

Superconductivity in Alkali Intercalated C₆₀

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ABSTRACT. A model for superconductivity in alkali intercalated C₆₀ is proposed. The key to the high observed transition temperatures is the molecular nature of fullerite. Two different energy scales $t_{\text{intra}}/t_{\text{inter}} \geq 5 - 10$ for electron hopping on the balls and between balls respectively allow for a large electron phonon coupling constant $\lambda = 2 N \cdot V$. Electron scattering occurs mainly by vibrations on the balls and is dominated by t_{intra} , while the density of states N is given by inter-ball hopping and $\sim t_{\text{inter}}^{-1}$. Combined with a high Debye frequency this results in high transition temperatures. First-principles and semi-empirical methods are used to calculate the relevant parameters. A comparison with intercalated graphite shows crucial differences resulting in much smaller T_c values.

Superconductivity with unusually high transition temperatures ($T_c \geq 30\text{K}$) has recently been discovered [1] and has raised intense theoretical speculations.[2-7] We have investigated the electronic structure of these materials and calculated the conventional electron-phonon coupling properties. We have found a very unusual situation in which the existence of two largely different energy scales, caused by the molecular nature of C₆₀ fullerite, can lead to an optimum electron-phonon coupling constant $\lambda = 2 N \cdot V$.

The strong bonding within the C₆₀ molecules dominates the electron scattering V which is given by the characteristic energy scale $t_{\text{intra-ball}}$ of (predominantly) π -electrons moving on an isolate C₆₀ molecule. Maximum scattering occurs if the molecular electron-state is degenerate. For conduction to occur, inter-ball hopping takes place on a much smaller energy scale $t_{\text{inter-ball}}$ which dominates the density of states at the Fermi-level $N(\epsilon_F)$ via $t_{\text{inter-ball}}^{-1}$. This leads to a large optimal λ . This is in strong contrast to the standard single band picture in which a single energy scale t determines both N and V

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and essentially cancels out. The optimal value of λ is combined in C_{60} with a high Debye frequency, the prefactor determining T_c . This again is due to the relatively stiff on-ball modes given by $t_{\text{intra-ball}}$ and to the light mass of carbon atoms. This situation is a direct consequence of the molecular nature of fullerite. It is important to realize that this picture requires relatively large molecular units (C_{60}) which are (isotropically) weakly coupled. For instance, sheets or chain structures will not fall into this category since here the density of states for conduction along the preferred directions is small and also determined by t_{intra}^{-1} as opposed to t_{inter}^{-1} . As to the optimal size of the molecular units, one may consider the following: Because of the particular nature of the conduction states of carbon fullerenes, the electron scattering matrix element V is enhanced for small structures. The conduction states are of predominantly π -character with some σ -admixture, increasing with increasing curvature of the molecular unit.[3] Since $t_\sigma > t_\pi$, V increases with decreasing fullerene size $\sim 1/R^2$. We stress, however, that we do not propose electron pairing localized on individual molecules. The measured coherence length [8] of $\xi \approx 25 \text{ \AA}$ delocalizes the Cooper pair over 10-20 molecules and the Coulomb interaction μ^* is not expected to be significantly enhanced over standard values. A detailed analysis of μ^* for C_{60} has, however, still to be carried out.

To emphasize the unique nature of our picture we contrast C_{60} alkali doped fullerite with alkali intercalated graphite. Both factors determining $\lambda = 2 N \cdot V$ are not enhanced in graphite. First N , being largely given by the intra-sheet hopping is smaller [9] than for C_{60} , although it is somewhat re-enhanced by the higher doping density of e.g. KC_8 as compared to e.g. K_3C_{60} . Secondly, V is smaller since the important vibrations couple less effectively to the π electrons in flat graphite sheets than on curved C_{60} balls. In particular, buckling-type vibrations do not couple at all to first order in graphite.[6] Our calculations, to be described below yield a λ value about a factor of five smaller for intercalated graphite as compared to C_{60} , a qualitative difference. This leaves us with a rather unique situation in C_{60} where N is given by intermolecular compound properties, largely dependent on the specific intercalation compound, to be multiplied by V which is a rather constant intra-molecular quantity unaffected by intercalation.

This simple picture is beautifully confirmed by several experimental observations. First, for a given compound, T_c decreases drastically with increasing pressure [10] which can be explained by the soft compressibility of fullerite resulting in decreased density of states values N with decreasing intermolecular distances. Secondly, the observed [11] increase in T_c with increasing alkali intercalant size again supports the same density of states argument. In fact, these observations can be explained quantitatively assuming simply $T_c \approx \hbar \omega_D \exp\left[-\frac{1}{\lambda - \mu^*}\right]$ and $\lambda = 2 NV$ with $N \sim t_{\text{inter}}^{-1} \sim d^2$ as is commonly done for p-electron overlaps. Then, the same value of $(\lambda - \mu^*)$ needed to explain the absolute value of T_c also quantitatively describes the variation of T_c between K_3C_{60} and $Rb_2C_8C_{60}$, solely on the basis of interball distance (d) variation.[11] A further confirmation of the picture can be found in the apparent disappearance of on-ball Raman phonon-lines with metallic intercalation.[12] The strong on-ball electron-phonon coupling V yields an increased phonon line-width, calculated by us to be of order 5%

which should wash out most of their spectral features.[7]

We now describe some of the detailed calculations done to support this picture. The electronic structure of C_{60} has been studied by many groups.[13] A simple picture emerges. C_{60} is insulating with a gap of order 1.5 - 2eV separating a five-fold degenerate h_u level (HOMO) from a three-fold degenerate t_{1u} level (LUMO). The levels near the gap derive from predominantly π -like states centered at the individual carbon atoms with some small s, p_σ admixtures due to the finite curvature of C_{60} . The C_{60} envelope of these orbitals has predominantly $\ell = 5$ character for states near the gap. When placed in an fcc lattice the C_{60} molecular levels weakly interact via t_{inter} resulting in a bandstructure with a -0.5eV wide conduction band, reasonably well separated from higher bands. Details of this band depend on the relative orientation of the C_{60} molecules which are so far unknown. Upon alkali intercalation, well ordered compounds like e.g. K_3C_{60} result with the alkali atoms occupying octahedral and tetrahedral fcc interstitial sites. Detailed calculations [3] show that the rigid band picture is a good first approximation and that the alkali (donor) electrons can be viewed as partially filling the C_{60} conduction band. This is also in accord with the observation that K_6C_{60} becomes an insulator, as expected from a complete filling of the t_{1u} derived conduction bands. We have carried out a series of Density Functional (LDA) calculations [14] for fcc C_{60} serving as anchor points for simpler empirical tight binding (ETP) calculations which we use to evaluate the electron-phonon coupling matrix elements. The ETB Hamiltonian is based on four orbitals (sp^3) per atom with its parameters fitted to a large database of carbon molecules and solid structures.[15] For C_{60} its predictions agree well with the LDA results. The fit of the empirical parameters contains also a d^{-2} distance dependence of all hopping matrix-elements which is an essential ingredient for the evaluation of the electron-phonon coupling. Interball hopping is only approximately described by this procedure. Quantities like the conduction bandwidth, the Fermi surface and the density of states $N(\epsilon_F)$, however, depend on details of these inter-ball interactions. We feel that these quantities cannot be determined reliably at present and we will, therefore, consider reasonable ranges of values when needed. To determine the phonon eigenmodes of C_{60} we use a simple Keating model [16] with two nearest-neighbor on-ball force constants with a variable ratio α/β of bond stretching to bond bending. We fix the overall scale to reproduce the highest modes of C_{60} observed near 1600cm^{-1} and we vary the ratio to best reproduce the spectrum of more elaborate vibrational calculations.[17] Final values for the electron-phonon coupling V are rather independent on the β/α ratio while details of the spectral distribution of mode coupling depend on it. The on-ball modes range from $\sim 300\text{cm}^{-1}$ up to $\sim 1600\text{cm}^{-1}$. Modes with predominantly radial displacements are at the lower end of the spectrum (the quadropolar deformation of C_{60} is the lowest, buckling modes are somewhat higher) while the high energy modes have mostly tangential displacements. There is a strong similarity to graphite where the optical layer stretching modes are near 1600cm^{-1} , while the layer buckling modes occupy the lower end of the spectrum.[17]

It is instructive and useful to first consider the static Jahn-Teller effect of C_{60} , which occurs when electrons are placed into the 3-fold orbital degenerate t_{1u} conduction state.

Group theory shows that only two symmetries of modes, the totally symmetric non-degenerate A_g modes and the five-fold degenerate H_g modes couple to t_{1u} . For C_{60} there are two A_g modes, the overall radial breathing mode (A_g^1) near 500cm^{-1} and a pentagon stretching mode (A_g^2) near 1500cm^{-1} . These A_g modes couple diagonally to the t_{1u} states and do not lift any degeneracies. The Jahn-Teller coupling problem of a 5-fold vibrational mode (d-like) to a 3-fold electronic state (p-like) is interesting and has been studied in detail.[18-19] The five distortion coordinates of H_g can be grouped into two sets, the trigonal and tetragonal distortions. For icosahedral C_{60} the coupling constants for the two sets are degenerate while for point-defects in tetrahedral semiconductors (e.g. the Si vacancy) this degeneracy is lifted. The analogy of t_{1u} of C_{60} to the T_2 state of the silicon vacancy is particularly instructive and has been discussed elsewhere.[19] For C_{60} the Jahn-Teller energy surface can be evaluated analytically [19] knowing the individual coupling matrix elements V_{ij}^m between states i,j of t_{1u} and the mode frequencies ω_m . Because of the high symmetry of C_{60} this energy surface is two dimensionally orientationally degenerate ("mexican hat") i.e. E_{JT} depends only on three of the five distortion coordinates.

For $n = 1, 2, 3$ electrons the Jahn-Teller energy lowering is $1, 4, 3 \times E_{JT}$ respectively, with $E_{JT} = \frac{2}{15} \sum_m \sum_{ij}^3 |V_{ij}^m|^2 / M\omega_m^2$. For more than half filling the problem is electron-hole symmetric. Among the eight H_g modes of C_{60} we calculate significant coupling to mainly two modes, a low energy buckling mode H_g^1 and a high energy optic mode H_g^2 . This strong "selection rule" is successively more relaxed as the strength of the bond-bending force constant β is increased. However, the sum over all modes remains remarkably invariant within a few percent for α/β ranging from 0.1 to 0.3. For $\alpha/\beta = 0.1$ we find dominant contributions of $\sim 12\text{meV}$ from H_g^1 , of $\sim 7\text{meV}$ from H_g^2 which together with a $\sim 2\text{meV}$ diagonal contribution from A_g^2 and some other minor contributions yield an overall energy lowering $\Delta E \approx 28\text{meV}$.

To test the numerical accuracy of these values we performed frozen phonon LDA calculations for the A_g^2 mode and obtained virtually identical results. Using the calculated value of E_{JT} we can evaluate the "negative U" contribution which measures the tendency towards charge disproportionation or electron binding on individual C_{60} molecules. For half-filling of t_{1u} we find $U \approx -60\text{meV}$ which is clearly too small to overcome classical Coulomb repulsion effects which can be estimated to be $\geq 0.5\text{eV}$ in agreement with experimental charging studies of C_{60} in electrolyte solutions.[20] While the static value of E_{JT} seems small, dynamically the same type of coupling can be significant for electrons travelling in Bloch states made from the t_{1u} orbitals.

The standard BCS expression for electron-phonon scattering is [21]

$$\lambda = 2N(\epsilon_F) \cdot V = 2N(\epsilon_F) \cdot \sum_m \frac{\langle\langle V_m^2 \rangle\rangle}{M\omega_m^2}$$

where the sum runs over all vibrational modes m of the extended system and where the double bracket denotes a double Fermi-surface average for electrons scattered from Bloch states k to k' . This average can be carried out analytically in the limit of vanishing dispersion or vanishing t_{inter} as

$V = \frac{5}{6} E_{JT}$. Details of the derivation of this remarkable equality are given elsewhere.[19] The $q = k - k'$ dependence of the scattering is generally not important since the strength is given by the relatively dispersion-less on-ball vibrations. For the H_g Jahn-Teller modes the scattering is dominated by the inter-band terms (within t_{1u}) including $q = 0$. For the A_g symmetric mode $q = 0$ scattering is zero since it corresponds to a coherent overall shift of all electronic levels. For finite wave vector $q \neq 0$, A_g mode scattering is strong, again given by the on-ball coupling. This situation is not unlike the electron scattering from diagonal disorder in random alloys. As a consequence of these results phonon linewidths should be broadened upon intercalation. For $q = 0$, only H_g modes should be affected, as clearly seen in Raman scattering, [12] and as predicted by Varma et al. [7] However, for finite q , A_g modes should also be affected.

The question of the size of $N(\epsilon_F)$ entering λ is largely unsettled at this point. Estimates range from values of ~ 2 states/eV-spin- C_{60} derived from photoemission data, [22] to values of $\sim 6 - 20$ derived from bandstructure estimates, [13] up to values of 10-15 and > 20 inferred from susceptibility [23] and NMR data [24] respectively. An average value of $N \approx 15$ yields a $\lambda \approx 0.6$ which with $\mu^* \approx 0.1 - 0.2$ yields transition temperatures in the 20 - 30K range. For this the average cutoff Debye frequency $\hbar\omega_{log}$ has been estimated to be of order $\sim 1400K$. The simple mode frequency averaging procedure [21] used here can be simply improved upon as described in the literature, [25] but we do not expect drastic differences.

We conclude from these calculations that the observed superconductivity in alkali intercalated C_{60} compounds can be understood in terms of conventional electron coupling, albeit strongly modified by the molecular nature of the material. While the electron-phonon coupling λ has been calculated in some detail, the opposing Coulomb repulsion μ^* has not yet been investigated on a comparable level. This remains to be done for systems with a several largely different energy scales and strong spatial inhomogeneities, to establish the validity of our model. Considerations for conventional materials are known lead to limiting cancelling effects between λ and μ^* . [26] A further caveat is in place because of the rather close proximity of the scales of t_{inter} and $\hbar\omega_{log}$ as well as the electrostatic on-ball Coulomb repulsion for C_{60} . This situation approaches the limits of validity for retarded electron-phonon scattering on one hand and the band picture on the other hand.

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