Physics of undoped and doped C\textsubscript{60} fullerene

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This paper contains a review of the physical properties of the undoped and alkali-doped C\textsubscript{60} materials, including their crystal structure, electronic, optical and vibrational properties and the effect of pressure on the crystal and electronic structure. The mechanisms of superconductivity in alkali-doped C\textsubscript{60} in terms of phonon mediated electron pairing vis-à-vis electronic interaction effects are discussed.

1 Introduction

The recent discoveries of a simple method\textsuperscript{1} for synthesising C\textsubscript{60} (fullerene)\textsuperscript{2} in bulk, and that conducting\textsuperscript{3} and superconducting\textsuperscript{4} materials are obtained by doping crystalline C\textsubscript{60} (fullerite) with alkali metals have generated an enormous surge\textsuperscript{5} of interest in these materials. In this article we review some aspects of the physics of these materials and the mechanisms that may be responsible for the superconductivity in alkali doped fullerene. The review is not comprehensive and does not cover the literature\textsuperscript{5} extensively (which would in any case be very hard in a field which is experiencing a period of explosive growth); it is intended more as a guide to the literature that we are familiar with (mostly the published papers). We also include brief discussions of our own work in this field.

The C\textsubscript{60} molecule is easily one of the most beautiful molecules known to us and has the structure of the “truncated icosahedron” (a modern soccer ball) shown in Fig. 1a, the “truncation of the icosahedron” being illustrated in Fig. 1b. The structure has 12 pentagonal faces, with six 5-fold axes running through their centres; and 20 hexagonal faces, with ten 3-fold axes running through their centres. The pentagons are regular, with a bond length of 1.46 Å, but the hexagons are not, and have alternatively long (1.46 Å) and short (1.40 Å) bonds: the short bonds, 30 in number, connect the pentagons and are shared between two hexagons; the long bonds, 60 in number, are shared between a hexagon and a pentagon. The nuclear diameter of the “ball” is about 7 Å.

A brief history of the discovery of these molecules and the development of materials containing C\textsubscript{60} is as follows\textsuperscript{5,6}. As early as 1984-85 studies of mass spectroscopy of carbon clusters by laser vaporisa-

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Fig. 1—(a) The truncated icosahedron or soccer ball structure of the C\textsubscript{60} molecule. (b) Illustration of the truncation of the icosahedron and the appropriate symmetry axes
tion of graphite revealed\textsuperscript{7} “magic numbers” of carbon clusters, just as in metal clusters. But the discovery of the special stability of $C_{60}$ (and $C_{70}$) is due to Kroto \textit{et al.}\textsuperscript{2}. They suggested that $C_{60}$ is very special and is formed in condensing carbon vapour, proposed the correct structure, the name\textsuperscript{8} “buckminsterfullerene” for it, and mentioned the possibility of trapping atoms inside the carbon cage. They also suggested that $C_{60}$ or its derivatives are responsible for the “Diffuse Interstellar Line Problem”\textsuperscript{2,6}. This work was followed by a spate of quantum chemical studies\textsuperscript{9} of the $C_{60}$ molecules (mostly unaware of earlier Hückel calculations\textsuperscript{10} for the $C_{60}$ structure). However, the experimental work in the field was hampered by the difficulty of making large amounts of $C_{60}$. The major breakthrough leading to a “mass production” of $C_{60}$ came through the work of Kratschmer \textit{et al.}\textsuperscript{1}. The discovery that metallic, conducting samples could be obtained\textsuperscript{3} by alkali doping, and the subsequent discovery\textsuperscript{4} of superconductivity in many such materials\textsuperscript{11-13} with rather high $T_c$’s (all in compounds with composition\textsuperscript{14} $A_2C_{60}$); the current record for $T_c$ is for Rb-Tl doping\textsuperscript{13} with $T_c = 42.5$ K] triggered the explosive growth\textsuperscript{5} of the field. Recently\textsuperscript{15}, ferromagnetism below a $T_c$ of 18 K was reported in materials obtained by doping $C_{60}$ with organic dopants.

It is easy to see that even apart from the superconductivity aspect, these are extraordinarily exciting developments, especially from the chemistry standpoint. For, they essentially open up an entirely new subfield of organic chemistry. There are such possibilities to be investigated as functionalisation by adding H, F, etc. to the ball, substitution of B, N, etc. for carbon, trapping of metal or other atoms inside the C-cage. The resulting materials have potential applications paralleling those of conjugated polymers, in areas of catalysis, energy storage, synthetic metals, semiconductors, etc. One can think of other exotic possibilities of $C_{60}$ balls acting as a microscopic ball bearings and lubricants, etc.

In this article, however, we focus on the physics aspects of the materials derived from $C_{60}$ (including their crystal structure, electronic structure, optical properties, vibrational properties, phase transitions; metallisation, superconductivity and ferromagnetism resulting from doping, etc.) which are interesting in themselves.

It is worth noting that $C_{60}$ and $C_{70}$ are only two of a large number of possible “fullerenes”, $C_{28}$, $C_{32}$, $C_{50}$, $C_{60}$, $C_{70}$, $C_{84}$, $C_{240}$, $C_{540}$, etc. All the structures can be thought of as finite sheets of graphite “wrapped up” into balls. In order to relieve the strain induced by the “wrapping up” procedure, one has to introduce pentagonal “defects”. It is interesting to note that precisely 12 pentagons are enough no matter how large is the ball\textsuperscript{16}.

The rest of this review is organised as follows: Section 2 contains discussions of the crystal structure, electronic structure, optical properties, vibrational properties and the effect of pressure on the crystal and electronic structure of pure $C_{60}$. The properties of alkali-doped $C_{60}$ are discussed in Section 3. Section 4 is devoted to discussions of interaction effects and the mechanisms of superconductivity.

2 Properties of pure $C_{60}$

2.1 Structure

The room temperature crystal structure\textsuperscript{1,17} of pure $C_{60}$ is an FCC lattice with a conventional unit cell size of $a_0 = 14.1$ Å, corresponding to a nearest neighbour distance of 10 Å. The corresponding powder XRD pattern is shown in Fig. 2. It can be noted that the (200), (400), . . . peaks are nearly absent, and there are other “deserts” of intensity compared to more conventional FCC scattering patterns. These features are due to the “molecular form factor” $S_m(Q)$ of a single $C_{60}$ ball. At the simplest level of approximation $S_m(Q)$ is well modelled by assuming that the carbon atoms on the $C_{60}$ ball are distributed uniformly on a spherical shell of radius $R = 3.52$ Å, leading to

$$S_m(Q) \propto f_0(Q) f_0(Q) = \frac{\sin QR}{QR}$$  \hspace{1cm} (1)

where $f_0$ is the X-ray form-factor of a single carbon atom.

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Fig. 2—X-ray diffraction intensity of pure $C_{60}$ (powder sample plus capillary) at 300 K and 11 K. Light (heavy) curve is data (model fits). The lower panel is a blow up of the top panel data in a small range of $Q$ (after reference 17).
Both the X-ray crystal structure\cite{17} and NMR evidence\cite{18} indicate a high degree of rotational disorder implying free rotation of the C\textsubscript{60} molecules at room temperature. This is not surprising since C\textsubscript{60} is a molecular solid with rather weak intermolecular interactions. Hence, the librational frequencies and the barriers that hinder rotations of the C\textsubscript{60} molecules are expected to be very low. So the room temperature phase is actually a "plastic crystal".

Even more interestingly\cite{17}, as the temperature is lowered below 250 K, pure C\textsubscript{60} undergoes a first order orientational freezing transition, or a plastic crystal → crystal transition, into a simple cubic (SC) phase with 4 bulky balls per unit cell. The cell constant \(a_0\) is essentially the same as before, showing basically that 4 originally equivalent bulky balls have now become inequivalent. The powder XRD evidence\cite{17} is shown in Fig. 2. Fig. 3 shows more detailed information\cite{17} about the transition, including some data about the temperature dependence of the single cubic order parameter, and the DSC data. The entropy change associated with the transition is \(\Delta S = 6.7 \text{ J/g} = \text{Rln} 8\). In the low temperature phase, the charge distribution on the C\textsubscript{60} ball is no longer spherically symmetrical but acquires \(Y_{6m}(\theta, \phi)\) terms adding terms proportional to \(j_6(OR)\) to \(S_m(Q)\). A detailed model of the orientational ordering in the SC phase consistent with the diffraction data has been proposed\cite{17}. Constant pressure molecular dynamics simulations have been done\cite{19} to calculate the rotational diffusion coefficients, etc., across the transition. The rotation diffusion coefficient is \(1.5 \times 10^{12} \text{ sec}^{-1}\) at 300 K (typical of rapid rotation) and it drops to zero below about 200 K. The freezing of the orientations is accompanied by appearance of new librational modes. The phonon density of states \(C(v)\) obtained from the Fourier transform of the velocity auto-correlation function at two different temperatures is shown in Fig. 4. The simulations also show that the rotational diffusion coefficient falls to \(5 \times 10^{10} \text{ sec}^{-1}\) at \(P = 17.5 \text{ kbar}\) at 300 K.

2.2 Electronic structure
The electronic structure of a single C\textsubscript{60} molecule has been extensively studied\cite{9} and is well described at the simplest level by a molecular orbital picture. The core \((1s)\) and \(2(sp)\) bonding (antibonding) orbitals\cite{10} are very tightly bound (antibound) and hence fully occupied (empty), and can be ignored for most

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Fig. 3—Top integrated intensity of the (451) X-ray line (forbidden for an FCC lattice) as a function of temperature. Bottom DSC data on C\textsubscript{60} powder (after ref. 17)

Fig. 4—Molecular dynamics simulation of the translational (bold lines) and librational (dotted) density of states at 340 and 100 K (after ref. 19)
purposes. The most important "valence" molecular orbitals, arise from the overlap of the 60 \((2sp)_\pi\) electrons on the "C\(_{60}\) lattice", with hopping amplitudes \(t \approx 2\) eV on the long bonds, and \(t' \approx (1-1.3)t\) on the short bonds. The corresponding spectrum is shown in Fig. 5, and gives a good zeroth level account of the spectroscopy of single C\(_{60}\) molecules (as seen in its gaseous phase, for example). The orbitals can be symmetry-classified according to the irreducible representations of the icosahedral group \(I_h\), as indicated in the figure. Had the electron distribution on the ball been completely smeared and spherically symmetric (as in the simple model for the X-ray structure factor alluded to earlier) then these orbitals could have been classified by the orbital angular momentum \(\ell\), with the energy scaling (in a continuum limit) as \(\ell(\ell+1)\). The icosahedral charge distribution, with its leading spherical harmonic component being \(Y_{6m}(\theta, \phi)\), splits these \(O(3)\) classified levels into the \(I_h\) classified levels as indicated in the figure.

In the neutral C\(_{60}\) molecule, 30 of these molecular orbitals are fully occupied with 2-electrons each (in a Hartree-Fock picture) as indicated in Fig. 5. A gap of \(\approx 1.5\) eV separates the 5-fold degenerate, \(h_\pi\), highest occupied molecular orbitals (HOMO levels) from the 3-fold degenerate \(t_{1u}\) lowest unoccupied molecular orbitals (LUMO levels). The three \(t_{1u}\) orbitals have wavefunctions which have \(p\) like reflection symmetry, and their amplitudes peak in belts around the \(yz\), \(zx\) and \(xy\) planes. We will label these with indices \(x, y, z\) or \(1, 2, 3\).

The band structure of the crystalline C\(_{60}\) (fullerite) has also been studied by many groups\(^{22-24}\) using a variety of techniques. Fig. 6 shows the calculated band structure of the FCC C\(_{60}\) lattice using the first principles, self consistent, orthogonalised linear combination of atomic orbitals techniques\(^{24}\). The results are similar to those obtained\(^{22}\) by using the local density approximation except for some difference in the ordering of the bands near the X-point. The calculated direct band gaps which are slightly underestimated are 1.34 eV at X-point and 1.87 eV at the \(\Gamma\) point. The bandwidths of the top valence band and the first set of conduction band are 0.55 eV, in agreement with the photoemission\(^{23}\) data. The density of states (DOS) spectrum from -6 to +6 eV is shown\(^{24}\) in Fig. 7. Fig. 7 also shows the calculated real part, \(\varepsilon_1(\omega)\), and imaginary part, \(\varepsilon_2(\omega)\), of the dielectric function, \(\varepsilon(\omega)\), and the energy loss function (ELF), \(\text{Im}(-1/\varepsilon(\omega))\). The fine features in \(\varepsilon_2(\omega)\) (shown in Fig. 7) centred at 1.8, 2.7, 4.3, 5.3 and 6.3 eV have been identified with various transitions arising from the occupied to the unoccupied bands shown in the DOS; e.g. feature A arises from the transition \(V_1 \rightarrow C_1\). The expanded \(\varepsilon_1(\omega)\) in the energy range 1.2 to 2.2 is also shown in Fig. 7. The static dielectric constant of \(\varepsilon_1(\omega = 0)\), equal to 4.4, is comparable to that of diamond.
The band structure of C\textsubscript{60} is well described in terms of tight binding wavefunctions obtained by linear combinations of the molecular orbitals. Note that the point group of the crystalline C\textsubscript{60} with fully oriented balls is not \textit{Ih}, but only a subgroup \textit{Th}, and the band structure splits the (3-fold) degeneracy of the (LUMO) molecular orbitals. The tight binding Hamiltonian for the LUMO band can be written as

$$\mathcal{H}_{TB} = \sum_{ijab} t_{ijab}(r_i-r_j) c_{ia}^+ c_{jb} + \varepsilon_0 \sum_{ia} c_{ia}^+ c_{ia} \quad \ldots (2)$$

where \( c_{ia}^+ \), \( a=x, y, z \), create electrons in the 3 LUMO orbitals at site \( i \). For the case of the oriented FCC C\textsubscript{60} [i.e. each C\textsubscript{60} in an identical orientation], the \( t_{ijab} \)s are characterised by four independent parameters\textsuperscript{25}, e.g.: \( t_{xx}(110) = t_1 \), \( t_{yy}(110) = t_2 \), \( t_{zz}(110) = t_3 \), \( t_{xy}(110) = t_4 \). (The other hopping matrix elements are permutations of these same 4 parameters apart from signs). The corresponding \( k \)-space version of the Hamiltonian can be written as

$$\mathcal{H}_{TB} = \sum_k [\varepsilon_0 \delta_{ab} - t_{ijab}(k)] c_{ka}^+ c_{kb} \quad \ldots (3)$$

The matrix \( t_{ijab}(k) \) can be written as the sum

$$t_{ijab}(k) = 4\cos \left( \frac{k_x a_y}{2} \right) \cos \left( \frac{k_y a_x}{2} \right) \cos \left( \frac{k_z a_z}{2} \right) \left( \begin{array}{cc} t_1 & 0 \\ 0 & t_2 \end{array} \right) \left( \begin{array}{cc} 0 & t_3 \\ 0 & 0 \end{array} \right) + 4\sin \left( \frac{k_x a_y}{2} \right) \cos \left( \frac{k_y a_x}{2} \right) \left( \begin{array}{cc} 0 & t_4 \\ 0 & 0 \end{array} \right) \quad \ldots (4)$$

and the other matrices \( t_{ijab}^{yy} \) and \( t_{ijab}^{zz} \) can be obtained by cyclic permutations of \( (k_x, k_y, k_z) \) and of the matrix entries. We find\textsuperscript{25} that the LUMO bands obtained by Saito \textit{et al.}\textsuperscript{22} can be well fitted by the choice \( t_1 = 0.0089 \text{ eV}, \ t_2 = 0.034 \text{ eV}, \ t_3 = -0.020 \text{ eV}, \ t_4 = 0.019 \text{ eV}, \ v_0 = 0.718 \text{ eV} \).

2.3 Optical properties

The optical absorption spectrum of C\textsubscript{60} dissolved in hexane is shown\textsuperscript{26} in Fig. 8. There are three ab-
Absorption features at 213, 257 and 329 nm. An unusually sharp but weak feature has been observed at 404 nm. The other weak features are centered at 500, 540, 570, 600 and 625 nm. The calculated visible-ultraviolet absorption spectrum which is proportional to the conductivity $\sigma(\omega) = \omega \varepsilon_2(\omega)/4\pi$ agrees with the main features of the observed spectrum, as shown in the inset of Fig. 7 (left panel).

Electronic transitions have also been observed by high resolution electron energy loss spectroscopy (HREELS) in the energy range of 1.5 to 30 eV, by X-ray photoemission (XPS) and ultraviolet photoemission (UPS). The results of various techniques have been summarised and compared in Fig. 9.

The other experimental probes of electronic excitations are photoluminescence and excitation spectroscopies. The photoluminescence spectrum of a single crystal of C$_{60}$ at 300 K is shown in Fig. 10. The onset of the emission occurs at about 1.80 eV and overlaps the absorption band of the solid C$_{60}$ reported by Reber et al.$^{30}$ The peak of the emission band at $\sim 13500$ cm$^{-1}$ (1.67 eV) is in the same energy region as the peaks in $\varepsilon_2(\omega)$ shown in Fig. 7a. The hump at $\sim 12500$ cm$^{-1}$ (1.55 eV) may be due to the excitonic transition as suggested by the calculations of Ching et al.$^{24}$.

Fullerene has delocalised $\pi$-electrons and, therefore, exhibits a sizeable ultrafast optical nonlinear response, similar to that in conjugated polymers like polyacetylene and polydiacetylene. Degenerate four-wave mixing experiments$^{31}$ in solutions of C$_{60}$ in benzene gave the magnitude of the nonlinear susceptibility per C$_{60}$ molecule as $\gamma = 1.5 \times 10^{-42}$ m$^5$V$^{-2}$, comparable to that observed in polydiacetylene. A simple model of 60 delocalised electrons on a spherical surface (circumference = 22 Å, electron shell width = 2.5 Å) gives $\gamma = 2 \times 10^{-42}$ m$5$V$^{-2}$ and
the first absorption at 550 nm, both the quantities in good agreement with the experimental data.

There have been very few studies of the optical properties of solid C\textsubscript{60} so far. Reber \textit{et al.}\textsuperscript{30} have reported the optical absorption at 20 K of solid C\textsubscript{60} deposited on Ca F\textsubscript{2}. The onset of absorption occurs at 1.74 eV and the weak feature at 1.79 eV has been attributed to be due to an electronic transition.

2.4 Vibrational Properties

There are 174 intramolecular vibrational modes of C\textsubscript{60} which transform under \textit{l\textsubscript{h}} symmetry as\textsuperscript{32}

\[
\Gamma = 2a_{g}(R) + 8h_{g}(R) + 4t_{u}(IR) + 3t_{g} + 4t_{g}
+ 6g_{g} + 5t_{1u} + 6g_{u} + 7h_{u}
\]

where (R) and (IR) refer to Raman and infrared active modes, respectively. The four IR active modes occur at\textsuperscript{1,33,34} 526, 577, 1182 and 1429 cm\textsuperscript{-1}. Bethune \textit{et al.}\textsuperscript{34} have measured the Raman spectra of chromatographically separated C\textsubscript{60} and C\textsubscript{70} films and based on the measured depolarization ratios have identified the following modes: \(a_{g}\) modes at 496 and 1468 cm\textsuperscript{-1}; \(h_{g}\) modes at 273, 437, 710, 774, 1099, 1250, 1428 and 1575 cm\textsuperscript{-1}. Fig. 11 shows the three dominant modes in our\textsuperscript{29} Raman spectra of single crystals of C\textsubscript{60}. In fact Raman fingerprints can be used to characterise the purity of C\textsubscript{60} with respect to the presence of C\textsubscript{70} because the latter has a strong Raman line at 1568 cm\textsuperscript{-1}. The Raman polarizability of this mode seems considerably higher than the corresponding mode at 1468 cm\textsuperscript{-1} in C\textsubscript{60} because a sample containing C\textsubscript{60}/C\textsubscript{70} = 2.1\textsuperscript{55} gives almost equal Raman intensities for both the lines\textsuperscript{55}.

Fig. 12 shows the neutron inelastic scattering (NIS) spectra\textsuperscript{36} wherein some more vibrational modes, not observed earlier by IR and Raman techniques, are seen because there are no group theoretic selection rules in NIS. The vibrational modes (11 of them) have also been observed by HREELS\textsuperscript{27} and Fig. 13 shows the comparison of the observed frequencies obtained by various techniques\textsuperscript{34,37} where the strong features in each spectroscopy are indicated by thick lines. All these intramolecular modes, in the frequency range 200-1600 cm\textsuperscript{-1}, can be classified\textsuperscript{36} according to whether their displacements are dominantly radial/buckling (200-80 cm\textsuperscript{-1} region) or tangential motion (880-1600 cm\textsuperscript{-1}). The lowest frequency intramolecular mode in C\textsubscript{60} at 273 cm\textsuperscript{-1}, called the squashing mode, corresponds to an ellipsoidal deformation of the C\textsubscript{60} pseudo-sphere whereas the 496 cm\textsuperscript{-1} mode corresponds to pure radial deformations. The high frequency intense mode at 1468 cm\textsuperscript{-1} is called the pentagonal pinch mode. The pentagons and hexagons of the icosahedron structure expand and contract in and out of phase for the 496 and 1468 cm\textsuperscript{-1} modes, respectively. In addition to these intramolecular modes, solid C\textsubscript{60} has intermolecular, librational and translational, external modes lying in the frequency range 5-200 cm\textsuperscript{-1} (in K\textsubscript{3}C\textsubscript{60} there are, in addition, K\textsuperscript{+}-C\textsubscript{60}\textsuperscript{-} vibrational modes in this range)\textsuperscript{36}.
implies that the reduction in volume decreases the pressures. It is likely that such transitions may occur at higher pressures under hydrostatic pressures. Under shock loading, it was found by Raman scattering that C\textsubscript{60} solid transforms to graphite at 17 GPa and 600°C. Recently\textsuperscript{42}, the electrical resistivity of solid C\textsubscript{60} powder has been measured up to 25 GPa using a Bridgman anvil apparatus. The magnitude of the semiconducting gap has been obtained at different pressures from the temperature-dependent resistivity. These measurements show that the resistivity and the gap decrease with increasing pressure but there is a sudden transition at 15-20 GPa to a more insulating phase. It will be worth reinvestigating these results because the gap extrapolated to ambient pressure in these experiments is only 0.45 eV, much smaller than the calculated band structure value (~1.5 eV) or that obtained from optical experiments. The low value of the gap suggests that the resistivity they are seeing is dominated by impurity conduction.

Sinha et al.\textsuperscript{38} have carried out resonance Raman scattering for the highest frequency pentagonal pinch mode in a C\textsubscript{60} film grown on Si and show that the Raman excitation profile has a peak at ~2.4 eV, indicating that the mode is predominantly interacting with electronic excitations of this energy.

Fig. 12 also shows\textsuperscript{36} the vibrational modes of K\textsubscript{5}C\textsubscript{60}. The following features are noteworthy: A prominent feature at 4.3 meV (i.e. 35 cm\textsuperscript{-1}), a broad band at 14 meV, a redistribution of intensities between the radial and tangential modes. The low frequency features have been suggested to belong to K\textsuperscript{+}-C\textsubscript{60}\textsuperscript{3} optic modes.

2.5 Effect of pressure

Room temperature powder X-ray diffraction studies have been done up to 1.2 GPa by Fischer et al.\textsuperscript{39} and up to 20 GPa by Duclos et al.\textsuperscript{40} The isothermal volume compressibility \(\kappa\) is found to be \(6.9 \times 10^{-2}\) (GPa\textsuperscript{-1}) by Fischer et al.\textsuperscript{39} and \((5.5 \pm 0.5) \times 10^{-2}\) (GPa\textsuperscript{-1}) by Duclos et al.\textsuperscript{40} who also quote a pressure derivative \(d\kappa^{-1}/dP = 5.7 \pm 0.6\). The isothermal compressibility of C\textsubscript{60} is about 3 times that of graphite and 38 times that of diamond\textsuperscript{39}. The linear compressibility of \(2.3 \times 10^{-2}\) (GPa\textsuperscript{-1}) is essentially the same as the inter-layer compressibility \(d(\ln \kappa)/d(\ln P)\) of graphite. This implies that the reduction in volume decreases the van der Waals separation between C\textsubscript{60} molecules and does not compress the individual molecule. This is consistent with the pressure dependence of the X-ray diffraction intensities\textsuperscript{39}.

It has been also shown by X-ray diffraction experiments\textsuperscript{40} that the symmetry of the FCC C\textsubscript{60} solid is lowered at 16 ± 1 GPa under non-hydrostatic pressures. It is likely that such transitions may occur at higher pressures under hydrostatic pressures. Under shock loading, it was found by Raman scattering that C\textsubscript{60} solid transforms to graphite at 17 GPa and 600°C. Recently\textsuperscript{42}, the electrical resistivity of solid C\textsubscript{60} powder has been measured up to 25 GPa using a Bridgman anvil apparatus. The magnitude of the semiconducting gap has been obtained at different pressures from the temperature-dependent resistivity. These measurements show that the resistivity and the gap decrease with increasing pressure but there is a sudden transition at 15-20 GPa to a more insulating phase. It will be worth reinvestigating these results because the gap extrapolated to ambient pressure in these experiments is only 0.45 eV, much smaller than the calculated band structure value (~1.5 eV) or that obtained from optical experiments. The low value of the gap suggests that the resistivity they are seeing is dominated by impurity conduction.

Sood et al.\textsuperscript{29} have carried out photoluminescence and optical microscopic observation of the single crystals of C\textsubscript{60} under hydrostatic pressures up to 5 GPa. Fig. 10 shows the red shift of the photoluminescence band with increasing pressure. The colour of the crystal also changed from red to black as seen visually in transmission geometry at ~3.2 GPa. The inset in Fig. 10 shows the pressure dependence of the peak position, marked as \(E_g\). The least square fitted pressure derivative \(dE_g/dP = -0.138\) eV/GPa. It is reasonable to interpret \(E_g\) as a band gap due to some conduction band → valence band transition, but it not clear as to which specific transition it is. The change in colour occurs because of an increase in the absorption coefficient of the visible light due to the significant reduction in the band gap. The reduction of the band gap with pressure is directly related to the broadening of the valence and conduction bands due to increased interband resonance interaction. At a simple level of approximation, taking equal dispersion for the two bands (of width \(W\)), \(\partial W/\partial(\ln a) = -\partial E_g/\partial(\ln a)\). Hence, using the known compressibility we can estimate a “deformation potential” \(\partial W/\partial(\ln a) \approx 6\) eV.

Aoki et al.\textsuperscript{33} have measured the pressure dependence of the four \(t_{2u}\) intramolecular IR modes of solid C\textsubscript{60}. The observed pressure derivative \(dW/dP\) of all the modes (except the lowest frequency) lies in the range 0.2 to 0.45, similar to that of the 1470 cm\textsuperscript{-1} mode of diamond \(dW/\partial P = 0.32\). It implies that the intramolecular force constants in C\textsubscript{60} and diamond are similar. A negative value of \(dW/dP\) for the lowest frequency IR active mode\textsuperscript{43} (which corresponds to radial displacements of the C\textsubscript{60} pseudosphere) is interesting and needs to be understood.

![Table of intramolecular vibrational mode energies of C\textsubscript{60} as obtained by various techniques. The strong features are indicated by thick lines (after ref.27).](image-url)
3 Properties of alkali doped C$_{60}$

Experimental evidence reported so far$^{12,14,44}$ indicates that homogeneous phases of alkali-doped C$_{60}$ form only at special compositions A$_3$C$_{60}$, A$_2$C$_{60}$, and A$_6$C$_{60}$ [when one mixes two types of alkali atoms, one can have A$_2$A'C$_{60}$ etc.] For intermediate compositions the doped material A$_x$C$_{60}$ seems to phase separate into the above materials.

The most interesting of these materials is A$_3$C$_{60}$ [or A$_2$A'C$_{60}$] which has the "cryolite" structure, shown in Fig. 14. This is an FCC structure with a basis of three alkali ions and one C$_{60}$ ball. The C$_{60}$ balls, now negatively charged, are in the same positions as in the pure C$_{60}$ crystal, but the lattice is now slightly expanded, with the lattice constants as indicated in Fig. 15 for a whole sequence of materials. With respect to the C$_{60}$ balls, the A$^+$ ions sit at octahedral sites (as in a Rocksalt structure) and at tetrahedral sites (forming an inner cube of size $a_0/2$) as indicated in Fig. 14. [A basis that corresponds to this structure, for example, is C$_{60}$ (0,0,0), A$^+$ (1,1,1), A$^+$ (1,1,1), A$^+$ (1,1,1)]. The C$_{60}$ balls are now no longer free to rotate, but are oriented with 8 of their (20) hexagonal faces perpendicular to the (111) directions. (This still leaves two equivalent orientations related by a 90° rotation around (100), which seem to be randomly chosen at room temperatures$^{44}$.)

The most remarkable physical property of A$_3$C$_{60}$, of course, is that it is metallic at room temperature and goes superconducting below critical temperatures in the range 18-40 K depending on the material. The transition temperature of the various materials are indicated in Fig. 15 together with their lattice constants. After the discovery of superconductivity in these materials, many studies$^5$ have been undertaken to determine a variety of their properties. We list below the principal results, referring the reader to the original papers for more details. (1) $T_c$ decreases dramatically with increasing pressure$^{45}$. $\left(\frac{dT_c}{dp}\right)_{T_c} = -0.78$ K/Kbar for K$_3$C$_{60}$. [This is consistent with the increase of $T_c$ with the lattice constant$^{12}$ as shown in Fig. 15. See ref. 12 and below for a more detailed analysis]. (2) Magnetisation measurements$^{46}$ in K$_3$C$_{60}$ lead to the following estimates for the extrapolated critical fields at zero temperature. $H_{c1}(0) \approx 49$ T and $H_{c2}(0) = 132$ oe. From these, if the pure superconductor expressions are used, one gets a coherence length \( \xi = \left[ \frac{\phi_0}{2\pi H_{c2}(0)} \right]^{1/2} \approx 26 \) Å, and using $H_{c1}(0) = \phi_0/4\pi\lambda^2 \ln(\lambda/\xi)$ one gets $\lambda \approx 2400$ Å. It is likely that the dirty superconductor expressions (e.g. $\xi = \xi^d/l$ where $l$ is the mean free path) are much more appropriate and the actual coherence length is much larger. In any case it is clear that A$_3$C$_{60}$ is an extreme type II superconductor. The critical current density estimated from the magnetisation measurements is $J_c(H = 10$ koe) \approx 1.2 \times 10^5$ amp/cm$^2$. (3) \( \mu \)-Spin rotation measurements$^{47}$ have also been carried out and these yield a somewhat larger $\lambda$ value of 4800 Å, which is probably more reliable as $H_{c1}$ tends to be generally overestimated in magnetic measurements due to effects of flux pinning$^{47}$.

![Fig. 14—Structure of A$_3$C$_{60}$ as viewed along with (100) axis. The shaded (open) small circles represent alkali atoms at octahedral (tetrahedral) sites as indicated (after ref.44)](image1)

![Fig. 15—Dependence of superconducting transition temperature $T_c$ on the lattice parameter $a_0$ (Å) for various alkali doped fullerenes (after ref.12)](image2)
It is reasonable to assume that the band structure of the $A_3C_{60}$ is essentially the same as that of pure $C_{60}$, with slightly reduced bandwidths (because of the expanded lattice). Furthermore, the alkali ions are likely to be just closed shell $A^+$ ions, contributing 3 electrons/C$_{60}$ to the LUMO bands. Hence, one expects a metal with a half-filled LUMO band. Using the density of states (DOS) obtained from our tight binding fit to the LUMO band discussed earlier, we find $\varepsilon_F = 1.734$ eV, DOS at the Fermi level $N_0 = 10.4$ spin/eV/C$_{60}$ (see Fig. 16a). The $k_z = 0$ section of the Fermi-surface (FS) that results (obtained using this same tight binding fit), is shown in Fig. 16b. The topmost of the LUMO bands is completely empty, and the FS has a hole-like simply connected piece centred at the $\Gamma$ point in the bottom-most LUMO band, and pieces with more complicated connectivities in the middle LUMO band. Recently, local density functional band structure calculations have been carried out for $K_xC_{60}$. The results are in agreement with the above observations. The calculated DOS is in good agreement with that measured from photoemission studies. The full 3-d Fermi surface is also given in ref. 49. Hamada et al.

4 Interactions, effects and mechanisms of superconductivity

The simplest mechanism that has been explored to explain the superconductivity in $A_3C_{60}$ is the conventional electron-phonon mechanism. Two recent papers that do this are by Varma et al. and Schluter et al., with somewhat different results.

It is clear that intramolecular electron-phonon couplings, between the $t_{1u}$ orbitals on a ball and the vibrational modes of that ball, are the most dominant of the electron-phonon interactions, since the intramolecular hopping amplitudes are much stronger than the intermolecular amplitudes. The interaction Hamiltonian can be written formally as

$$\mathcal{H}_{el-ph} = \sum_{i,m,a,h} h_{ab}^{m} Q_{ma}^{i} c_{ia}^{\dagger} c_{ib}$$

$$... (5)$$

Here $Q_{ma}^{i}$ is the $m$th vibrational mode with degeneracy index $\mu$, of the ball at site $i$. (These modes were discussed earlier in Section 2.4). Under the icosahedral symmetry, the direct product group $t_{1u} \otimes t_{1u}$ breaks up as $a_g + t_{1g} + h_g$. The $t_{1g}$ mode is asymmetric so it cannot couple. The $a_g$ mode does not lift the degeneracy between the $t_{1u}$ orbitals, and hence is like a local chemical-potential term. Its effects are argued to be much less important than the coupling with the $h_g$ modes, which are the most dominant. As discussed in Section 2.4, there are 8 $h_g$ modes, each 5-fold degenerate. For each of these modes, symmetry considerations completely determine the form of the coupling $\Sigma_{\mu} h_{ab}^{m} Q_{m\mu}$ as the $3 \times 3$ matrix.

$$h_{m} = \frac{g_{m}}{2} \begin{pmatrix} Q_{m1} - \sqrt{3} Q_{m4} & -\sqrt{3} Q_{m1} & -\sqrt{3} Q_{m2} \\ -\sqrt{3} Q_{m1} & Q_{m5} + \sqrt{3} Q_{m4} & -\sqrt{3} Q_{m3} \\ -\sqrt{3} Q_{m2} & -\sqrt{3} Q_{m3} & -2Q_{m5} \end{pmatrix}$$

with a single characteristic coupling constant $g_{m}$ for each $h_g$ mode. The coupling constants and frequencies calculated by Varma et al. for the 8 $h_g$ modes using the quantum chemical MNDO semi-empirical technique are shown in Table 1.

For a static distortion corresponding to the $m$th mode, it can be shown that the matrix $h_{m}$ can be written as $R^{-1} H(Q_{m}) R$ where $R$ is a rotation matrix and $H(Q_{m})$ is diagonal, depending only on the
“radial” displacement $Q_m = (\sum \mu Q_{mul}^2)^{1/2}$, and it splits the three $t_{1u}$ orbitals into a singlet (label 1 say) with energy $-gQ_m$ and a doublet (labels 2 and 3 say) with energy $gQ_m/2$. The resulting lowering of the electronic energy is then governed by an effective Hamiltonian $-(g^2/\omega_m)[a^+_1 a_1 - 1/2(a^+_2 a_1 + a^+_3 a_1)]^2$. If $g^2/\omega_m$ were much larger than the band width $W$ of the $t_{1u}$ band, this effect would have led to static Jahn-Teller distortions and a “local pairing” scenario. However, in the current context, as is evident from Table 1, $\omega_m (g^2/\omega_m) \ll W$, and the traditional picture of retarded electron-electron interactions due to dynamic, virtual (Jahn-Teller) effects, with no static distortions, is more appropriate. Neglecting the dispersion of the phonon bands, and neglecting interband scattering due to the electron-phonon interaction, Varma et al. have argued that the effective electron-phonon coupling strength governing the superconducting transition is simply

$$\lambda = \sum_m \frac{N_g g_m^2}{M \omega_m^2} = 2 N_0 \sum_m V_m = \sum_m \lambda_m.$$  

The coupling energies $V_m = g^2/(2M \omega_m^2)$ for the different modes calculated by them are summarised in Table 1. From an approximate solution of the Eliashberg equations along traditional lines, they calculated $T_c$ using the McMillan formula

$$T_c = (\omega_v/1.2) \exp\{-1.04(1 + \lambda)/\lambda - \mu^*(1 + 0.62 \lambda)\}.$$  

but with the effective phonon frequency which appears as a prefactor, being given by the nonstandard expression $\omega_v = \exp[\sum_m (\lambda_m/\lambda) \ln(\omega_m(1 - \lambda_m))]$ because most of the coupling strength is in the two highest lying modes. The $\mu^*$ in Eq. 7 is the coulomb-pseudopotential parameter, which is not easily estimated. Fig. 17 displays the $T_c$ that results as a function of $N_0$ and $\mu^*$. In order to get the right $T_c$ for the alkali-doped $C_{60}$, with $N_0 \approx 12/eV/C_{60}/spn$, one needs $\mu^*$ values that are in the range 0.01.

Table 1 also summarises the results of the calculations of Schluter et al., which are similar in spirit but different in detail. For them the largest electron-phonon coupling involves the low frequency ($\approx 400$ cm$^{-1}$) radial surface buckling mode with $h_g$ symmetry. The total coupling strength is somewhat larger, but the effective $\omega_{av}$ would be much smaller. Clearly the discrepancies between the two sets of calculations need to be resolved.

The $\lambda$ values involved above ($\approx .4$) are substantial, and would have other measurable conse-

<table>
<thead>
<tr>
<th>Vibrational mode symmetry</th>
<th>$\omega_{av}$(cm$^{-1}$)</th>
<th>Theory (Ref. 51)</th>
<th>Theory (Ref. 52)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_m$ (cm$^{-1}$)</td>
<td>$g_m$ (eV/\lambda)</td>
<td>$V_m$ (meV)</td>
</tr>
<tr>
<td>$h_{1g}$ (1)</td>
<td>273</td>
<td>263</td>
<td>0.1</td>
</tr>
<tr>
<td>$h_{2g}$ (2)</td>
<td>437</td>
<td>447</td>
<td>0.1</td>
</tr>
<tr>
<td>$h_{2g}$ (3)</td>
<td>710</td>
<td>711</td>
<td>0.2</td>
</tr>
<tr>
<td>$h_{4g}$</td>
<td>744</td>
<td>924</td>
<td>0</td>
</tr>
<tr>
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<td>1575</td>
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</tr>
<tr>
<td>$a_{1u}$ (1)</td>
<td>496</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{2u}$ (2)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total $V$ (meV)</td>
<td></td>
<td>17.1</td>
<td>21</td>
</tr>
</tbody>
</table>

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Fig. 17 — $T_c$ as a function of the density of states $N_0$ and of the coulomb pseudopotential $\mu^*$ (after ref. 51)
quencies, e.g., they would lead to a strong decrease in the phonon frequencies and a corresponding increase in their linewidth according to \( \Delta \omega \propto \lambda^{-1} \), i.e., one expects a suppression of 20% in the frequency of the high \( h \) modes and an increase of \( \sim 200 \text{ cm}^{-1} \) in line widths in going from pure C\textsubscript{60} to A\textsubscript{3}C\textsubscript{60}. In contrast, the \( a \) modes would shift and broaden by a factor of \( \Omega(W_{\text{band}}/W_{\text{inter}})^2 \) less compared to the \( h \) modes according to this mechanism. The recent\textsuperscript{16} inelastic neutron scattering data on K\textsubscript{3}C\textsubscript{60} can be interpreted as indicating a softening (by \( \sim 6\% \)) and broadening of the \( h \) modes, and an apparent disappearance of the \( h \) when compared to C\textsubscript{60} (cf. Fig. 12). However, a detailed comparison must await higher resolution data and more detailed mode assignments.

Some additional insights into the viability of the electron-phonon mechanism of \( T_c \) can be gleaned\textsuperscript{29} from an analysis of the lattice constant dependence\textsuperscript{12} of \( T_c \) discussed in Section 3 (cf. Fig. 15). Ignoring for simplicity the coulomb pseudopotential \( \mu^* \), using the weak coupling approximation for \( T_c \) and keeping the lattice constant dependence only of \( N_0 \), \( \mathrm{d} \ln T_c/\mathrm{d} \ln a = -\lambda / \mathrm{d} \ln N_0/\mathrm{d} \ln a = \lambda^{-1} \) \( \mathrm{d} \ln W/\mathrm{d} \ln a \) where \( W \) is the bandwidth of the \( t_{1u} \) band. A simple interpretation of the pressure dependence of the photoluminescence peak as discussed earlier in Section 2.5, together with the value \( \lambda = 0.5 \text{ eV} \), translates to \( \mathrm{d} \ln W/\mathrm{d} \ln a = 12 \). Assuming that this same value holds for A\textsubscript{3}C\textsubscript{60} and using the measured value\textsuperscript{12} for \( \mathrm{d} \ln T_c/\mathrm{d} \ln a \) (cf. Fig. 15) of \( +0.2 \), we can estimate a \( \lambda \) value of 0.3, which is in agreement with the values discussed above\textsuperscript{51,52}.

We note that such a conventional electron-phonon mechanism for \( T_c \) would imply values of \( 2\Delta/k_B T_c = 3.6 \), the BCS value\textsuperscript{55}. In a recent tunnelling spectroscopic study\textsuperscript{60} of A\textsubscript{3}C\textsubscript{60}, much larger values of \( 5.03 \pm 0.2 \) for K\textsubscript{3}C\textsubscript{60} and \( 5.2 \pm 0.3 \) for Rb\textsubscript{3}C\textsubscript{60} have been reported for \( 2\Delta/k_B T_c \). If these results are confirmed by more studies, than the simple electron-phonon mechanism scenario cannot be the entire story.

For the electron-phonon coupling mechanism discussed above to be reasonable, the coulomb pseudo-potential \( \mu^* \) has to be smallish (<1), although \( \omega_{av} \) is perhaps much larger than its value in more conventional superconducting materials, and \( \lambda \) is substantial. Indeed the rather larger \( T_c \) that are calculated depend on this, as is clear from Fig. 17. However, the question of the size of \( \mu^* \), and hence of the mechanism responsible for superconductivity, is controversial. In a recent paper\textsuperscript{57} that reiterates his earlier stand\textsuperscript{58}, P.W. Anderson has argued that \( \mu^* \) can not be small in the fullerenes as the conduction band is much too narrow, and the \( \ln(E_F/\omega_{av}) \) factor that is necessary\textsuperscript{55} for the suppression of \( \mu^* \) is not big enough. Hence, he has argued, an electronic mechanism for \( T_c \) must be operative.

In an interesting set of papers, Chakravarty and Kivelson\textsuperscript{59} and Baskaran and Tosatti\textsuperscript{60} have suggested that there is an effective intra-C\textsubscript{60} pairing or attractive interaction between the \( t_{1u} \) electrons on a single C\textsubscript{60} ball which arises due to a large repulsive coulomb repulsion energy U to the tight binding \( \langle t-t' \rangle \) model of a single C\textsubscript{60} ball discussed in Section 2.2. A straightforward calculation\textsuperscript{59} of the energies of the (negatively) charged states of C\textsubscript{60} in perturbation theory leads to the results shown in Table 2 (for the case \( t=t' \)). From these it is clear that while the leading order results are in accordance with conventional Hund's rules and repulsive effective interactions, the second order results can lead to their reversal if U is large enough. Specifically there is an antiferromagnetic (Hunds rule reversal) instability that lowers the energy of the spin-singlet \( \langle 1A_g \rangle \) state relative to the spin-triplet \( \langle 3T_2 \rangle \) state in the doubly charged sector for \( U \geq 2.94 t \). This is followed by a pairing instability, which makes \( E_2-\langle 1A_g \rangle \leq 2E_1 \) for \( U > 3.25 t \). One can argue\textsuperscript{59,60} in favour of similar effects for large U, when one has a \( \langle t' \rangle -J(1') \) model on the C\textsubscript{60} lattice, by invoking RVB-related ideas that arose in studies of the Hubbard and \( t-J \) models in the context of the cuprate superconductors\textsuperscript{61}. Needless to say, these arguments are no proof that such effects do exist in the Hubbard model on the C\textsubscript{60} lattice, but recent exact numerical diagonalisation studies of the Hubbard model on smaller sized molecules\textsuperscript{62} are suppotive.

Purely on symmetry grounds, one can write the following effective Hamiltonian\textsuperscript{63} for excitations involving just the \( t_{1u} \) orbitals on a single C\textsubscript{60} ball:

\[
\mathbf{H} = \epsilon_0 \sum_{\mu} c_{\mu}^+ c_{\mu} + U_0 \sum_{\mu \neq \nu} (c_{\mu}^+ c_{\mu})(c_{\nu}^+ c_{\nu})
- \frac{J}{8} \sum_{\mu \neq \nu} (c_{\mu}^+ \sigma_{\mu \nu} c_{\mu})(c_{\nu}^+ \sigma_{\nu \mu} c_{\nu})
+ \frac{U_1}{3} \sum_{\alpha} (c_{\alpha}^+ c_{\alpha}^+ c_{\alpha})(c_{\alpha} c_{\alpha} c_{\alpha})
\]  

\ldots (8)
Here \( a, b = 1-3 \) are the orbital indices and \( \mu, \mu' \), \( \nu, \nu' \) are spin indices. \( U_0 \) is essentially the effective coulomb or charging energy; \( J \) is the spin-exchange energy that would lead to the spin Hund's rule if it were positive; \( U_1 \), if positive, would lead to the orbital Hunds rule. The key question is that of the magnitudes and the signs of the effective interactions \( U_0, J \) and \( U_1 \) for the real \( C_{60} \) ball. For the Hubbard model on the \( C_{60} \)-ball, the perturbative results for the energies in Table 2 translate to:

\[
U_0 \equiv 0.02 \frac{U}{t} + 0.129 \frac{U^2}{t^2}; \quad U_1 \equiv 0.03 \frac{U}{t} - 0.128 \frac{U^2}{t^2};
\]

Clearly, \( U_0 \) is positive; but \( J \) while ferromagnetic for small \( U \), becomes antiferromagnetic for large \( U \); and \( U_1 \) also becomes attractive for large \( U \). However, it is not clear whether \( U \) on the carbon sites is large enough for these instabilities to be operative. Some estimates suggest that \( U \approx 5 \) eV, which would put it (for \( t = 2 \) eV) below even the antiferromagnetic instability. Furthermore, the effects of the rest of the (i.e. inter-site on the \( C_{60} \) lattice) coulomb interactions are not included in the above results for \( U_0, J \) and \( U_1 \). The ferromagnetism that has been observed in the dilutely doped (with organic dopants) \( C_{60} \) materials would seem to suggest that the Hunds rule correlations implying a positive \( J \) are not reversed. The viability of the pairing mechanism of Chakravarty and Kivelson and Baskaran and Tossatti is hence unclear. It is worth noting, however, that \( U_0 \) is strongly suppressed relative to \( U \), arising from the fact that the \( t_{1u} \) orbitals are spread out over the \( C_{60} \) ball.

There is yet another, more exotic, electronic attractive mechanisms that may well be operative in the \( A_3C_{60} \); if not to cause the pairing, at least to reduce the effective electron-electron repulsive interactions, and hence leading to a smaller \( \mu^* \). This is the “excitonic” mechanism due to intramolecular and intermolecular polarisability effects, which ought to be quite large in the \( C_{60} \) based materials, and is similar to the one proposed by Little. The intramolecular effects make important contributions in determining the renormalised coupling \( U_0 \), etc., in the effective Hamiltonian for a single ball. To understand the intermolecular polarisability effects, one should start from the reference ionic state \( \overline{A}_3C_{60} \) where there are no average electric fields or polarisations. Now as the conduction electrons in the \( t, u \) bands hop around from ball to ball dynamical charge imbalances leading to local electric fields and polarisations are induced. In an adiabatic approximation where the hopping is slow compared to the time scale in which polarisations respond, there is an effective reduction in energy or effective Hamiltonian equal to

\[
- \sum_j \left( \frac{1}{2} \sum_{j' \neq j} e^2 \alpha_j |r_{ij}|^{-4} \right)
\]

which implies a negative contribution to \( U_0 \) (cf. Eq. 8) of order

<table>
<thead>
<tr>
<th>Charge</th>
<th>&quot;LS&quot; classification</th>
<th>( I_a ) classification</th>
<th>Energy in the &quot;Hubbard model&quot;</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>( ^1S (L=0 \ S=0) )</td>
<td>( ^1A_g )</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>( ^2P (L=1/2 \ S=1) )</td>
<td>( ^2T_{1u} )</td>
<td>0.139t + 0.5U + 0.0082U^2/t</td>
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<tr>
<td>2</td>
<td>( ^2P (L=1 \ S=1) )</td>
<td>( ^3T_{1g} )</td>
<td>0.278t + 0.0189U^2/t</td>
</tr>
<tr>
<td>'D</td>
<td>( L=0 \ S=2 )</td>
<td>( ^1H_g )</td>
<td>0.278t + 1.02U + 0.0129U^2/t</td>
</tr>
<tr>
<td>'S</td>
<td>( L=0 \ S=0 )</td>
<td>( ^1A_g )</td>
<td>0.278t + 1.05U + 0.0010U^2/t</td>
</tr>
</tbody>
</table>
\[
\frac{e^2}{2a_0} \left[ \frac{\alpha(C_{60}^-)}{a_0^3} \sum_j (r_j/a_0)^{-4} + \frac{\alpha(A^+)}{a_0^3} \sum_j' (r_j/a_0)^{-4} \right]
\]

where \( \Sigma' \) and \( \Sigma'' \) run over all the \( C_{60}^- \) and \( A^+ \) sites respectively. This term is easily a fraction of an eV. Since the values of \( U_0, J \) and \( U_1 \) resulting from all other sources are not known precisely, it is difficult to say conclusively whether the net effect is attractive or not; but the mechanism will, at the least, lead to a suppression of the \( \mu^* \) and in the way may play an important role in the superconductivity of the fullerenes.

To summarise, the mechanism of superconductivity in doped fullerenes is far from being well understood. The field of fullerenes is still very young and holds promise for exciting future developments.

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References

5. For a comprehensive list of papers in this area see Smalley E R, Buckminsterfullerene bibliography (Chemistry Depart- ment, Rice University, Houston T X 77251) (available via E-mail by sending the message SUBSCRIBE to bucky @Soll. rusm. upenn. edu).
6. For a more detailed account of the history of the subject see ref. 5; also Huffman D R, Physics Today, Nov 91, p. 22 and Smalley R E, The Sciences, 31 (1991) 22.
8. After Buckminster Fuller of the Geodesic Dome fame who studied such structures; e.g. see Synergetics dictionary-The mind of Buckminster Fuller, edited by E D Applewhite (Garland Publishing, New York), 1986.
16. This follows from the Euler theorem \( V - E + F = 2 \) for a convex polyhedron with \( E \) edges, \( F \) faces and \( V \) vertices. Given a structure with \( n \)-petagonal and \( m \)-hexagonal faces and with every vertex 3-fold coordinated, \( V = (5n + 6m)/3 \), \( E = (5n + 6m)/2 \) and \( F = n + m \). Then the theorem forces \( n = 12 \); but \( m \) is arbitrary and \( V = n = 20 + 2m \). The special stability of \( C_60 \) for particular values of \( n \) is connected with closed electronic shells.
20. We note that in graphite the \( \sigma \)-bonding in the planes is by \( sp^3 \) hybridised orbitals, and the \( \pi \) bonding in the planes is due to \( p \) orbitals. Here, because of the curvature of the surface of the ball, the two sets of orbitals get admixed. The situation is intermediate between \( sp^3 \) and \( sp^2 \) hybridisation.