

Fulleride Superconductors are Three-Dimensional Members of the High- T_c Family

A_3C_{60} (A = alkali metal) superconductors adopt face-centred cubic (*fcc*) structures and their superconducting T_c increases monotonically with increasing interfullerene spacing, reaching a 33 K maximum for $RbCs_2C_{60}$ – this physical picture has remained unaltered since 1992. Trace superconductivity (s/c fraction < 0.1%) at 40 K under pressure was reported in 1995 in multiphase samples with nominal composition Cs_3C_{60} . Despite numerous attempts by many groups worldwide, this remained unconfirmed and the structure and composition of the material responsible for superconductivity unidentified. Thus the possibility of enhancing fulleride superconductivity and understanding the structures and properties of these archetypal strongly correlated molecular solids close to the Mott-Hubbard metal-insulator (M-I) transition had remained elusive.

It was evident to us that new synthetic ideas coupled with detailed property measurements were needed to remove this bottleneck. We developed qualitatively new synthetic protocols employing new solvents to access high-symmetry hyperexpanded alkali fullerides in the vicinity of the M-I boundary and at previously inaccessible intermolecular separations; we then used the accumulated synthetic expertise to specifically target high-symmetry (i.e. retaining t_{1u} orbital degeneracy in the solid) fullerides with varying C_{60} orientations and packings (i.e. tuning geometrical frustration) in order to enhance molecular superconductivity. This approach culminated in the discovery of pressure-induced bulk superconductivity at 38 K in body-centred-cubic (*bcc*) structured A15 Cs_3C_{60} (Fig. 1) – the highest T_c known for any molecular material [1]. This is also the first example of a superconducting C_{60}^{3-} fulleride with non-*fcc* sphere packing – this single non-*fcc* material has a higher T_c than all the *fcc* A_3C_{60} fullerides studied over the past 18 years. Moreover, we found that the electronic ground state in competition with superconductivity, and found at ambient pressure, not only contains magnetic moments localised on the C_{60}^{3-} anions but is antiferromagnetically ordered with $T_N = 46$ K – this is the hallmark of strong electron correlations [2]. High-resolution synchrotron X-ray powder diffraction at 14.6 K (beamline **BL10XU**) showed that the application of hydrostatic pressure to the cubic-localised electron C_{60}^{3-} antiferromagnetic insulator (AFI) with the *bcc*-derived A15 structure (space group $Pm\bar{3}n$) produces no structural change over the range 1 bar to 25 kbar [2]. The effect of

increased pressure is thus solely to decrease the interfullerene contact distances isotropically, thereby increasing the overlap between t_{1u} orbitals on neighbouring C_{60}^{3-} anions and thus the bandwidth W , favouring electron delocalisation. Therefore the antiferromagnetic insulator-superconductor transition maintains the threefold degeneracy of the active orbitals in both competing electronic states, and is thus a purely electronic transition to a superconducting state. The dependence of the transition temperature on pressure-induced changes of anion packing density is not explicable by BCS theory – once the superconducting state is established, T_c initially increases with decreasing V in complete contrast to the behaviour of the conventional *fcc* fullerides under pressure. Then above ~ 7 kbar, the sign of $\partial T_c / \partial V$ changes to positive. The resulting maximum in T_c as a function of the inter- C_{60} separation – unprecedented in fullerene systems but reminiscent of the T_c vs hole density behavior of atom-based cuprate superconductors – is attributed to the key role of strong electronic correlations near the onset of the M-I transition (Fig. 2).

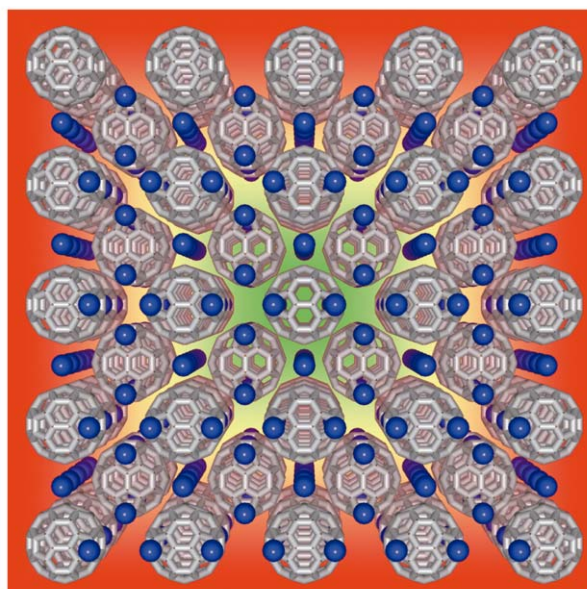


Fig. 1. Crystal structure of A15 Cs_3C_{60} (space group $Pm\bar{3}n$) based on *bcc* anion packing with orientationally ordered C_{60}^{3-} anions. Cs^+ cations are shown in blue. The lower density of the body-centred packing offers more spacious sites (with four fulleride neighbours) for the large Cs^+ cation when compared to *fcc* A_3C_{60} fullerides.

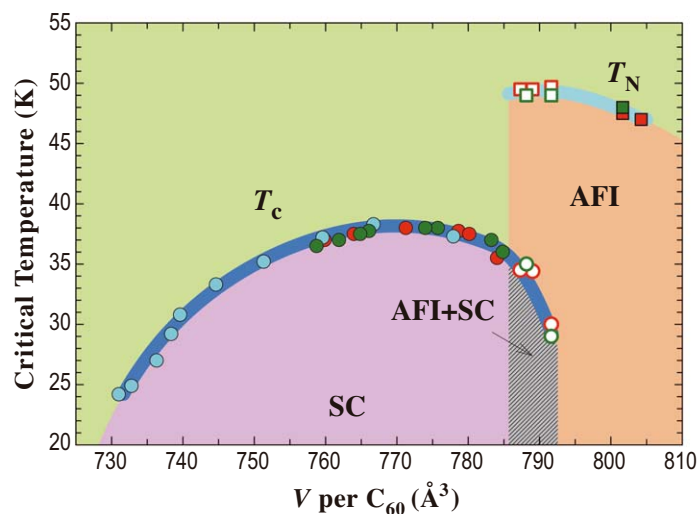


Fig. 2. Electronic phase diagram of A15 Cs₃C₆₀ showing the evolution of the Néel temperature, T_N (squares) and the superconducting transition temperature, T_c (circles) and thus the isosymmetric transition from the ambient pressure antiferromagnetic insulating (AFI) state to the high pressure superconducting (SC) state as a function of volume occupied per fulleride anion, V at 14.6 K. Different symbol colours represent data obtained for different sample batches. Open symbols represent data in the AFI-SC coexistence regime.

The high symmetry of the C₆₀ building unit imposes a robust cubic three-dimensional structure on A15 Cs₃C₆₀ free of positional, chemical, or orientational disorder with a fixed charge state in which magnetism is transformed into superconductivity solely by changing an electronic parameter, the extent of overlap between the outer wave functions of the constituent anions. The pressure-induced transition in A15 Cs₃C₆₀ from a localized electron AFI to a superconductor with two distinct dependences of T_c on packing density is purely electronic in nature, driven by increased overlap between the C₆₀³⁻ anions and the associated enhanced tendency to delocalise the t_{1u} electrons. The unconventional nature of the superconducting state that emerges from the AFI can be associated with its proximity to the M-I transition where conventional Fermi liquid theories are not expected to be valid, and quasi-localized effects produced by electronic correlation enhancing the role of intramolecular Jahn-Teller (electron-phonon) and Hund's rule (electron-electron) coupling are directly controlled by the persistent orbital degeneracy in both the insulating and superconducting states, clearly traceable to the molecular origin of the electron states. The observed superconductivity dome is consistent with theoretical treatments [3], which explicitly take account of the orbital degeneracy and the repulsion between the electrons as well as the classical electron-phonon coupling. These effects are not seen in the conventional *fcc* A₃C₆₀ systems, which are too far from the M-I transition for differences from the conventional

BCS predictions of the dependence of T_c on $N(E_f)$ to become apparent. Therefore, A15 Cs₃C₆₀ emerges as an ideal material for understanding the interactions producing superconductivity in structurally and chemically complex correlated electron systems such as the cuprates and oxypnictides as it allows the isolation of the influence of only electronic factors (including orbital degeneracy) without any other complications.

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