

Research Article

Phonons in A_3C_{60} Lattice and Structural Dynamics

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The critical temperature (T_C) of superconductivity in A_3C_{60} compounds is generally lower smaller with alkali atoms (A). Furthermore T_C decreases with applied pressure. In the BCS model, these trends are explained by the lower density of states at the Fermi level for a decreased lattice constant (R). There is more than one counterexample, however, suggesting that BCS does not give the whole truth. The most important one is that the compound with the largest lattice constant, Cs_3C_{60} , is not superconducting at all at ambient pressure. In this paper we derive a novel model where a negative lattice contribution to Hubbard U , proportional to $1/R$, is taken into account. It is possible to explain why A_3C_{60} compounds with $A = Li$, and Na have a low T_C or are not superconducting at all, and why Cs_3C_{60} is superconducting only at applied pressure and then with the highest T_C of all C_{60} alkali fullerenes. It is concluded that the density of states mechanism derived in the BCS model is in doubt. Nevertheless superconductivity in A_3C_{60} depends on electron-phonon coupling. The dominating phonon is the bond stretching A_g phonon, a breathing phonon for the whole fullerene molecular ion.

1. Introduction

The discoveries of conductivity and superconductivity (SC) in K_3C_{60} and Rb_3C_{60} were great events in science during the 1990s [1–5]. SC was later discovered in a number of other A_3C_{60} compounds, where A stand for alkali atoms: Li, Na, K, Rb, or Cs. Generally, increase of the lattice constant leads to a higher critical temperature T_C . Some of the A_3C_{60} compounds ($A = Li, Na$) with the smallest lattice constants are not superconducting [6–8]. Only C_{60} fullerenes have proven to be superconducting (SC).

Remarkably, the compound with the highest lattice constant does not follow this trend [9–11]. Disorder-free Cs_3C_{60} is an antiferromagnetic insulator at ambient pressure. However, already at the quite modest pressure of 3 kbar (≈ 3000 atm), it turns into a superconductor (SC) with the highest T_C known for any fullerene [9–11]. At temperatures above T_C Cs_3C_{60} passes directly into a semiconducting and antiferromagnetic phase. This system thus needs an explanation model which is not depending on the existence of free electrons, as in the BCS model. Takabayashi et al. further point out [11] that transfer from SC to antiferromagnetic phase appears to be “purely electronic”, thus seemingly explicable without resorting to nuclear dynamics.

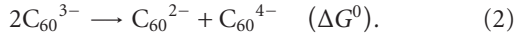
There are a number of peculiarities in experimental data in general, as summarized by Gunnarsson [12], Rosseinsky [13], Margadonna and Prassides [14], and Iwasa and Takenobu [15]. A widely accepted approach is to treat the metallic alkali C_{60} fullerenes as metals and apply the BCS model [12–15]. In the latter model, T_C increases if the density of states at the Fermi level increases. In the case of A_3C_{60} the Fermi level is in a narrow band, so the conclusion is that if the band width further decreases, the density of states will increase and hence also T_C . However, contrary to this deduction, Cs_3C_{60} is not superconducting at all.

Expansion of the lattice by intercalation of molecules leads to a higher density of states and to a higher T_C . Lattices of several A_3C_{60} compounds have been expanded by intercalating NH_3 and this improved the SC properties [16–18] for some of them, but in K_3C_{60} and Rb_3C_{60} , SC was lost and antiferromagnetism appeared instead.

SC A_3C_{60} is a “molecular metal”. If so, one should be able to derive (Hubbard) $U = 0$ for the solid, using molecular data. The molecular Hubbard U is defined by

$$U = I - A, \quad (1)$$

where I is the ionization energy and A is the electron affinity [12–15]. ΔG^0 is the adiabatic energy [19] for charge disproportionation according to:



U is thus the corresponding vertical energy. Usually $U > 0$ for a molecule or insulator, but it is still possible to have $\Delta G^0 = 0$, that is, oxidation state degeneracy according to (2). The reason is that ΔG^0 corresponds to the optimum geometry of the products, in the present case for C_{60}^{2-} and C_{60}^{4-} , in (1). $\Delta G^0 < 0$ means that the sites are differently occupied in a pair of electrons [charge alternant phase or charge density wave (CDW) phase].

In the CDW phase, equivalent sites may exchange electron pairs, but there may be an activation barrier. The activation barrier may be removed due to interaction with the C_{60}^{3-} state [19]. Interaction with C_{60}^{3-} is maximized when $\Delta G^0 = 0$. For K_3C_{60} , most estimations of U end up with values larger than 1 eV. This is too large to reach $\Delta G^0 = 0$. Below we will find that if the lattice contribution to U is taken into account, it is possible to achieve $\Delta G^0 = 0$.

As another or complimentary cause of SC, one has often referred to the Jahn-Teller effect. The Jahn-Teller effect does not include the degeneracy of (2), however. A possible rational for involving the Jahn-Teller effect at electron transport is that it is different for different site charges, but that effect must be of minor importance in comparison with the degeneracy between site oxidation states, directly related to the Mott-Hubbard problem and the structural dynamics generated by nonconserved oxidation states.

On the basis of the Jahn-Teller effect, one has concluded that a single H_g mode is important. In contradistinction, it will be argued here that the A_g breathing mode is the very cause of structural dynamics leading to SC.

In this paper we will use a mixed-valence model for three oxidation states (MV-3) [19–22]. “Valence” here meant the charge on the C_{60} molecule. The negative lattice contribution to Hubbard U is inversely proportional to the lattice constant R . Contraction of the lattice, for example by applied pressure [23–25] therefore leads to a lower U , a more negative ΔG^0 in (2), and reduced T_C . T_C in Rb_3C_{60} decreases almost linearly with applied pressure [25]. For Rb_3C_{60} ΔG^0 is negative already ambient pressure but for Cs_3C_{60} ΔG^0 is positive. This makes Cs_3C_{60} an antiferromagnet at ambient pressure, but applied pressure decreases the lattice constant enough to make ΔG^0 negative and therefore an almost perfect SC.

Finally we will discuss electron-phonon interactions, which are of fundamental importance for SC, in MV-3 as well as BCS theory. We will see, using MV-3, that the same electron-phonon coupling is applicable to all C_{60} fullerenes, including Cs_3C_{60} .

2. Molecular Electronic and Vibrational Structure

It was early established that the valence electrons of the alkali atoms are transferred to the threefold degenerate, lowest unoccupied (LU) t_{1u} molecular orbital (MO) of

C_{60} , thereby forming $A_N C_{60}^{N-}$ where N is the number of electrons in LUMO. We will only be interested in the case with incompletely filled LUMO ($N < 6$). Due to the spherical symmetry, the electronic states for a single C_{60} may be compared to the multiplet states of a single atom in the second row with incompletely filled 2p shell. The $2s^2 2p^2$ configuration of carbon produces the states: 3P , 1D , 1S . According to Hund’s rule, the ground state has the highest possible spin, therefore 3P . In the C_{60} anions the energy difference between high spin and low spin states is very small [26–28]. For C_{60}^{2-} , the reason is that the exchange integrals are numerically small, of about the same size as the relevant integrals for the $t_{1u}^2 \rightarrow t_{2g}^2$ correlation effect [29–31].

The low spin ground state of C_{60}^{2-} , C_{60}^{3-} , and C_{60}^{4-} is a prerequisite for superconductivity according to the MV-3 model. If in addition (2) also holds with a negative ΔG^0 , the diamagnetism of C_{60}^{3-} can be explained. Jahn-Teller effects and electron-phonon coupling are of minor importance in this case compared to electron correlation effects.

Another prerequisite for SC is that electron pair transfer (EPT) from a C_{60}^{4-} site to a C_{60}^{2-} site can take place without activation energy, or, in other words, that the electron pair is not trapped at the C_{60}^{4-} site. This has been discussed by Duščas and the author, and it was found that the reorganization energy is only 0.24 eV for adding two electrons to C_{60}^{2-} [32]. The reason for this is that the bond length change is very small.

Typical for π systems is that occupation of the bonding π MOs up to and including HOMO tends to shorten some of the CC bonds. The shortened bonds are said to have “double bond character”. In C_{60} the shorter bonds are the thirty ($3 \times 20/2$) bonds that are common to two hexagons (Figure 1). Occupation of LUMO lengthens these bonds, since LUMO tends to be antibonding in the double bonds. Full occupation of the t_{1u} LUMO to form C_{60}^{-6} leads to a lengthening of the double bonds of C_{60} to almost equal bond lengths over the whole molecular ion [32].

We are thus looking for a mode where the t_{1u} LUMO is stabilized on one molecule and at the same time destabilized on the other. The vibrational mode coupled to EPT between t_{1u} orbitals on different sites is the one that shortens the double bonds and lengthens the single bonds. This is the breathing mode of the strong bonds in Figure 1.

Experimentally, breathing modes have been found to be involved in superconducting systems [33]. The theory [19, 29, 30] is equivalent to the Holstein diatomic model for a single electron [34, 35]. In neutral C_{60} the relevant phonon should be the A_g phonon at 1470 cm^{-1} [12].

Gunnarsson pointed out that it is the size, not the mass of the alkali ion that determines T_C [12]. We therefore do not expect large contributions to the electron-phonon coupling due to the motion of the metal ions. The A_g breathing mode is very likely the phonon that couples to the electrons in SC. The H_g modes tend to increase some double bonds while decreasing the corresponding ones on the opposite side of the molecule, thus should be unimportant for EPT.

Next we will study EPT between two adjacent molecular ions A and B. The fundamental assumption in the chemical model for SC is that electrons and phonons are coupled

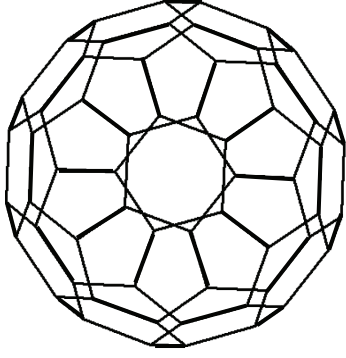


FIGURE 1: C_{60} molecule. The most relevant electron-phonon interaction mode for EPT is the in-phase bond stretch for the short and strong bonds, drawn with thick lines.

in a motion that makes the electron pair oscillate between adjacent sites (in a time-dependent treatment). For this to happen, the activation barrier has to be sufficiently low. The exact wave function for the electron pair transferring between A and B may be complicated to write down, in particular since the relevant states are correlated and cannot be represented by single Slater determinants. If the t_{1u} LUMO is called “a” on site A and “b” on the adjacent site B, there are three spin singlet states, where two electrons are localized on site A (aa), on site B (bb) or where the two electrons are localized on different sites (ab + ba). The symmetrized form of the former are $aa + bb$ and $aa - bb$. $ab + ba$ corresponds to the spin-coupled antiferromagnetic state [or spin density wave state (SDW)]. $aa + bb$ and $aa - bb$ are the necessary states for EPT, thus for SC.

It is interesting that the three A_3C_{60} systems which are not superconducting at ambient pressure, $NH_3K_3C_{60}$, $NH_3Rb_3C_{60}$, and Cs_3C_{60} with large lattice constant R , are all antiferromagnetic, thus with the $ab + ba$ ground state [9, 36, 37]. The latter wave function cannot superconduct since the electrons are fixed one on each site.

3. Hubbard U and Lattice Interactions

Estimation of U from molecules leads to a molecular U in the range 2.7–3.1 eV [12, 13, 38, 39]. For the solid there are experimental estimates of U in the range 0.8–1.27 eV [39–43]. This refers to a crystal where all site charges are the same, say Z . The charge disproportionated CDW phase, where the charges $(Z - 1)$ and $(Z + 1)$ alternate, is favored by an additional negative contribution according to the Born model. The Born radius R can be taken as the lattice constant. The decrease of the Born free energy is (atomic units)

$$\Delta G(\text{Born}) = -\frac{(Z-1)^2 + (Z+1)^2 - 2Z^2}{2R} = -\frac{1}{R}, \quad (3)$$

(neglecting the Born exponent). R is about 20 Bohr for fullerenes. $\Delta G(\text{Born})$ is thus equal to $-1/20$ Hartree or -1.3 eV. This lowers the energy difference between the SDW and CDW state, thus Hubbard U decreases. After this correction we obtain roughly $U \approx 0$ for the A_3C_{60}

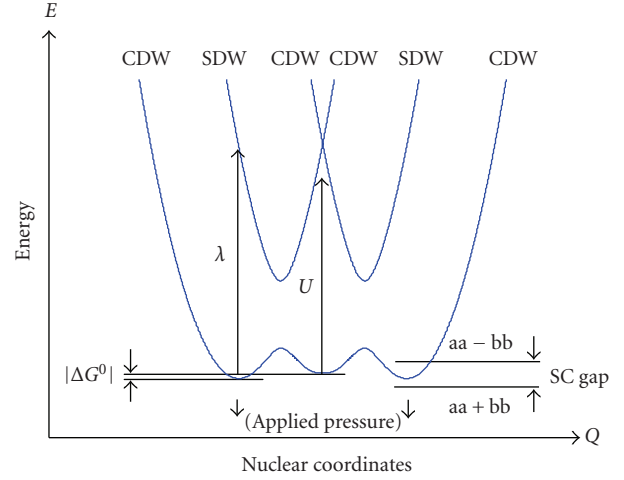


FIGURE 2: PESs of the MV-3 model. Curvatures are exaggerated. λ is reorganization energy. The fat horizontal bars are vibronic energy levels. $aa + bb$ and $aa - bb$ denote approximate wave functions for the given energy levels. For $NH_3K_3C_{60}$, $NH_3Rb_3C_{60}$, and Cs_3C_{60} , the SDW-PES is lower than CDW-PES. Fat arrows show the behavior of CDW-PES at applied pressure. $|\Delta G^0|$ is defined by (2).

fullerenes. In conclusion, Hubbard U is less smaller with lattice constant.

High pressure in A_3C_{60} systems leads to a smaller lattice constant. Thus the CDW phase with C_{60}^{2-} and C_{60}^{4-} is favored compared to the SDW phase with C_{60}^{3-} sites. If on the other hand the lattice is expanded, the SDW phase wins and becomes the ground state. SC cannot occur since the ground state is mainly $ab + ba$.

Figure 2 shows a total energy potential energy surfaces (PES) at the molecular level, as a function of a collective breathing mode for the carbon atoms. In the case given in Figure 2 the outer minima are lower, and this corresponds to the CDW case, the case that applies to all A_3C_{60} systems except Cs_3C_{60} .

The important thing is that the inner PES, corresponding to the SDW, is present slightly above the CDW-PES. In most cases there is an interaction between CDW and SDW that opens a gap. The lower state is $aa + bb$ mixed with $ab + ba$. This energy level is denoted as $aa + bb$ in Figure 2. The $aa - bb$ is the upper state. Provided the lower state has a major component of $aa + bb$, the gap is a true SC gap. If, however, the SDW-PES is below the CDW-PES, the $ab + ba$ component will be the major one in the lower state. Since $ab + ba$ is the wave function which put an electron on A and one on B, EPT is not possible and hence there is no SC.

We arrive at the picture sketched in Figure 3. As the lattice constant (R) increases the CDW states, denoted $aa + bb$ and $aa - bb$ in Figure 3 are increasing in energy due to the numerically smaller lattice energy contribution according to (3). $aa + bb$ interacts with $ab + ba$, and this interaction is maximized at the crossing point (Figure 3). The ground state is mainly of $aa + bb$ type except for Cs_3C_{60} . In Cs_3C_{60} the ground state has a very large component of $ab + ba$, which means that the antiferromagnetic phase wins

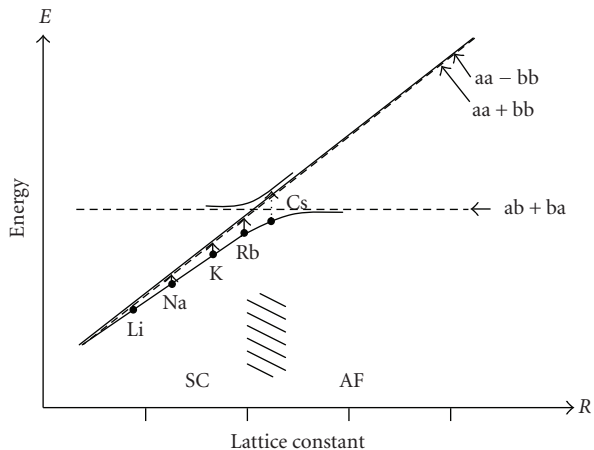


FIGURE 3: Free energies for the SDW and CDW states as a function of lattices constants in (3). Arrows at the symbol for the element show the superconducting gap. Cs_3C_{60} is in the antiferromagnetic region (AF) where the gap is a pseudogap.

over SC phase. High pressure decreases the lattice constant for Cs_3C_{60} , changing the composition of the ground state. Interestingly, when the pressure is sufficient to change the phase into a SC phase, T_C is the largest one, corresponding to $\Delta G^0 = 0$ in Figure 2.

A number of experiments have been carried out on NH_3 -doped fullerides [16–18]. NH_3 intercalates without causing any other change than increasing the lattice constant [13]. As a function of volume/ C_{60}^{3-} the critical temperature T_C increases monotonically. If the increase in lattice constant is too large, the minimum of the SDW-PES appear below the minimum of the CDW-PES and the SC is lost. Instead the antiferromagnetic phase appears. This is very clear from Figure 3. As we move to the right in the diagram the ground state wave function gets increased character of $ab + ba$, equivalent to antiferromagnetic coupling.

The structural change at electron transfer is associated with a total energy lowering denoted as “reorganization energy” (λ). Large λ is directly related to high effective mass in the Holstein model [34, 35]. For fullerenes λ has proven to be comparatively small in the cases examined, or about 0.05 eV for single electron transfer [32]. As a comparison, λ is about 0.22 eV in polyacetylene [44]. The Jahn-Teller effect or modifications due to chemical bonding between the fullerene molecules may modify some distances, but this is usually of little importance for λ .

The coupling in the case of electron pair transfer is well defined and different from the coupling in single electron transfer and, of course, different from magnetic couplings. The most important difference is that the a^2 and b^2 states do not couple directly, but assume the presence of the SDW $ab + ba$ state. In principle the coupling may be calculated in a quantum chemical calculation that includes two molecules.

An important problem is to understand why A_4C_{60} is an insulator. A_4C_{60} with an unfilled shell-like A_3C_{60} has

a different Hubbard U . Equation (3) corresponds to the following equation:



We now see that the right member consists of two odd-electron systems, while A_4C_{60} itself has an even number of electrons, of course. Referring to the fact that systems with an even number of electrons generally have lower energy than systems with an odd number of electrons, it is quite simple to understand why (3) has a ΔG^0 close to zero, while ΔG^0 for (4) is decidedly positive. In any case this may be verified in quantum chemical calculations which involve two adjacent molecules.

Knupfer and Fink have used electron energy loss spectroscopy (EELS) for A_4C_{60} systems and found that Mott-Hubbard behavior with ΔG^0 is larger than the one for the A_3C_{60} systems [45]. Iwasa applied reflection techniques to A_3C_{60} , verifying the metallic properties with $\Delta G^0 \approx 0$ [46]. Other experiments show a similar trend [47].

The reason why A_4C_{60} systems are nonSC may be large Hubbard U , as discussed by Rosseinsky [13]. Another important possibility may be that Jahn-Teller effect splits the t_{1u} level as shown in STM experiments [48]. The lower level is fully occupied [49], making charge transfer impossible.

4. Discussion

In this paper we have shown that a molecular model provides a satisfactory explanation of the dependence of T_C on lattice constant in A_3C_{60} systems. The model is based on the structural dynamics that is connected to EPT and oxidation state degeneracy. Decrease of the lattice constant in Cs_3C_{60} due to increased pressure leads to appearance of SC. If the pressure is further increased, T_C increases at first, but eventually Cs_3C_{60} shares the fate of the other C_{60} fullerides, so that T_C decreases with increased pressure. The fact that T_C increases with increased pressure at first is a problem not only in the BCS model but also in the present model. Since this problem has to do with the properties of the ground state wave function [($ab + ba$) versus ($aa + bb$) character], it would be unwise to dig deeper into this problem without accurate calculations.

In the BCS model too, decrease of the lattice constant leads to a lower T_C , but in that case the reason is decrease of the density of states. The BCS mechanism is doubtful to say the least, as has been shown during the historical development of the SC phenomenon. In the A_3C_{60} fullerides it is a quite successful model but it does not predict the nonSC behavior for Cs_3C_{60} . It also does not explain why $NH_3K_3C_{60}$ and $NH_3Rb_3C_{60}$ are antiferromagnets. The phase change from SC to antiferromagnetic is driven by the composition of the ground state wave function, which in its turn depends on the lattice constant.

The Jahn-Teller effect is overrun by intermolecular bonding or at least strongly modified. In the molecular SC model the importance of the Jahn-Teller effect is superceded by the oxidation state degeneracy (disproportionation). However, the Jahn-Teller effect (combined with the chemical

bonding effect) may well explain why A_4C_{60} systems are not superconducting, as illustrated in the STM experiments by Wachowiak et al. [48] and further detailed by O'Shea [49]. The t_{1u} degeneracy is split and the lower MO is fully occupied, thereby making SC impossible. An interesting discussion of the Jahn-Teller effect in C_{60} fullerenes and the dependence of lattice constant on superconductivity have recently been given by Capone et al. [50]. Some conclusions are different from those of this paper, however.

Another, or contributing reason for the absence of SC in A_4C_{60} compounds may be the large Hubbard U for these compounds as compared to the A_3C_{60} compounds. An important task is to obtain an accurate value of U , as has in fact been the goal in previous review articles [12–15]. The description here introduces the nuclear coordinate into the Mott-Hubbard problem. Thereby it becomes possible to discuss the vibronic states of importance in superconductivity. The distinction between ΔG^0 and U is important.

Phonons lower the energy in the SC phase where they interact with the electrons. The motion of the electron pair is correlated with the nuclear coordinates in the breathing mode. The vibration motions of the nuclei “pump” the electron pairs between the sites without expense of energy. This happens in a quantum mechanical manner and leads to an energy lowering that stabilizes the SC phase with an energy gap to the first excited state. The antiferromagnetic phase cannot behave in the same way, since the charge distribution is inert and almost independent of the exact positions of the nuclei. The relevant breathing phonon in the case of A_3C_{60} is very likely a double-bond stretching phonon with symmetry A_g .

In this paper the difference in lattice energy between the CDW and SDW phases has been pointed out as a general explanation of SC in A_3C_{60} . The BCS model on the other hand states that T_C depends on the density of states, but this does not hold for Cs_3C_{60} . Takabayashi et al. therefore concluded that SC in Cs_3C_{60} is of a different type, more similar to SC in cuprates with CuO_2 plane [10, 11, 51]. This is possible, not least considering the change of crystal structure from fcc in most A_3C_{60} fullerides to A15-bcc in Cs_3C_{60} . Of particular importance is that in Cs_3C_{60} the density of states at the Fermi level is higher than in the A_3C_{60} fcc fullerides and should have a higher T_C rather than not being SC at all.

In model used here change of structure leads to different Born model contributions to the CDW state in (3) shifting the onset pressure of SC. Since it is not known which onset pressure would apply to the fcc phase, a detailed discussion of this problem would not be successful at this stage. To complicate matters further, change of structure also leads to differences in coupling between the SDW and CDW states.

The author firmly believes that the BCS model is a kind of rough limit model for the transition between ordinary metals (e.g., alkali metals and coinage metals at normal pressure) and SC metals. The presence of free electrons is there guaranteed. The BCS model should not be used in cases where insulating phases play roles [52]. In any case the BCS model appears to be too crude a model to allow adequate parametrization. In the BCS model the binding energy of a pair of electrons determines whether SC

appears, whereas in reality the binding energy depends on the presence of positive nuclei and the mobility on the structural reorganization energy versus coupling [52].

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