Structural and Electronic Properties of Lithium-doped Fullerides

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The small Li ion dimension makes the lithium intercalated fullerides Li_xC_{60} display quite a large doping range (x = 1-30). This, together with the lack of superconducting properties, makes them different from other better known alkali doped fullerides. Furthermore, the formation of polymerised C_{60} structures is often observed, especially at low lithium concentrations.

The physical properties of these systems, in particular the structural and the electronic properties, have been extensively investigated using neutron and X-ray diffraction, NMR and Raman spectroscopies.

At high doping levels ($x \geq 15$) both diffraction and multiple-quantum NMR [1] clearly show the formation of lithium clusters intercalated in the largest interstices of the C_{60} lattice. On decreasing the lithium concentration, C_{60} units begin to polymerize (in a 1D or 2D network), as shown by X-ray diffraction [2], Raman spectroscopy and confirmed also by ^{13}C NMR lineshape analysis [3], which indicates the presence of sp^3 carbons.

The charge transfer between lithium and fullerene has been investigated by Raman spectroscopy. Assuming a linear dependence of the $A_g(2)$ mode energy on the C_{60} charge, the extent of charge transfer per Li atom decreases exponentially as Li doping is increased and, unlike other alkali metals, is never complete.
The Raman spectrum of the monomer form of $Li_{15}C_{60}$ can be interpreted as a two-phase system consisting of C_{60}^{6-} and C_{60}^{8-} charges, observable also for higher dopings.

The mobility and dynamics of Li ions have been studied by ^7Li and ^6Li NMR lineshape and spin lattice relaxation.

Some compounds in the low doping region ($x<15$) can exhibit, depending on different preparation conditions, either monomer or polymer phases both stable at room temperature. Recent results on Li_4C_{60} are presented where the structural and electronic properties of the two different forms are compared.

References:

1. M. Tomaselli, B. H. Meier, M. Riccò, T. Shiroka and A. Sartori, J. Chem. Phys., **115**, 472 (2001).
2. T. Shiroka, M. Riccò, F. Barbieri, E. Zannoni and M. Tomaselli, Phys. Solid State, **44**, 521 (2002).
3. M. Tomaselli, B.H. Meier, M. Riccò, T. Shiroka and A. Sartori, Phys. Rev. B, **63**, 113405 (2001).