Buckyballs

ELECTRONIC STRUCTURE AND SUPERCONDUCTIVITY

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Electron-phonon coupling may be responsible for superconductivity in alkali metal interstitial alloys based on "buckyball", or buckminsterfullerene C_{60}, the almost spherical carbon molecule, the third known form of crystalline carbon found recently in macroscopic quantities in graphite soot.

Perfect geometrical shapes with high symmetries have always been found fascinating. The synthesis in 1990 of crystals containing cabon-60, a molecule with icosahedral symmetry where all the 60 carbon atoms are equivalent, generated excitement in the physics, chemistry and materials science communities. The study of these crystals has yielded surprising discoveries including a new family of superconductors with high critical temperatures T_c, notably $T_c = 31.3$ K for Rb_2-CsC_{60}. We shall review briefly the electronic properties of C_{60} and its compounds.

The truncated icosahedron shape for C_{60} was first postulated by R. Smalley's group in 1985. They observed that carbon clusters with 60 atoms were uniquely stable and abundant in molecular beams generated with a laser vaporization source. Searching for an explanation for this unusual stability, they found the 60-atom structure shown in Fig. 1. This structure is unique in its high symmetry and satisfies the basic rules of carbon chemistry. The twelve pentagons and twenty hexagons of the truncated icosahedron are familiar to most of us as the shape of a football. This isomer of C_{60} was named "buckminsterfullerene" after the architect Buckminster Fuller who designed geodesic domes with icosahedral symmetry. Owing to its almost spherical shape, the molecule is familiarly called a "buckyball".

Subsequent molecular beam experiments have confirmed the cage structure, but the icosahedral symmetry of C_{60} was only established after Krätschmer,

Huffman, and co-workers produced macroscopic quantities using an electric arc discharge between two graphite rods. With solid C_{60} ("fullerite") available, the nuclear magnetic resonance (NMR), infrared, Raman, X-ray diffraction, and photoelectron spectra were soon measured, and all showed characteristics of the highly symmetric shape of a truncated icosahedron. For example, the NMR signal contains a single line, demonstrating that all 60 atoms occupy equivalent sites in the molecule.

Crystalline Carbon

Carbon's ability to form covalent bonds from atomic configurations with different degrees of s-p hybridization is responsible for the enormous variety of organic and biological molecules. Yet, pure carbon was thought to occur in only two crystalline forms: graphite and diamond. Graphite, which has sp^2 hybridization, is a layered compound (Fig. 1): each graphite layer has a hexagonal honeycomb structure with short, strong bonds between carbon atoms. The interlayer distance is large and the interaction between the layers is weak. Diamond (and its hexagonal variety lonsdaleite) has sp^3 hybridization and forms a tetrahedral network of strong bonds (Fig. 1).

C_{60}-fullerite is a new, third form of crystalline carbon. The C_{60} molecule resembles a graphite layer wrapped around a sphere with twelve pentagonal "defects". These are required by geometrical constraints to close a hexagonal graphitic network onto itself. The bond lengths in C_{60}

are 1.40 Å and 1.46 Å, and the separation between "balls" is 3 Å. These values are close to the 1.42 Å intralayer bond length and 3.35 Å interlayer separation in graphite. The curvature of the bonding network mixes some sp^3 character to the mostly sp^2 atomic hybridization in the C_{60} molecule. Three of the four valence electrons of each carbon atom are shared in the 90 σ bonds that are along the edges of the truncated icosahedron. The remaining valence electron is in the π orbitals. These are formed from radially oriented atomic orbitals that are mostly p with ≈ 8% mixing of s character. The π bonds are delocalized (aromatic), although they are somewhat stronger in the hexagon-shared edges of the truncated icosahedron.

The C_{60} molecule has a quasi-spherical shape with a cage diameter of 7 Å. Its "surface" should be "slippery" and unreactive like graphitic sheets. Solid C_{60} has a cubic dense packing of molecules, with a 10 Å separation between molecular centres. The orientation of the molecules in the crystalline phase is one of the interesting aspects of C_{60}, because the weak interaction between molecules means that very small energy barriers exist between a large number of symmetrically equivalent orientations. Thermal analysis shows two phase transitions at ≈ 220 K and ≈ 250 K. The high temperature phase has a face-centered cubic (fcc) lattice and is orientationally disordered. The low temperature phase has a simple cubic lattice and is an orientationally ordered superstructure of the high temperature phase. "Jumps" between molecular orientations

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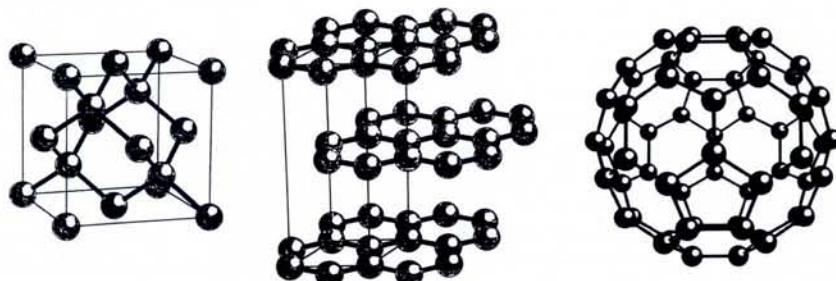
Fig.1 — Basic structures of carbon crystals: from the left, the tetrahedral network of diamond, the hexagonal layers of graphite, and the buckyballs of fullerite.

have been studied as a function of temperature by NMR and neutron diffraction. The "rotational" motion of the C_{60} molecules in the crystalline phase is one of the interesting physical properties of fullerite.

Electronic Spectrum

The electronic spectrum of C_{60} has been observed by photoemission and inverse photoemission spectrometry for occupied and empty states, respectively. The calculated density of states is in excellent agreement with the experimental spectra (Fig. 2). The sharp spectral features in Fig. 2 are due to the high degeneracy of the molecular states and the small band dispersion in fullerite. Neither diamond nor graphite have such a large number of sharp spectral features.

The electronic structure of C_{60} can be simply understood if we use the quasi-spherical shape and high symmetry of the molecule. Fig. 3a shows a contour plot of the amplitude of the wavefunction of the lowest unoccupied state of C_{60} on a surface of a sphere with 3.2 Å radius. The polar coordinates of the figure are similar to latitude and longitude in world maps: the contour lines are the equivalent of altitude in geographical maps. Fig. 3b shows a contour plot of a combination of spherical harmonics with angular momentum $l = 5$ that belong to a t_{1u} representation of the I_h icosahedral point group. The similarity between the wavefunction and the spherical harmonic is striking, particularly if we look at the the topology of the nodes of the two functions.

The molecular wavefunction shown in Fig. 3a is important in understanding superconductivity in the alkali fullerides because their conduction bands are derived from that molecular state. The symmetry of the three-fold degenerate state is t_{1u} in the I_h icosahedral point group. We can recognize in Fig. 3a that the wavefunction has a ring-like pattern around the "equator" where the three degenerate t_{1u} wavefunctions correspond to three mutually perpendicular "rings". This t_{1u} state is a π orbital and is related to an $l = 5$ spherical harmonic: we shall call it a π_5-t_{1u} orbital.

Alkali Fullerides

All the alkali elements form interstitial alloys with solid C_{60}. We find again a similarity with graphite which forms intercalated compounds where the alkali atoms are sandwiched between the graphite layers. The highest alkali (A) concentration is achieved for A_6C_{60}. The crystal structure of K_6C_{60}, Rb_6C_{60} and Cs_6C_{60} is a body-centered cubic (bcc) packing of C_{60} molecules with the alkali atoms occupying all the quasi-tetrahedral interstitial sites. The bonding between the alkali atoms and C_{60} is ionic, with the alkali valence electron transferred to the
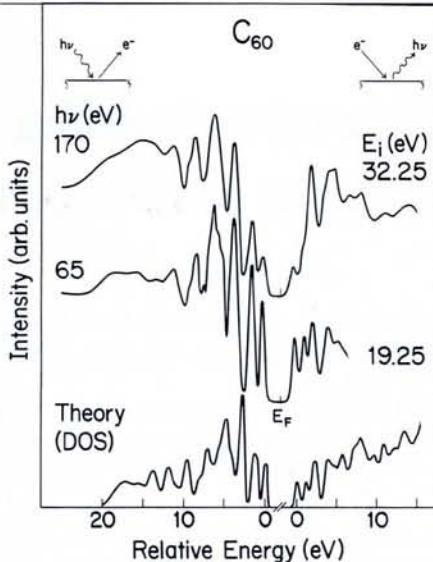

Fig. 2 — Calculated density of states (DOS) compared with the measured photoemission and inverse photoemission spectra. The DOS curve shown in the lower part was Gaussian broadened. The photoemisson energy distribution curves are shown in the left of the upper part for two different incident photon energies $\hbar\omega$. The inverse photoemission photon distribution curves are shown on the right of the upper part for two different incident electron energies E_i. The photoemission and inverse photoemission processes are sketched on the top of the figure.

C_{60} molecules. With six alkali atoms per C_{60} molecule, the lowest set of empty bands of C_{60} is filled and the compounds are insulators. The K_3C_{60} and Rb_3C_{60} compounds have a face-centered cubic packing of C_{60} molecules with the K and Rb atoms occupying both the octahedral and the tetrahedral interstitial sites. The bonding is ionic and the bands derived from the lowest empty state of C_{60} are half filled with the alkali valence electrons.

The A_3C_{60} compounds are metallic and have a high superconducting critical temperature T_c. K_4C_{60} and Rb_4C_{60} form tetragonal structures that are derived from the bcc A_6C_{60} compounds by selectively filling a fraction of its tetrahedral sites: these structures are insulating. Li and Na also form insulating compounds with stoichiometries close to two, but their structure has not yet been determined. Apparently Li, Na and Cs do not form the A_3C_{60} metallic phase. The determination of A_xC_{60} phase diagrams for the different alkali atoms is one of the steps which will help answer questions of phase stability.

Superconductivity Mechanisms in Alkali Fullerides

In A_nC_{60} alkali fullerides, the separation between the molecules is large and overlap between the π_5-t_{1u} molecular orbitals that form the conduction band is small. This leads to a narrow band (see the narrow peaks in the spectra of Fig. 2), and
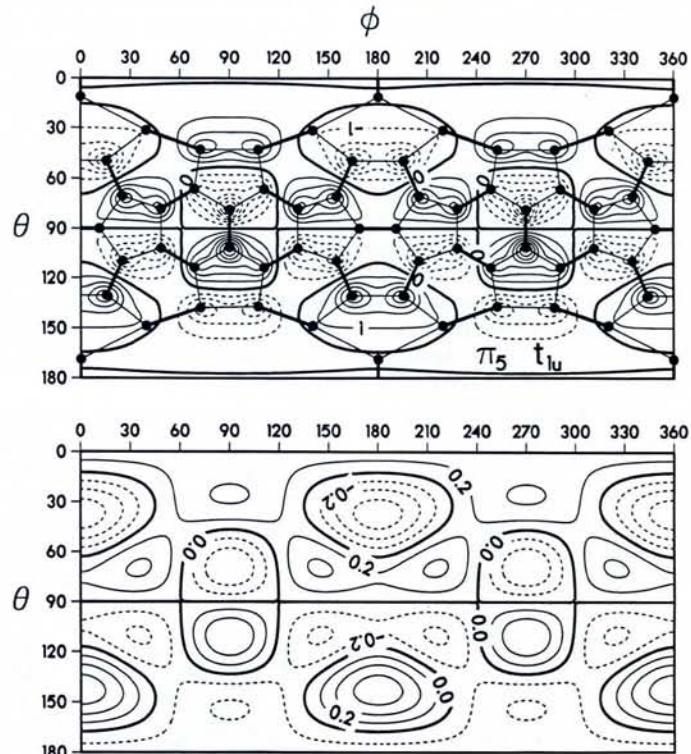
Fig. 3 — Contour plot of (a, upper) the wavefunction amplitude of the lowest unoccupied state of C_{60} and (b, lower) a linear combination of spherical harmonics with $l = 5$ that transforms with the t_{1u} representation of the I_h icosahedral point group. The C_{60} wavefunction is plotted at the surface of a sphere of 3.2 Å radius as a function of azimuthal and polar angles. The dots and straight lines in (a) are the projection onto the sphere of the carbon atoms and bonding network, respectively. The thick contour lines emphasise the nodes of the functions.

electron correlation effects that are not included in the traditional mean-field (e.g., local density) band structure calculations should have an important influence on the electronic properties. In particular, some of the alkali fullerides with stoichiometries lower than six and different from three could be Mott insulators. Note that the electronic system cannot be treated as an isolated narrow band, because the π_5-t_{1u} electrons have a strong spatial overlap with the remaining π and σ electrons. These electrons must be considered, for example, in the calculation of screening properties.

The many purely electronic mechanisms for superconductivity that have been proposed in the past for highly correlated electrons in a narrow conduction band may be responsible for superconductivity in the alkali fullerides at high temperatures. However, current experimental evidence indicates that superconductivity in alkali fullerides may be due to the traditional electron-phonon interaction. But the evidence is preliminary, and identifying the origin of the superconductivity in the alkali fullerides remains an important open question.

Electron-phonon interaction

The superconducting transition temperature T_c of a material can be estimated from the (logarithmic) average phonon frequency ω_{log}, the strength of the electron-phonon interaction, and the effective Coulomb interaction parameter μ^*, using the Allen and Dynes version of the McMillan equation,

$$T_c = (\hbar\omega_{log}/1.20 k_B) \quad (1)$$
$$\exp[-1.04(1+\lambda)/(\lambda-\mu^*-0.62\mu^*)]$$

Carbon-carbon bonds are strong and the carbon atomic mass is small, so the C_{60} molecule has very high vibrational frequencies, with a maximum vibration energy of $\hbar\omega_{max} = 0.2$ eV, and the value of $\hbar\omega_{log}/k_B \approx 1100$ K is quite high. Using a typical value for metals of $\mu^* \approx 0.1$ and the observed $T_c = 18$ K, Eq. (1) gives $\lambda \approx 0.5$ for K_3C_{60} (for aluminum, $\lambda \approx 0.43$ and for lead, $\lambda \approx 1.55$). The high critical temperatures observed for alkali fullerides do not require an unusually strong electron-phonon interaction, but can be explained by the high molecular vibrational frequencies.

The usual microscopic expression for the electron-phonon interaction parameter is $\quad \lambda = 2N(E_F)\, \bar{V},$

where $N(E_F)$ is the density of states per spin at the Fermi energy and $\bar{V}$ is the average attractive electron-electron potential due to the electron-phonon interaction. The calculation of $\bar{V}$ requires an average over all the allowed scattering processes between two electron states by phonon absorption and emission. Recent theoretical estimates give $N(E_F) \approx 8$ states per

eV per spin per C_{60}, and $\bar{V} \approx 30$ meV, hence $\lambda \approx 0.48$. This is the right order of magnitude considering the uncertainties in the theoretical estimates.

It has been observed that the critical temperature scales linearly with the lattice constant, a, of the alkali fullerides. If superconductivity is due to the interaction with the C_{60} vibrations, then $\bar{V}$ does not depend on the lattice constant, and T_c depends on a through $N(E_F)$. The gradient of dT_c/da is consistent with current estimates of $dN(E_F)/da$. This scaling of T_c with a is one of the experimental observations that should be explained by any valid mechanism for superconductivity in the alkali fullerides.

The strongest evidence for a phonon coupling mechanism is the disappearance in metallic K_3C_{60} of Raman lines that are observed in both insulating C_{60} and in K_6C_{60}. By a lucky coincidence, the t_{1u} molecular orbitals belong to the vector representation of the point group I_h. Thus the vibrational modes which induce scattering between the conduction electrons of K_3C_{60} are also those which are Raman active. One consequence of the electron-phonon interaction is a reduction of the phonon lifetime, and consequent broadening of the phonon lines. The disappearance of the phonon lines in K_3C_{60} can be explained by a broadening sufficiently large to make the lines indistinguishable from the background noise. One crucial experiment would be to search for a narrowing of the Raman lines below T_c where the superconducting gap will restrict the phonon decay channels.

An objection which can be raised to the phonon mechanism of superconductivity is that alkali intercalated graphite, which

shows many similarities with alkali fullerides, has much smaller critical temperatures. There is, however, a crucial difference between the two types of compounds: The π electrons of C_{60} are sp hybrids whereas the π electrons of graphite are of pure atomic p character. This p character closes by symmetry many of the available electron-phonon channels in graphite. In particular, there is no coupling to the transverse phonon modes. With the strong dependence of T_c on the electron-phonon coupling λ, large differences in critical temperatures can be achieved if some of the scattering channels are closed. If the hypothesis that sp hybridization is important is confirmed, then it would be the curvature of the bonding network which is responsible for the high T_c in the alkali fullerides.

Conclusions

The C_{60} and A_nC_{60} crystals have electronic and vibrational structures which can be simply understood once we consider their molecular character and the high symmetry and quasi-spherical shape of C_{60} molecules. There remains much to learn about superconductivity in highly correlated systems from the study of these beautiful compounds.

FURTHER READING

The field was recently reviewed by R.F. Curl and R.E. Smalley in *Scientific American* (October 1991) and by D.R. Huffman in *Physics Today* (November 1991). For an extensive list of the C_{60} literature, send an e-mail message to the "Bucky News Service", bucky@sol1.lrsm.upenn.edu, with the single word "INTRO" in the first line.