

Face-centered-cubic structured Cs_3C_{60} : the Holy Grail of fulleride superconductivity

The structural and electronic properties of C_{60} -based solids have been exhaustively explored in the last 20 years. They have been long recognized as archetypal examples of molecular superconductors with superconducting transition temperatures (T_c) as high as 33 K. The superconducting T_c of the face-centered cubic (fcc) A_3C_{60} ($A = \text{alkali metal}$) fullerides has been shown to increase monotonically with the inter C_{60} separation, which is in turn controlled by the sizes of the A^+ cation intercalants. However, following these seminal discoveries many years ago, the established fulleride chemistry had chronically failed to deliver new materials. Very recent work in our laboratories based on new synthetic ideas and coupled with detailed structural and electronic property measurements has removed this bottleneck. We specifically targeted 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 bcc-structured A15 Cs_3C_{60} , the highest T_c known for any molecular material. This was 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 20 years [1]. Our subsequent work showed 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 a Néel temperature, $T_N = 46$ K – this is the hallmark of strong electron correlations [2]. The antiferromagnetic Mott-Hubbard insulator-superconductor (AFMI-SC) transition maintains the threefold degeneracy of the active t_{1u} orbitals in both competing electronic states, and is thus a purely electronic transition to a superconducting state with a dependence of the transition temperature on pressure-induced changes of anion packing density that is not explicable by conventional BCS theory.

In our most recent work, we have now isolated the fcc polymorph of Cs_3C_{60} (Fig. 1) to show how the spatial arrangement of the electronically active units controls the competing superconducting and magnetic electronic ground states. We found that unlike all the other fcc A_3C_{60} solids, the most expanded fcc-structured fulleride, Cs_3C_{60} is not a superconductor but a magnetic insulator at ambient pressure, and becomes superconducting under pressure [3]. The

antiferromagnetic ordering occurs at an order of magnitude lower temperature in the fcc polymorph ($T_N = 2.2$ K) than in the bcc-based packing ($T_N = 46$ K). The prime reason for the suppression of the well-defined transition to magnetic order in contrast to the bcc-based A15 material is the geometrical frustration of the fcc lattice. The isotropic molecular structure and weak spin-orbit coupling in the C_{60}^{3-} anion should make the fcc Cs_3C_{60} phase a good example of the nearest neighbor Heisenberg fcc lattice, where the ground state is infinitely degenerate, preventing long-range antiferromagnetic order. As magnetic anisotropies are very small in fullerides, the observed gradual crossover to a highly disordered frozen state over a broad temperature range followed by the onset of magnetic long-range order but of an extremely disordered nature at a much lower temperature can be assigned to the suppression of the frustration globally via the next-nearest neighbor exchange interactions, coupled with the presence of merohedral (orientational) disorder, which locally removes the frustration. The qualitative contrast with the sharp transition to magnetic long-range order on the non-frustrated bipartite bcc lattice is very clear.

Magnetization measurements under pressure reveal that fcc Cs_3C_{60} becomes superconducting upon the application of moderate applied pressures. Superconductivity is initially observed with a rapidly increasing T_c , which rises to a maximum of 35 K (lower than the 38 K T_c found for the A15 polymorph) at ~ 0.7 GPa before decreasing upon further pressurization. The resulting variation of T_c with P shows a rather broad maximum. Synchrotron X-ray powder diffraction

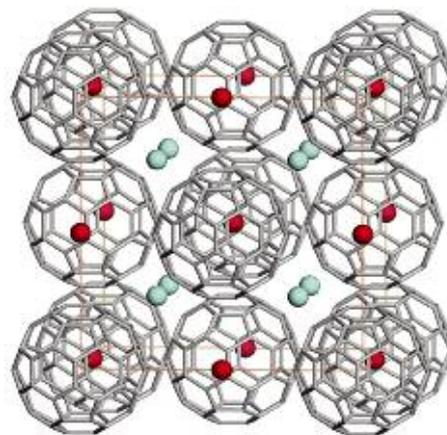


Fig. 1. Face-centered cubic structure of Cs_3C_{60} . Two orientations related by 90° rotation about $[100]$ occur in a disordered manner (merohedral disorder) - only one of these orientations is shown for clarity.

measurements (beamline **BL10XU**) at the pressures used in the magnetization measurements and at temperatures below the observed T_c show that the fcc structure is preserved at all relevant T and P . The low temperature, high pressure diffraction results allow the superconducting T_c to be related to the C_{60} packing density measured by V . After peaking at 35 K for $V = 759.6 \text{ \AA}^3/C_{60}^{3-}$, the $T_c(V)$ dependence at the highest pressures (lowest volumes) correlates well with that observed for the less expanded fcc A_3C_{60} superconductors at ambient pressure (Fig. 2(a)).

The different sphere packings in the fcc and A15 bcc-based Cs_3C_{60} polymorphs produce distinct dome-like $T_c(V)$ relationships (Fig. 2(a)). Within each polymorph, the packing density V represents the ratio of U to the bare bandwidth W , which controls the metal-insulator transition, as expansion reduces W . At the same V the bcc-based polymorph has a higher T_c , consistent with band structure calculations [4]. The bandwidths W in the less dense A15 phase are also higher, allowing the metallic state to remain stable to larger V than is possible in the fcc phase – the details of the intermolecular overlaps in the two sphere packings allow this combination of larger W and higher $N(E_F)$ in the bcc packing, which, in combination with orientationally ordered anions and considerably reduced static positional disorder on

the Cs positions, give a higher T_c . As W_c is controlled by the lattice packing, we can use this parameter to scale T_c in the two polymorphs by replacing V – which represents U/W within each polymorph but does not allow direct comparison between sphere packings – with $(U/W)/(U/W)_c = (W_c/W)$. Both Cs_3C_{60} polymorphs have the same dependence of T_c on this reduced variable, showing that T_c is controlled by proximity to the metal-insulator transition independent of the sphere packing adopted.

Normalization to the maximum T_c in each family permits the mapping of all the bcc and fcc C_{60}^{3-} superconductors onto a single packing-independent dome-shaped universal curve (Fig. 2(b)), suggesting that it is the separation from the competing localized electron ground state that determines T_c in fullerenes, with the absolute values observed depending on the details of the molecular overlap within the two different sphere packings. Electron correlations are also important in high- T_c superconductors like the cuprates, where the packing of the electronically active ions is essentially identical (two-dimensional square) in all known superconducting families. Cs_3C_{60} is unique as the same electronically active unit can be packed in two distinct lattice motifs to reveal that T_c scales in a lattice-independent manner with proximity to the correlation-driven metal-insulator transition.

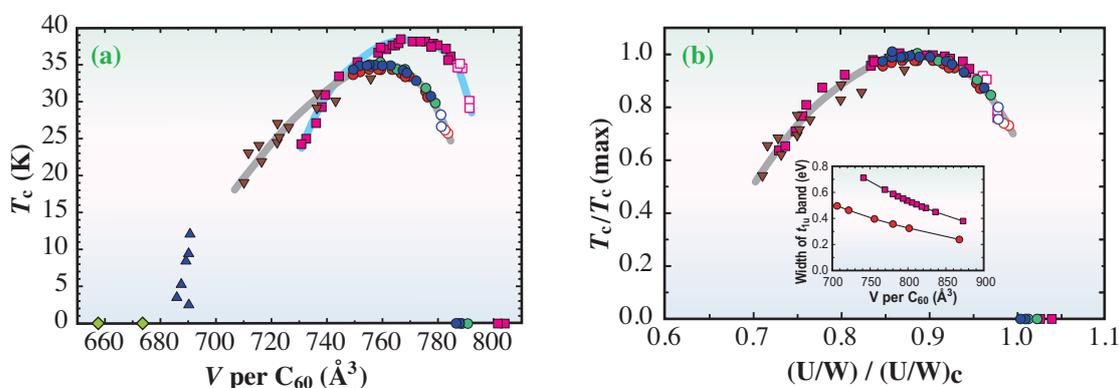


Fig. 2. (a) T_c as a function of volume occupied per fulleride anion, V , at low temperature in the two sphere packings of A_3C_{60} superconductors. The red/green/blue circles and pink squares correspond to the bulk $T_c(V)$ behavior observed in fcc- and A15-structured Cs_3C_{60} , respectively. Open symbols represent data at pressures where trace superconductivity is observed and where in the A15 phase superconductivity coexists with antiferromagnetism. The yellow rhombi, dark blue triangles and brown inverted triangles correspond to the ambient pressure T_c of fcc C_{60}^{3-} anion packings with Li_2CsC_{60} , $Pa\bar{3}$ symmetry, and $Fm\bar{3}m$ symmetry, respectively. (b) Normalized superconducting transition temperature, $T_c/T_c(\text{max})$, as a function of the ratio (U/W) divided by the critical value $(U/W)_c$ required to produce localization in the A_3C_{60} fulleride structures with fcc- and bcc-sphere packings. Inset, dependence of the t_{1u} conduction bandwidth on volume occupied per fulleride anion, V , for fcc-sphere (red circles) and bcc-sphere (pink squares) packings, as determined by electronic structure calculations.

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