Doping-Induced Distortions and Bonding in K_6C_{60} and Rb_6C_{60}

Wanda Andreoni, François Gygi, and Michele Parrinello
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

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Using the Car-Parrinello method we have investigated theoretically the properties of K_6C_{60} and Rb_6C_{60} crystals. Our results are in very good agreement with available experimental data. We find an interesting pattern of relaxations both in the C_{60} fullerene cage and in the position of the K ions with respect to an ideal configuration. The relaxation energy gain is ≈ 1 eV and is due in comparable amounts to the C_{60} and the K's. These energy gains are achieved by relatively small ionic displacements. Analysis of the electronic charge density reveals non-rigid-band effects. Similarities and differences with graphite intercalation compounds are discussed.

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The discovery first of conductive behavior in alkali-doped C_{60} crystals [1] and then of their superconductivity when doped with K [2] and Rb [3] has added great momentum to the field of fullerene-derived crystals which was already booming after the breakthrough discovery of an easy way to produce macroscopic amounts of C_{60} [4]. Although no direct evidence for the crystal structure of the superconducting phase at low temperature exists, it has recently been established that its composition is K_3C_{60} [5,6] and that the C_{60}'s at room temperature form an fcc lattice [7] which is also generally believed to be the structure of the superconducting phase [2,7]. However, soon after the discovery of the superconductivity of K_3C_{60}, another crystalline phase was shown to play an important role [8]. Upon further doping by alkali metals the C_{60} sublattice changes from fcc to bcc and the existence of a bcc phase of composition K_6C_{60} has been demonstrated [8]. Although such a phase is expected to be insulating [9], it is clear that understanding this structure and its interplay with the fcc crystal will have important consequences for the ongoing process of unveiling the superconductivity mechanism. We have performed an *ab initio* molecular-dynamics simulation in order to understand the origin of this structure. Our results are in very good agreement with available experimental data and show that energies in the range of ≈ 1 eV can be gained by ionic relaxations that involve small displacements.

The structure of C_{60} is well known and has been shown to consist of a truncated icosahedron [10,11]. In spite of their fivefold axes the C_{60} molecules can be arranged into a bcc lattice still preserving the T_h point-group symmetry [12]. In this arrangement the eight (111) hexagons in different molecules face each other in a perfectly parallel manner. This is to be contrasted with what happens in the fcc arrangement where the closest contact points between neighboring molecules are oddly oriented single bonds if the same orientation of the C_{60} molecules is kept. This is the likely origin of the reported low-temperature fcc→sc (simple cubic) transition which is caused by a reorientation of four nonequivalent C_{60}'s in a sc cell [13]. The bcc structure can accommodate up to six K atoms in the tetrahedral interstitial sites, while only three K atoms can be placed in the more densely packed fcc lattice by filling all the tetrahedral and octahedral sites. In the bcc structure the tetrahedral sites lie at the corners of the square faces of the primitive cell, i.e., at positions of the type $a(0,\frac{1}{4},\frac{1}{2})$. These elementary geometrical considerations justify the occurrence of the bcc structure when the crystal is fully doped. The structure of the fully doped K_6C_{60} compound has been studied experimentally in some detail [8]. The C_{60}'s form a bcc lattice of lattice constant $a = 11.39$ Å and the K's sit at $a(0,\frac{1}{4}\pm\delta,\frac{1}{2})$ and symmetry-derived positions, i.e., slightly away from the tetrahedral sites. In the case of Cs_6C_{60}, the value of δ is 0.03. The positions of the C atoms reported in Ref. [8] for Cs_6C_{60} were determined under the assumption that all C-C bond lengths are equal, which implies that all C atoms lie on a sphere. The radius of this sphere which best fits experimental results is 3.57 Å. The structure of K_6C_{60} is found to be essentially the same as that of Cs_6C_{60} apart from the value of a.

We have investigated in detail the effects of doping on the structural and electronic properties of this system using the Car-Parrinello method [14]. In this scheme the local-density approximation (LDA) to the density-functional theory is used. The density is expressed conventionally in terms of Kohn-Sham (KS) orbitals. The minimization of the density functional is then performed with a dynamical scheme which allows simultaneous relaxation of the electronic and ionic degrees of freedom. We expand the KS orbitals into plane waves with an energy cutoff of 35 Ry and use only the $k=0$ point of the Brillouin zone. In order to check the convergency relative to the k-point sampling we have repeated the calculation in a simple cubic supercell containing two formula units, and obtained very similar results. Only the valence electrons are treated explicitly and their interaction with the ionic cores is described via a fully nonlocal pseudopotential. Such a scheme was proven to provide a very accurate description of electronic and ionic properties of C_{60} [15]. For a report on tests of convergence with respect to the energy cutoff we refer to Ref. [16] where calculations were performed on carbon microclusters as well as diamond and graphite. For K and Rb we have used a local pseudopotential [17]. However, given their large ionic cores it has proven essential to include nonlinear core corrections in order to obtain accurate results [17]. While we present here only results for K_6C_{60} we have also performed calculations on the Rb compound and obtained very similar results.

TABLE I. Fractional coordinates of the carbon atom positions in K_6C_{60} ($a=11.39$ Å).

	x	y	z
C_1	0.0	0.064	0.309
C_2	0.102	0.126	0.267
C_3	0.063	0.228	0.202

We have started from an ideal bcc configuration ($\delta=0$) in which the C_{60} molecule is undistorted relative to its ideal icosahedral arrangement [15] shown in Fig. 1(a). We use the experimental bcc lattice parameter $a=11.39$ Å [8]. We expect this to differ by only a few percent from the theoretical equilibrium lattice constant (see, e.g., for the case of C_{60}, Ref. [18]). Relaxation of the ionic positions leads first to a significant distortion of the fullerene cage and then to a much slower potassium relaxation. This indicates the presence of low-frequency K modes and of a larger Debye-Waller factor for the potassiums, a fact that is borne out by experiments [8]. The distortion pattern of the fullerene cage is shown in Fig. 1(b). It is a highly symmetric distortion which preserves the T_h symmetry. The deformation can be described in a first approximation as an elongation of the C_{60} cage along the three Cartesian axes. Consistent with the T_h symmetry, there are three sets of nonequivalent atoms C_1, C_2, and C_3, shown in Fig. 1(b). Their fractional coordinates are given in Table I. These three sets of atoms lie now at different distances from the center of the molecule $R_{C_1}=3.59$ Å, $R_{C_2}=3.55$ Å, and $R_{C_3}=3.54$ Å. This is at variance with the isolated C_{60} molecule where all the atoms sit on the surface of a sphere of radius $R=3.53$ Å [15]. In agreement with the experimental results of Ref. [8], we observe a slight breathing of the C_{60} molecule. Note that the cubic distortion that we find is not allowed in the structural refinement reported in Ref. [8]. However, it falls within the experimental uncertainty. The single bonds which had equal lengths in the isolated C_{60} molecule are now split into three groups of slightly different lengths (as shown in Table II). More remarkably, the six double bonds that point towards the Cartesian axes undergo substantial lengthening to the point of becoming the largest ones. The average bond length is 1.436 Å, in agreement with the value of 1.44 Å obtained from the constrained fit in Ref. [8].

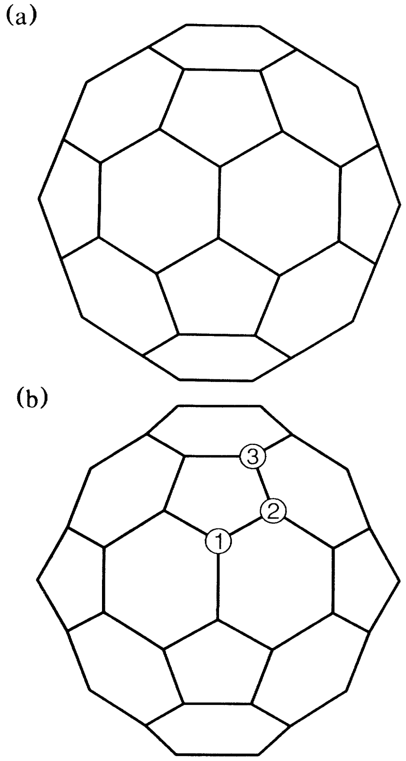

FIG. 1. C_{60} viewed from a twofold symmetry axis: (a) isolated molecule; (b) in the K_6C_{60} crystal. The atomic displacements have been amplified by a factor of 5 to make them more clearly visible.

The potassium atoms also relax and at equilibrium we find $\delta=0.033$, which is in striking agreement with the experimental results. In a separate calculation we have relaxed the structure of a hypothetical undoped bcc C_{60} and found that distortions—with respect to the C_{60} molecule—are smaller than 5×10^{-3} Å. This indicates that the larger relaxations of C_{60} observed in K_6C_{60} are induced by doping. Furthermore, in undoped bcc C_{60} the cost of inducing the distortions described above is large and amounts to ≈ 0.6 eV.

Preliminary calculations on fcc K_3C_{60} [19] show that the pattern of C_{60} deformations is very similar but displacements from ideal positions are much less pronounced. This is also in very good agreement with the structural data reported in Ref. [7]. These doping-induced structural changes are on average comparable to those described in graphite intercalated compounds

TABLE II. Bond lengths in Å in isolated C_{60} [15], solid C_{60} [24], and fully doped K_6C_{60}. Note that in isolated C_{60} only two different bonds are present.

Bond	C_{60} (theory)	fcc C_{60} (expt.)	K_6C_{60} (theory)
C_1-C_2	1.447	1.45	1.443
C_2-C_3	1.447	1.45	1.442
C_3-C_3	1.447	1.45	1.436
C_1-C_1	1.390	1.40	1.447
C_2-C_3	1.390	1.40	1.420

[20,21]. However, changes in individual bonds can be much larger than those predicted, e.g., in Li intercalated graphite [22]. This suggests much larger electron-lattice coupling in doped fullerenes.

The relaxation of K_6C_{60} described above yields an energy gain of 1 eV, which can be decomposed in various contributions. In a calculation in which the K's are fixed in their ideal ($\delta=0$) positions we find that the C_{60} displacement pattern is qualitatively similar to that described above. The energy gained in this process is only 0.66 eV, so that the remaining 0.34 eV is to be associated with the displacement of the K's. This last energy gain can be understood in part on the basis of simple geometrical considerations: The K atoms sit at positions in which they face two hexagons and two pentagons of the C_{60} neighbors. The displacement $\delta=0.03$ is such as to center the K's better relative to these four faces. More intriguing is the observation that, in this process, the energy gain is primarily due to a reduction in the electronic kinetic energy which indicates an important role of the K displacement in the delocalization of the electronic wave functions. Most of the energy gained (≈ 0.66 eV) in the relaxation of the C_{60} molecule comes from nonspherical distortions. In fact, only ≈ 0.1 eV can be gained if only radial relaxations are allowed.

Calculations performed with two C_{60}'s per unit cell produced the same average bond length (1.436 Å) although some difference in the relaxation pattern was observed. Finally, the energy gain was also $\approx$ (1 eV)/C_{60}. This leads us to conclude that our results do not depend on k-point sampling.

In order to understand better the electronic structure of this compound we have calculated the difference in charge density between the doped and undoped bcc crystals. In Fig. 2 we show this difference in charge density $\Delta\rho(r)$, angularly averaged relative to the center of the fullerene molecule, and the total excess charge $\Delta n(r) = 4\pi\int_0^r \Delta\rho(r')r'^2 dr'$. We decompose $\Delta\rho(r)$ into a contribution coming from the t_{1u}-derived orbitals and one coming from the polarization of the inner valence states. The large contribution coming from valence polarization provides a measure of the non-rigid-band effects. The shape of the t_{1u} states is hardly affected by "doping." We have not found evidence among the low-lying unoccupied states of one delocalized between the fullerenes.

We draw attention here to the similarity between Fig. 2 and the layer-averaged electronic density in higher stage Li intercalated graphites [23], where non-rigid-band effects have also been described. This similarity also holds quantitatively if one takes into account the different geometry of the two systems. In either case about 90% of the excess charge is located in the occupied interstitial sites. These are defined here as the regions external to the C_{60} spheres and in the intercalated graphites as the alkali-metal-filled volume between adjacent carbon planes.

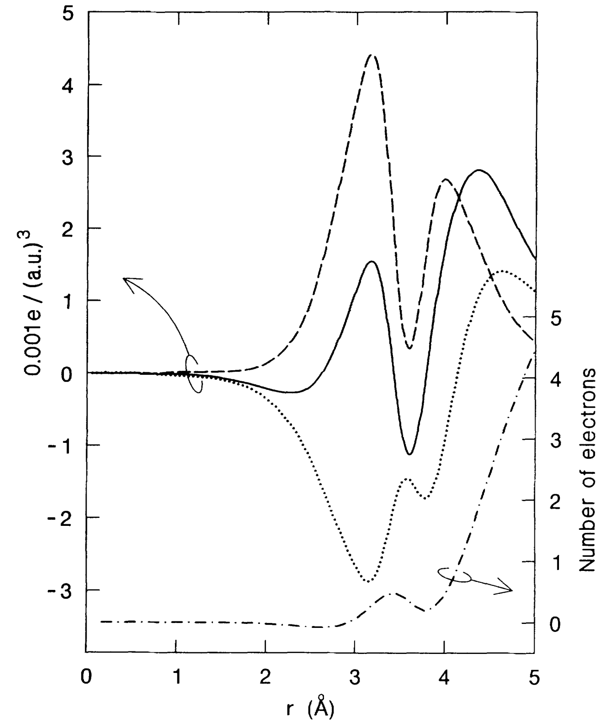

FIG. 2. Solid curve: $\Delta\rho(r)$. Dashed curve: density associated with the t_{1u}-derived state. Dotted curve: valence-state-polarization contribution. Dash-dotted curve: $\Delta n(r)$. These curves have been computed with the undoped bcc crystal with distorted C_{60} as reference.

In conclusion, we have determined theoretically important details of the K_6C_{60} structure. Our findings are in very good agreement with available experimental data [8] and in addition predict a new pattern of distortions which could be detected in a more sophisticated experiment. The calculation presented here is not of the superconducting compound itself. Yet it provides solid information on some of the relevant energy scales involved. This information will certainly be important in the construction of theoretical models for this intriguing new class of superconductors.

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