C_{60}: Physical Properties and Superconductivity

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In 1985, Smalley discovered that the laser vaporization of graphite in a pulsed jet of helium spontaneously forms C_{60} in a condensing carbon vapor [1]. Under certain experimental conditions C_{60} is essentially the only carbon species formed and Smalley proposed that C_{60} must adopt a special structure in order to account for this unusual selectivity. The structure he proposed was a truncated icosahedron, known informally as "Buckminsterfullerene" (Fig. 1). In 1990, Krätschmer reported a simple macroscopic preparation of this first reported crystalline molecular allotrope of carbon [2], and subsequently a flurry of activity in research laboratories around the world was initiated. The originally proposed truncated icosahedral structure of C_{60} was strongly supported by ^{13}C NMR [3], IR [2], and Raman spectra [4], however determination of the exact structure of the molecule by single crystal X-ray diffraction was frustrated by the rapid isotropic rotational motion of the spherical molecules in the crystal down to temperatures of 100 K [5]. This obstacle was overcome by osmylating C_{60} thus producing rotationally ordered crystals of a 1:1 C_{60} osmium tetraoxide adduct. The resulting single crystal X-ray structure of this C_{60} derivative confirmed its soccerball geometry [6].

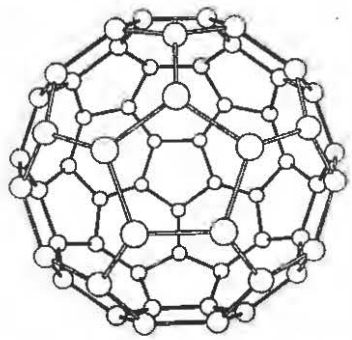

Figure 1: Truncated icosahedral structure of Buckminsterfullerene

Hückel molecular orbital calculations carried out by Hadden in 1986 suggested that C_{60} would exhibit an exceptionally high electron affinity, reflecting its relatively low-lying triply degenerate π t_{1u} LUMO [7]. This prediction was confirmed experimentally: cyclic voltammetric studies show that C_{60} readily undergoes three reversible one-electron reductions [8]. Other researchers have shown that C_{60} readily undergoes a Birch reduction to $C_{60}H_{36}$ [9], and that it produces deep red-brown solutions of diamagnetic polyanions upon reaction with lithium in tetrahydrofuran [10]. The electron deficient character of C_{60} determines much of its chemistry, and is reflected in its reactivity towards low-valent late transition metals, such as Pt(0) [10] and Ir(I) [11].

In situ measurements of the electrical conductivity of C_{60} films doped with alkali metal vapors establish that the doped films behave as organic metals and exhibit conductivities at ambient temperature comparable to those of n-type doped polyacetylene. Doping to saturation, however, always results in the formation of an insulating phase [13]. Low temperature investigations of the highly conducting potassium-doped phase, in the form of both thin films and polycrystalline powders, indicate that the highly conducting state undergoes a phase transition to a superconducting state at 18 K (Fig. 2) [14]. Carefully controlled reactions establish there is a single superconducting phase of composition K_3C_{60} [15]. Structural data are consistent with this formulation, corresponding to complete filling of all the interstitial sites in a face centered cubic lattice of C_{60} units [16]. Photoemission [17], ^{13}C NMR [18], and Raman spec-

troscopy [13] as well as powder X-ray diffraction data [19] support the formulation of the insulating phase as K_6C_{60}, which adopts an intercalated body centered cubic structure [19].

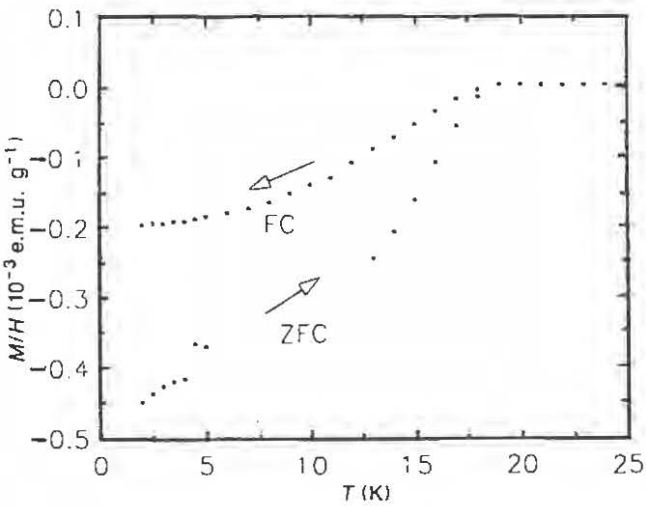

Figure 2: Temperature dependent magnetization of a K_xC_{60} crystalline sample. The direction of temperature sweep in the field-cooled (FC) and the zero-field-cooled (ZFC) curves is indicated by the arrows.

A key investigation of the pressure dependence of the superconducting transition temperature in K_3C_{60} established that $dT_c/dP = -0.78$ K/kbar. This decrease in the critical temperature (T_c) with increasing pressure is unusually large for a superconductor and is entirely reversible upon decreasing the pressure [20]. The critical temperature is also dependent on the size of the alkali metal dopant and increases significantly if larger alkali metals are used [21]. These trends in the variation of T_c can be rationalized in terms of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity, which in its simplest form leads to the following quantitative relation,

$$T_c = \theta_d \exp[-1/VN(E_F)]$$

where θ_d is the Debye temperature, V is the electron-phonon interaction, and $N(E_F)$ is the density of states at the Fermi level [22]. Since increasing the pressure decreases the density of states at the Fermi level, while doping with successively larger alkali metals increases the density of states at the Fermi level, BCS theory accounts qualitatively for the changes observed in T_c. Extended Hückel band structure calculations of the density of states for the alkali doped fullerides account almost quantitatively for the observed changes in T_c on doping with successively larger alkali metals and support the conclusion that the density of states at the Fermi level is the controlling factor that governs T_c [23].

The reduced state adopted by the superconducting phase is consistent with the electron deficent character of C_{60} which defines much of its chemistry. Although the mechanism of superconductivity in C_{60} is not established with certainty, the evidence supports a conventional BCS type mechanism. Further advances leave open the possibility of even higher superconducting transition temperatures.

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