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Fullerene Molecule and Alkali Fullerides
(A belated report paper)

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On the advent of the C_{60} fullerene molecule[1] we are in the presence of a new microscopic object: a hollow, highly-symmetrtic, (quasi-) spherical molecule, consisting of a large number of carbon atoms. Molecular physics can therefore borrow standard methods for treating such an object from solid-state and condensed matter physics.

To the first approximation the fullerene molecule may be viewed as a spherical, elastic shell of atoms; having derived its elastic energy, one may obtain the corresponding vibration spectrum. The linear elasticity of a spherical thin film has to be established from first principles. The oscillation modes of this sphere can be classified into four classes, out of which a few particular modes only can be computed analytically. The vibrations are coupled to rotations, the main effect of this coupling however being static deformations beyond the harmonic approximation. If such a molecule is being to blow up during rotation, this would happen for certain polar angles on the sphere; a situation never reached, however, for the fullerene molecule. The dynamical anharmonicities of such an elastic, hollow sphere are, nevertheless, an extremely intriguing subject.

Carbon is a life element (is our life carbonic?). We know it, mainly, as sp^2-hybridizations in graphite layers, or sp^3-hybridizations in diamond. Is the fullerene molecule a curved, spherically-shaped graphitic layer? The electron affinity of carbon is 1.26 eV, while the electron affinity of the C_{60} fullerene molecule is much higher, about 2.65 eV. Any standard theory of chemical bonding would have basic difficulties in accounting for this discrepancy. How does a fullerene molecule react to an electron moving in the vicinity of its surafce? One may think that the molecule gets polarized, and bound states would appear for the moving electron. The electronic spectrum of such a quantal assembly is a hydrogen-like spectrum, in agreement with the experimental indications of the single-charged fullerene anion. Highly-charged anions could also be treated within such a simplified model, at least in principle.

Layered structures of graphite have been doped in the past with alkali cations, which are easily accommodated in-between the layers, with the hope, among others, to fabricate electric charge batteries. Solid-state fullerites accept easily alkali cations, too, and form stoichiometric compounds to various degrees. The best known among these alkali fullerides are A_3C_{60}, where A denotes Rb, K, Cs, or even Na and Li. These compounds have a fcc-structure, with two distinct coordination sites for the alkali cations, one tetrahedral, the other octahedral. These two types of sites look like fullerenic cages wherein alkali cations are accommodated. The tetrahedral coordination is rather tight, so that the relatively small-size alkali cations occupy central positions inside. On the contrary, the octahedral coordination is pretty wide, and, while large alkali cations like Cs are central in these coordinations, small- and medium-size alkali cations, like Li, Na, and, respectively, K are placed off centre, along the structural directions of high symmetry. For instance, a K cation may occupy one of the eight corners of a small cube centered on the octahedral coordination. Detailed computations using inter-ionic potentials confirmed this picture, leading to the conclusion that octahedrally coordinated alkali cations in some fcc-alkali fullerides may acquire off-centre sites placed along the (111)-symmetry directions. These off-centre positions of the alkali cations in alkali fullerides give certainly rise to a certain disorder, though not a competely undetermined one, *i.e.* this disorder is only a partial one, preserving to a certain degree the original ordering of the host latice. This circumstance is rather singular, in any case not very common in solids, and its effects on the transport phenomena, thermal properties, local electronic structure, etc remain to be investigated. In particular, diffusion of the interstitial impurities on off-centre sites may exhibit new, universal features, still unknown, to a large extent.

The off-centre sites may degenerate in highly-doped alkali fullerides into clusters of small-size alkali cations built inside the octahedral cages. Tetrahedral-, cubic-shaped and even cubic-centered Na clusters (*i.e.* Na_4, Na_8 and, respectively, Na_9) have been reported in alkali-doped fullerites, and the question of their stability, the nature of their chemical bonding, the degree of ionicity, the extent of their metallic behaviour, etc have been rightly raised. These atomic systems are very complex to be approached by any specific theoretical method, even a numerical one. We are left, for the time being, with approximate models, able to give only a qualitative understanding of these micro-objects. Such an approach is the Thomas-Fermi model, where the electronic cloud moves in a self-consistent potential, usually of high symmetry. The Thomas-Fermi model for this situation tells us that the tetrahedral cages are too small to permit clusters building; that the alkali clusters in the octahedral cages are only formed in the presence of the cage walls which give rise to huge, repulsive electronic potentials; in other words, these clusters are actually groups of alkali cations strongly squeezed inside the fullerenic cages; this squeezing generates a high degree of collectivization of the alkali electrons, so that we may view these micro-objects as small metallic drops; whose ionicity is not very high, however: the Na_4 cluster, for instance, has a total charge of about +2.7 eletronic charges, the Na_9 cluster is almost neutral, while the Na_8 clsuter seems to be rather unstable. Alkali clusters in highly-doped fullerides may exhibit their own molecular dynamics, wich is worth-testing by various spectroscopical methods.

There is no perfect solid, and the alkali fullerides are no exception. Usually, the defect concentration increases with increasing temperature. However, upon certain conditions of preparing the sample, when the preparation involves an equilibrium process, a slight defect concentration may appear, which is independent of temperature, and this seems to be the case for some alkali fullerides. In these compounds there seems to exist a small concentration of alkali vacancies in the tetrahedral coordination, which give rise to an aditional line in the NMR spectra of ^{87}Rb and ^{39}K. This phenomenon is know as the $T-T'$ splitting of the NMR spectra of the alkali cations in Rb_3C_{60} and K_3C_{60}, and the mechanism of alkali vacancies migrating through the lattice seems to explain the occurrence of the additional T'-line, beside the T- and O-lines originating in the two distinct types of coordination (tetrahedral and octahedral) of a perfect compound.

The octahedral off-centre positions of the alkali cations in these compounds may also distort the shape of the alkali NMR lines originating in the tetrahedral coordination. Usually, the off-centre sites generate a quadrupolar coupling whose effect in the NMR spectrum is averaged out by the tunneling of the atoms between the highly-symmetric off-centre sites. However, in the case of K_3C_{60}, the alkali cations in the tetrahedral sites are polarized by the octahedral off-centre cations, in such a way that a net effect is obtained in the form of an assymmetric shape of the tetrahedral NMR line. This seems again to be a rather unique situation, pertaining to the fullerenic compounds.

References

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