.2 [9], but there is one report of $2\Delta/T_c \simeq 3.53$ [10]. For pure C_{60}, the numbers 3.3 to 3.8 have been published [11].

For single element materials, BCS theory predicts a T_c dependence on the mass of the nucleus, M; the isotope used affects the transition temperature according to $T_c \sim M^{-\alpha}$ where $\alpha = 0.5$. Experiments have found no effect on T_c for different alkali isotopes, while the latest measurement of α is about 0.21 for complete substitution of C-13 for C-12 [12]. Partial substitution levels have given contradictory results.

Many other properties of superconducting C_{60} have been measured or estimated, including the critical fields (C_{60} is a Type II superconductor), the coherence length, and the penetration depth, as well as the resistivity for non-superconducting

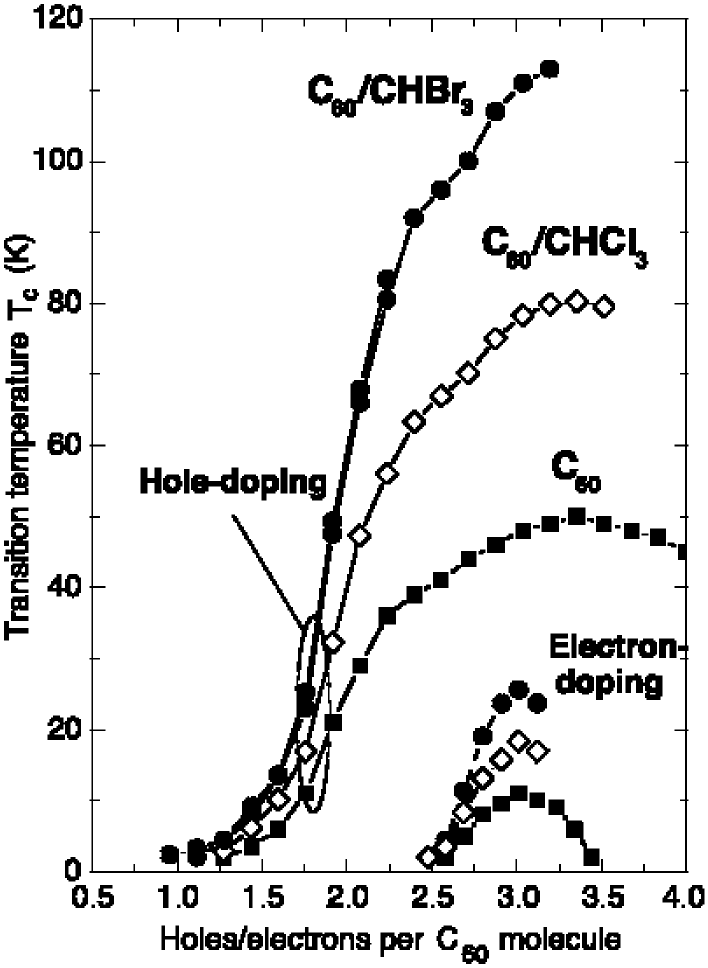

Figure 5: Effect of positive and negative charge carrier concentrations on T_c for three lattice spacings: 14.16 Å, 14.28 Å, and 14.43 Å. This graph is from reference [1].

conditions. Many of the calculated values have wide uncertainties, and researchers are actively working on improving the measurements.

4 Theoretical Considerations

There does not appear to be debate on the broad class of superconductors to which C_{60} belongs — it is a classical s-wave superconductor; however, what causes the pairing of the electron is up for debate. There are two possible mechanisms that could mediate the superconductivity of C_{60}: electron-phonon interactions and electron-electron interactions. Both possibilities have been seriously considered, and if phonons are the important arbiters, the question of which phonons becomes important. While the tangential intramolecular phonons have received the most attention, there is not a universal a consensus on this matter.

Many theoretical considerations use the McMillan formula of 1968 for estimating the transition temperature:

$$T_c = \frac{\omega_{ln}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \tag{1}$$

where ω_{ln} is a typical phonon frequency, λ is the electron-phonon coupling, and μ^* is the Coulomb pseudopotential. This formula is based on the Migdal-Eliashberg theory (1958 and 1960, respectively) which ignores the vertex corrections for the electron-phonon interactions and is assumed to be valid for phonon frequencies that are much smaller than the electron energy scales involved. Its validity is unclear for C_{60} compounds. Various methods have been used to calculate the values in the McMillan formula. It is argued that the tangential intramolecular phonons are most important because they are the most energetic, although not all agree.

Values for λ have been estimated as

$$\lambda \sim N(0)\sum_{\nu\alpha}\frac{\Delta\varepsilon_{\nu\alpha}^2}{\omega_\nu^2} \tag{2}$$

where $N(0)$ is the density of states, α is the energy level, ν is the phonon coordinate, $\Delta\varepsilon$ is the energy shift due to the phonon displacement, and ω is the phonon frequency. See reference [2] for justification and more details. There is not agreement on which terms in the sum are dominant, and theoretical and experimental estimates of the density of states cover a range of values, generally between 5 and 10 per eV and spin. Some of the estimation methods are questionable because of the theoretical assumption that phonon energies are much less than the bandwidth, which is not true if the intramolecular phonons are the important ones. Estimates of the coupling between electrons and the intramolecular phonons as of 1997 ranged from 0.009 to 0.059 eV.

The approximation for λ of equation 2 is used to explain the dependence of T_c on the lattice parameter: the further apart the C_{60} molecules, the less their band structures overlap; therefore the energy bands are narrower and the density of states higher. There is, however, recent contradictory evidence concerning the relationship between the density of states and the lattice parameter in the field-effect transistor configuration [13].

The Coulomb pseudopotential, μ^* is a reduction of the dimensionless Coulomb potential, μ, due to retardation effects, the correlated scattering of electrons into higher energy states. μ is the product of a typical Coulomb repulsion energy, U, of 1–1.5 eV, and the density of states, $N(0)$. Simple models yield the following equation:

$$\mu^* = \frac{\mu}{1+\mu\ln\left(B/\omega_{ph}\right)}. \tag{3}$$

B is a typical electron energy (half the bandwidth) and ω_{ph} is a typical phonon energy. If $B/\omega_{ph} \gg 1$, then the Coulomb potential can be significantly reduced. Some theorists argue that the relevant width B includes all the bands, on the order of 30 eV, in which case μ^* is about 0.2 eV, not much larger than for conventional superconductors; if the appropriate width is that of a single band, this theory is inadequate and other mechanisms must be taken into account. While this formula was derived within the Eliashberg model, it has recently been reported that the formula is still valid when vertex corrections are taken into account, when B represents the Fermi energy, and ω_{ph} is properly rescaled [14].

In a 2001 article, E. Cappelluti, *et al.* claim that the experimental evidence for Rb_3C_{60} can not be made to fit the Migdal-Eliashburg equations, in light of more precise measurements of the isotope effect and the superconductivity gap [9]. They do not, however, reject the idea that phonons mediate the superconductivity, and they offer some testable theories [15].

Other explanations of the superconductivity of C_{60} have been offered. Soon after its discovery, an attractive electron-electron interaction was theorized by several groups. If the Coulomb pseudopotential is reduced to the point where it becomes negative, then electron-electron coupling could be used to explain the behavior. A model incorporating both phonon and electronic effects into the pairing mechanism has been proposed which the authors claim can explain some of the experimentally based calculations of the coupling constant λ and the pseudopotential μ^* [16]. Both of these effects have been considered by others, as well — see the section on Jahn-Teller effects beyond the Migdal-Eliashberg treatment in Gunnarsson's review article [2], and more recently in reference [17]. Other proposals include a model for A_xC_{60} based on a bond between neighboring alkali atoms [18].

5 Conclusions

Research on superconducting C_{60} is a very active field for both theorists and experimentalists. Higher and higher transition temperatures are being reached, and the properties of these materials need to be better characterized so as the better understand the mechanism — or mechanisms — of superconductivity. Most broadly speaking, we want to know how to explain the superconductivity of C_{60} and how to raise the transition temperature even higher.

In explaining the superconductivity, there is the question of what mediates the electron pairing. If it is phonons, which ones are important? Can the conventional phonon-based theories be made to explain the data? If not, can they be satisfactorily modified? Perhaps electron-phonon coupling is not the dominant mechanism; if this is the case, can electron-electron interactions explain the superconductivity? Or do we need new theories altogether? Can a theoretical explanation assist in figuring out how to further raise the transition temperature?

Given the increasingly high observed transition temperatures, how far can this go? Since there is a correlation between the lattice constant and T_c in most observations to date, what can be done to further increase the lattice constant? The field effect configuration is an innovative way of adjusting the density of charge carriers; are there other alternative experimental approaches that could yield large gains? Perhaps C_{60} is not the best molecule — superconductivity has been reported in C_{70} [19] as well, although at less impressive temperatures. It has been proposed that fullerenes smaller than C_{60} may have higher transition temperatures than those reported for C_{60} [20]; one published calculation predicts room-temperature T_c for C_{28} [21]! It will be interesting to follow advances in this field as the fullerenes try to rival the cuprates for dominance in the high-T_c world.

References

[1] J. H. Schön, Ch. Kloc, B. Batlogg, *Science*, **293**, 2432 (2001).

[2] O. Gunnarsson, *Rev. Mod. Phys.* **69**, 575 (1997).

[3] H. W. Kroto, J. R. Heath, S. C. O'Brian, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).

[4] H. W. Kroto, A. W. Allaf, and S. P. Balm, *Chem. Rev.*, **91**, 1213 (1991).

[5] M. Kosaka, K. Tanigaki, K. Prassides, S. Margadonna, A. Lappas, C. M. Brown, A. N. Fitch, *Phys. Rev. B*, **59**, R6628 (1999).

[6] P. Dahlke, M. S. Denning, P. F. Henry, M. J. Rosseinsky *J. Am. Chem. Soc.*, **122**, 12352 (2000).

[7] J. H. Schön, Ch. Kloc, B. Batlogg, *Nature*, **408**, 549 (2000).

[8] V. M. Loktev, *Low. Temp. Phys.*, **27**, 414 (2001).

[9] E. Cappelluti, C. Grimaldi, L. Pietronero, S. Strassler, G. A. Ummarino, *Eur. Phys. J. B*, **21**, 383 (2001).

[10] R. Hesper, L. H. Tjeng, A. Heeres, G. A. Sawatzky, *Phys. Rev. Lett.*, **85**, 1970 (2000).

[11] J. H. Schön, Ch. Kloc, H. Y. Hwang, B. Batlogg, *Science*, **292**, 252 (2001).

[12] M. S. Fuhrer, K. Cherrey, A. Zettl, M. L. Cohen, V. H. Crespi, *Phys. Rev. Lett.*, **83**, 404 (1999).

[13] R. E. Dinnebier, O. Gunnarsson, H. Brumm, E. Koch, P. W. Stephens, A. Huq, M. Jansen, *Science*, **296**, 109 (2002).

[14] T. H. Park, H. Y. Choi, *Phys. Rev. B*, **65**, art. no. 052504 (2002).

[15] C. Grimaldi, E. Cappelluti, L. Pietronero, S. Strassler, *Phys. Solid State*, **44**, 454 (2002).

[16] J. W. Yoo, T. H. Park, H. Y. Choi, *Physica C*, **364**, 66 (2001).

[17] S. Suzuki, S. Okada, K. Nakao, *J. Phys. Soc. Jpn.*, **69**, 2615, (2000).

[18] A. I. Chaban, *J. Supercond.*, **14**, 599 (2001).

[19] J. H. Schön, C. Kloc, T. Siegrist, M. Steigerwald, C. Svensson, B. Batlogg, *Nature*, **413**, 831 (2001).

[20] M. Côté, J. C. Grossman, M. L. Cohen, S. G. Louie *Phys. Rev. Lett.*, **81**, 697 (1998).

[21] N. Breda, R. A. Broglia, G. Colo, G. Onida, D. Provasi, E. Vigezzi, *Phys. Rev. B*, **62**, 130 (2000).