Quantum-chemistry evidence for metallic fcc fullerite[60] under high pressure

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The problem of high-pressure and high-temperature (HPHT) fullerite materials has many faces. Among them are theoretical efforts to predict or explain an insulator-metal transition following certain structure transformation. Since pressure-polymerized fullerite phases are experimentally best-studied, they have become the main target for electronic-structure calculations, e.g. [1,2]. Several-step fullerite production, when one of studied polymerized phases is chosen for the next HPTP topochemical step, leads to various 3-dimensional crystalline phases [3]. In our research it is suggested, that during some HPHT experiments there exist conditions (maybe in small regions of a sample) for such quick approach of fullerene molecules, that topochemical interactions do not succeed to distort spherical shape of molecules before they achieve an equilibrium of covalently bonded slightly deformed fullerenes. So, we propose, that the most symmetric $\mathbf{T}_h$ face-centered cubic crystalline phase of C_{60} exists not in its usual van der Waals form, but with interactions of covalent strength. Since ideal-shaped fullerenes have no steric possibilities to form well-directed covalent crystalline bonds, the principal argument for our hypothesis is the metallicity of strongly constricted $\mathbf{T}_h$-C_{60}, that can provide molecular attraction with small demands to their atomic structure.

Electron-structure calculations were fulfilled by restricted Hartree-Fock open-shell method (ROHF) with INDO parametrization for supercell (periodic) fcc models with 1 and 4 fullerenes[60] in the unit cell. Electronic terms of configurations $(t)^n$ were taken for self-consistent calculations by choosing of initial set of occupied one-electron states, where 3-fold degenerate state t was occupied by n=2,4,6 electrons (closed shell in the last case). Such independent self-consistent total-energy calculations (ROHF with term-defined spectral coefficients) are likely to have an advantage over widely used density-functional methods (including [1-3]), which leave it unknown before calculation, what structure will outcome, metallic or insulator [4]. It is found, that crystal constriction to around 80% (relative to pristine value), i.e. overcoming of the van der Waals barrier, leads to equilibrium with binding energy 0.5 eV/atom (relative to pristine energy), if fullerenes are not deformed (unrelaxed geometry). However, unrelaxed geometry has almost equal total energies of closed- and open-shell configurations. The second step was to shift atoms off unrelaxed positions preserving crystal symmetry. New equilibrium was found, it has an open-shell electronic configuration and energy advantage 0.4 eV/atom (relative to unrelaxed geometry). Directions and values of atomic shifts well agree with the above proposition of metallic character of the crystal binding in constricted phase: (1) the shifts are small (less than 10% of the fullerene radius); (2) those atoms, that could form [2+2] cycles, do not shift much, while their neihgbours do (back bonds are usual for metallic bonding).

In conclusion, the existence of constricted metallic fcc fullerite regions in HPTP phases may explain their magnetic properties [5]. The experimental evidence for such regions could be found by means of direct and inverse Auger spectroscopy [6].

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