Absence of Metal Clusters and Appearance of New Electron States in Na_6C_{60}

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We calculate the structural and electronic properties of the Na_6C_{60} fulleride using the Car-Parrinello method as well as standard local density approximation band structure calculations. In contrast to previous claims we find that metal clusters do not form but, like the potassium and rubidium fullerides, sodium intercalation gives rise to a conventional ionic compound. Unlike the case of heavier alkali fullerides, a characteristic new kind of low-lying electron state appears that is not the C_{60} state. Effects of temperature on the electronic nature of the compound are discussed as well as consequences of these findings for higher fullerides.

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The physical and chemical properties of alkali-metal fullerides have recently attracted much interest [1–3]. K_xC_{60} and Rb_xC_{60} compounds have been investigated widely, with emphasis on the $x = 3$ phases, which are superconducting at relatively high temperatures. Although a Na_3C_{60} phase was observed in the earliest report on alkali-metal intercalated C_{60} [4], intercalation of the fullerite with Na has been pursued systematically only more recently [5–8] and has given rise to Na_xC_{60} compounds with properties remarkably different from those of the heavier alkali fullerides of the same stoichiometry. In particular: (i) The $x = 3$ compound does not have a superconducting phase at low temperatures. Instead, at $\approx$ 250 K, it undergoes a transformation, which has not yet been uniquely characterized. (ii) Unlike K and Rb, Na forms continuous solid solutions at least from $x = 1$ to $x = 3$ [8]. (iii) Na_6C_{60} is an insulator [6] as are K_6C_{60}, Rb_6C_{60}, and Cs_6C_{60}. However, while the latter three are bcc [9,10], Na_6C_{60} is fcc. (iv) While for the heavy alkalis the maximum possible metal content of the intercalated compounds is $x = 6$, Na intercalation is possible up to $x \simeq 10$ and the fcc structure is retained [7].

In determining the difference in structure and composition limit, the ionic size plays a major role. Na atoms can more efficiently occupy the interstices of the C_{60} fcc solid, while the larger sizes of K and Rb drive the transformation to more open structures (bct for $x = 4$, bcc for $x = 6$) and cause instability at concentrations higher than 6. Other factors, such as the difference in ionization potential ($\simeq$ 1.6 eV higher in Na than in K), may, however, also be relevant. Eventually, the anomalous behavior of the Na fullerides is caused by the interplay between structural and electronic properties. Understanding this point requires *ab initio* theoretical approaches. Here we study *ab initio* the structural and electronic properties of the Na_6C_{60} phase, believed to be stable in a wide temperature range. The crystal structure is fcc [5], and the lattice constant at 10 K (14.248 Å) is only slightly larger than that of the pristine fullerite at room temperature (RT). Among the sets of interstitial sites [11], the octahedral (O, one per molecule) and the tetrahedral sites (T, two per molecule) are the largest voids. These are the positions occupied by the heavy alkalis in the $x = 3$ compounds. For $x = 6$, no obviously preferred distribution exists for the guest atoms. Refinement of x-ray diffraction (XRD) data [5] yields a structure with one Na atom (Na_1) on each T site and the remaining four (Na_2) forming a tetrahedral cluster (tetramer) centered at the O site, and occupying the two equivalent orientations with equal probability. According to Ref. [5], this picture is consistent with covalent bonding in the Na tetramers and with a net charge transfer to the C_{60}'s weaker than that in K_6C_{60}, for which several calculations show full ionization of the K atoms [12–16]. To support this view, two experimental data are reported, namely, the doping-induced shift of the Ag(2) Raman mode, which is, however, smaller than that of K_6C_{60} by only 5 cm^{-1}, and the shift of the NMR ^{13}C line, which is 13 ppm larger [17]. The parameters of the refined geometry are listed in Table I (d^*). We notice that the Na_2 atoms are well isolated from the Na_1 atoms (4.455 Å) and form a rather squeezed tetramer, their distance being as small as 2.8 Å. This value is 0.3 Å smaller than in the Na dimer (3.079 Å [18]) and $\approx$ 0.5 Å smaller than the smallest Na-Na distance in NaF [19]. The quality of

TABLE I. Na_6C_{60}: Interatomic distances in Å. The three nonequivalent C atoms in the fcc are here split into five due to the symmetry lowering. Overbar means "average." For comparison, the calculated values in the molecule d_m are also listed. See also text.

i	j	d	d^*	d_{mol}
Na_1	C	3.26	3.26	
Na_2	C	2.65–2.72	2.79–2.89	
Na_1	Na_2	3.63	4.455	
Na_2	Na_2	4.14	2.8	
C_1	C_1	1.428		1.390
C_1	$\overline{C_2}$	1.447		1.447
$\overline{C_2}$	$\overline{C_3}$	1.417		1.390
$\overline{C_2}$	$\overline{C_3}$	1.438		1.447
$\overline{C_3}$	$\overline{C_3}$	1.437		1.447

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such a refinement is, however, not so high, which leaves ample room to improve the structural determination.

The structural determination we report here is the result of computer simulations performed with the local density approximation (LDA)-based Car-Parrinello (CP) method [20], which has been used extensively on pure and doped fullerenes [21] and also on Na clusters [22]. For structural optimization, we have globally relaxed the atomic positions and used simulated annealing for the Na configurations. We propose a new structural model for the Na atoms in Na_6C_{60}, which, while having the same topology as the one in Ref. [5], differs drastically in the values of the interatomic distances (by as much as $\approx 50\%$ at 10 K). This changes the picture dramatically. Metal clusters do not form. A complex network of highly ionized Na atoms forms instead in the interstices of the fullerite. While the relaxation of the molecular structure and the chemical bonding are similar to K_6C_{60}, Na intercalation generates a new kind of localized electron state in the lowest unoccupied band. These states do not arise from the *s*-electrons of the alkalis. Nevertheless, they are associated with the presence of the tetrahedron of Na ions.

The computational details can be found in Ref. [13]; we used nonlocal atomic pseudopotentials [22,23] to describe the valence-core interaction and to expand the wave function into plane waves. The unit cell is fcc, with the 10 K experimental lattice constant, and one formula unit. CP simulations of the above periodically repeated cell [which corresponds to the only $k = 0$ point in the Brillouin zone (BZ)] were used for the first and basic steps to optimize the structure. We then further relaxed the atomic positions within a self-consistent scheme by using two Chadi-Cohen k points in the BZ [24]. The choice of the unit cell does not allow us to describe the orientational disorder of the Na atoms on the two tetrahedra, which would require a large supercell. Our main concern here, however, is the nature of the chemical bonding of the Na fulleride and its main structural features, an issue that is not affected by being restricted to an ordered type of arrangement, as we will also deduce from the final discussion of the chemical bonding.

Starting with the structure proposed in Ref. [5], we used a combined steepest descent method to relax only the molecular structure first and then all the atomic positions. The Na_1 atoms did not move, while the Na_2 atoms spontaneously moved away from each other by $\simeq 1.3$ Å, thus causing an energy gain of 1.6 eV. The stability of this configuration was also confirmed by a simulated annealing search for the Na coordinates. In order to enhance confidence in our optimization, we also considered an ordered arrangement of the Na atoms on the d sites [11] (6 per molecule) and relaxed the entire structure again. This results in a local energy minimum $\simeq 1.3$ eV higher than our optimized structure, owing in part to the smaller Na-Na distances (3.5 Å).

Figure 1(a) shows how the energy varies as a function of the Na_2-Na_2 distance (each point corresponds to a full relaxation of the molecular structure). Flatness ($\Delta E \simeq 0.1$ eV) is confined to an interval of ≈ 0.25 Å around the optimal value. A huge difference exists between the calculated Na-Na distances (Table I) and those proposed in Ref. [5]. In particular, the large expansion of the tetrahedron makes the Na_2 atoms much closer to the Na_1 atoms than to each other. The theoretical geometry is consistent with the Na atoms being strongly ionized. This agrees with the high electron affinity of C_{60} and with the strongly ionic character of the chemical bonding of the other alkali-metal fullerides. Simulations at about RT show no significant variation of the structural properties. The average configuration of the Na atoms remains unaltered, and the fluctuations of the Na_2-Na_2 distances do not exceed 0.1 Å.

Only a weak and delocalized electron density exists around the Na network [see Fig. 2(a)]. Although the residual density is weak, the Na_2 atoms are less ionized than the Na_1 atoms. This difference is subtle but probably detectable in NMR experiments. The integral $I_{Na}(R)$ of the total electron density $\rho(r)$ over a sphere of radius $R = 1$ Å centered at the Na sites is $\approx 0.02e$ for Na_1 and $\approx 0.05e$ for Na_2. Figure 2(b) illustrates the quantity relevant to describe the charge transfer, namely, $\Delta\rho(r) = \rho(r) - \rho_m(r) - \rho_{Na}(r)$, where $\rho_m(r)$ is the electron density of C_{60} in the deformed structure of the fulleride (see Table I) and $\rho_{Na}(r)$ is the superposition of the atomic Na densities. There is no bond-charge formation between the Na atoms. Instead, the charge flows away almost completely from the cations and localizes mainly on the C_{60} molecules and in part on the interstitial region. The integral $D_{Na}(R)$ of $\Delta\rho(r)$ calculated on spheres centered at the Na atoms is more negative for Na_1 starting at $R \approx 1$ Å, thus confirming the site dependence of the charge transfer. The distribution of the

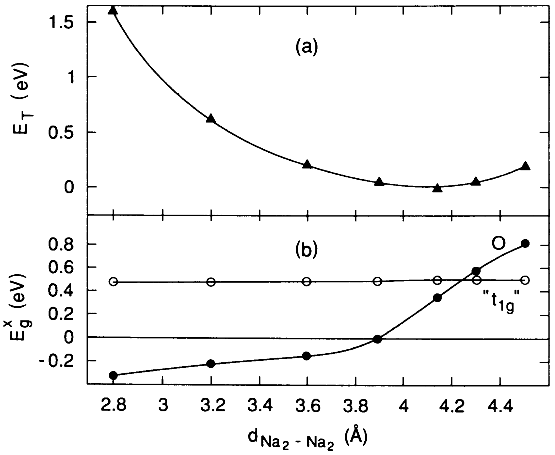

FIG. 1. (a) Total energy as a function of the Na_2-Na_2 distance. (b) Filled and open circles represent the energy of the O and of the t_{1g}-derived states referred to the t_{1u}-derived one, at X.

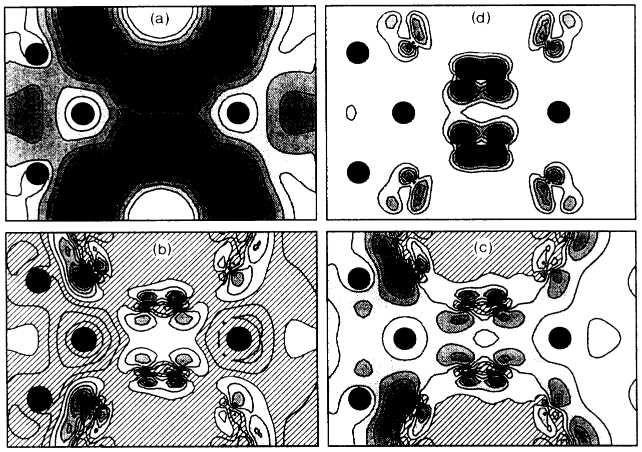

FIG. 2. Na_6C_{60} (110) plane: (a) $\rho(r)$ normalized to the unit cell volume. Contours scale logarithmically from 0.001 to 0.1; (b) $\Delta\rho(r)$, (c) $\rho_e(r)$, (d) $\rho_{t_{1u}}(r)$ (see text). In (b)–(d) contours vary linearly with 0.001 spacing. White: 0–0.001, hatched: < 0.

excess electron density $\rho_e(r) = \rho(r) - \rho_m(r)$ [Fig. 2(c)] is much more complex than that of the t_{1u}-derived band states of C_{60} [Fig. 2(d)], due to the strong polarization of the occupied states of C_{60}. This finding contradicts what one would expect in a naive rigid band picture, and is fully analogous to our results for K_6C_{60} [13,16].

From this same analysis performed on K_6C_{60}, we deduce that both the degree and the localization of the transferred charge are similar for the two fullerides. Such considerations are necessarily qualitative, however, since a quantitative description of the charge transfer and *a fortiori* of the comparison of two systems is not possible. As an estimate, the values of the integrated $\Delta\rho(r)$ at half-distance between the alkali atom and C are $D_{\rm K}$ (1.60 Å) $= -0.13e$, $D_{\rm Na_1}$ (1.63 Å) $= -0.18e$, $D_{\rm Na_2}$ (1.34 Å) $= -0.075e$. The lengthening of the double bonds (see Table I), which reflects the charge transfer to antibonding orbitals, is the same in both compounds [16]. The molecular structure is modified significantly and, as expected, more so than in K_3C_{60} [16]. The relaxation of the molecule yields an energy gain of 0.47 eV in Na_6C_{60} and 0.55 eV in K_6C_{60}. The binding energy is about 2.2 eV, comparable to the value of 2.8 eV calculated [16] for K_6C_{60} [25].

In agreement with experiment [6], the LDA band structure of Na_6C_{60} in Fig. 3(a) corresponds to an insulator. The fundamental gap is direct at X as in pristine C_{60} but strongly reduced (from $\simeq$ 1.1 eV to 0.35 eV). Although a detailed comparison with K_6C_{60} is not possible due to the difference in structure, some useful information can be obtained. The reduction of the energy gaps between the bands derived from the highest occupied and lowest unoccupied molecular orbitals of C_{60}, which also depends on the charge transfer, is of the same order in the two compounds [25]. However, in contrast to K_6C_{60} [12,14,16], the band structure of Na_6C_{60} does not retain the sequence of levels of C_{60} beyond the t_{1u}-derived bands. An interesting new feature appears in the lowest empty states, namely, a simple and rather flat band, which in Fig. 3 is slightly lower than the bands derived from the t_{1g} states of C_{60}. It is not derived from the Na atomic states, but is strongly related to the arrangement of the Na_2 ions. Figure 3(b) shows the probability density corresponding to the lowest unoccupied state (Γ_1) at the Γ point. This is localized at the empty O site which is the center of the tetrahedron of the Na ions and corresponds to a minimum of the Hartree potential seen by an excess electron. The localization properties do not change with the k point, consistent with the small dispersion of the band. We shall refer to them as the O states (band). This kind of electron state does not exist in K_6C_{60}. The center of the four-K-ions motif (center of the cube face) is the counterpart of the O site here. This, however, does not correspond to a minimum of the Hartree potential because an accumulation of the electron density between the molecules takes place.

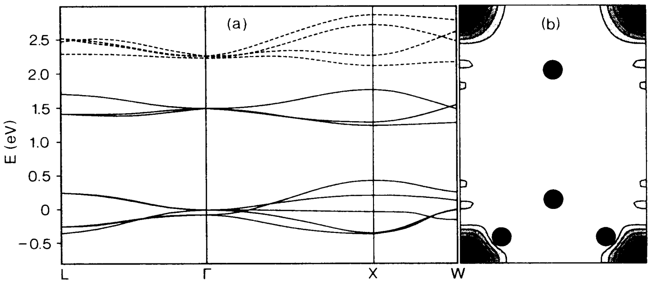

FIG. 3. Na_6C_{60} (a) band structure and (b) probability density of the O state at Γ on the (110) plane. Contours as in Figs. 2(b)–2(d).

An intriguing issue is to what extent the energy and nature of the O states depend on the geometry of the Na ions. We have calculated the band structure for different sizes of the Na tetrahedron. The O state lowers with decreasing Na_2-Na_2 distance, and eventually crosses the t_{1u}-derived bands. This is shown in Fig. 1(b) at X, which corresponds to the smallest energy gap. Therefore, squeezing the tetrahedron leads to the transformation from an insulator to a zero-gap semiconductor and eventually to a metal. In particular, the configuration proposed in Ref. [5] would correspond to a metal, since the O states are so low that they hybridize with the t_{1u}-derived ones, and part of the excess electron density accumulates within the Na tetramer. Such a configuration, however, is energetically very unfavorable. We stress that the calculated equilibrium distance is very close to the closing of the gap at the X point and that within the LDA one cannot determine precisely when this takes place. Therefore, at least around X, the occupation of the O state may well depend on, e.g., the temperature of the sample. Figure 1(b) also shows that expansion of the tetrahedron drives a crossing between the O and the t_{1g}-derived states. As expected, we find that closing of the gap also occurs for decreasing lattice constant. $d(Na_2\text{-}Na_2)$ scales superlinearly with it, so that a rapid insulator-metal transition can be expected under pressure, provided that the crystal structure is preserved. Unfortunately, experimental data on Na_6C_{60} under pressure are not yet available [26].

Detection of the O states by either optical measurements or inverse photoemission (IPES) is not easy. Being confined to the environment of the O site, their overlap with any of the occupied states, which are initial states in the transitions and are all localized on the C_{60} molecules, is negligible. In particular, although not forbidden by selection rules, the electron excitations to such states from the highest occupied (t_{1u}-derived) ones are characterized by a relatively weak dipole moment. Calculations performed at several k points show that this is at least one order of magnitude lower than the dipole moment corresponding to the transition to the t_{1g}-derived states. IPES, not angularly resolved [6], does not reveal any special features, which is also due to a lack of sufficient energy resolution (0.3 eV). Being that the O band is essentially dispersionless, angle-resolved IPES may still be able to characterize it.

Although the situation may at first sight be reminiscent of an anomalous low-lying empty band in LiC_6 [27], the nature of the electron states in the two cases is completely different. In LiC_6, they are interlayer bonding states, free-electron-like and their existence is not related to the presence of the intercalating cations. Here, the O states are strictly related to the presence of the Na ions and are spatially highly localized.

In conclusion, we have determined *ab initio* the Na structure of Na_6C_{60} and shown that this reflects an ionic type of chemical bonding between the alkalis and the C_{60} molecules. The charge transfer to C_{60} from the Na atoms is high, and only slightly less than in K_6C_{60}, in agreement with indications from Raman and NMR data. Therefore, the main structural characteristics will not be altered if we consider the orientational disorder of the tetrahedra. This, however, may in reality lead to the formation of domains, and, together with the rotation of the balls, which is shown by the narrowness of the ^{13}C NMR line (observed at least at RT [5,28]), may be a source of difficulty for any structural determination from XRD. In order to establish the Na configuration, Na-sensitive probes such as ^{23}Na NMR are highly desirable. Nonisoelectronic behavior is seen in the presence of new low-lying electron states that originate in the characteristic structure of the Na ions in the fcc host structure. This finding provides a clue to understanding the anomalous electronic properties of Na fullerides at least for $x \gtrsim 6$. For $x = 6$, although probably empty at low temperatures, such states are so low that their occupation at specific points in the BZ may well fluctuate with temperature and also depend on the stoichiometry and on the degree of purity of the sample. In the higher Na fullerides, which also retain the fcc structure, such states may become fully occupied so the common assumption that electron doping simply corresponds to filling the empty states of C_{60} should no longer be valid.

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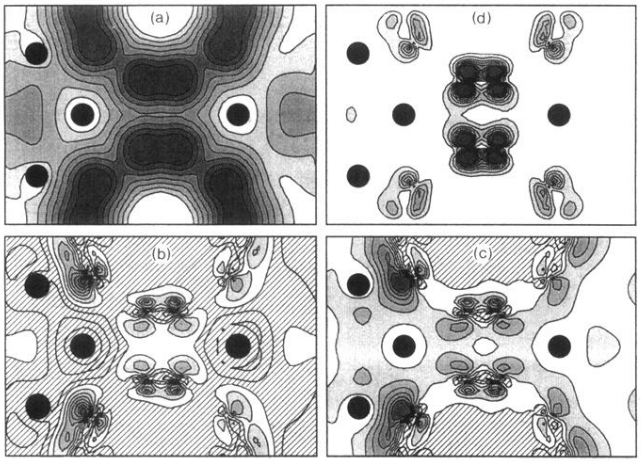

FIG. 2. Na_6C_{60} (110) plane: (a) $\rho(r)$ normalized to the unit cell volume. Contours scale logarithmically from 0.001 to 0.1; (b) $\Delta\rho(r)$, (c) $\rho_e(r)$, (d) $\rho_{t_{1u}}(r)$ (see text). In (b)–(d) contours vary linearly with 0.001 spacing. White: 0–0.001, hatched: < 0.

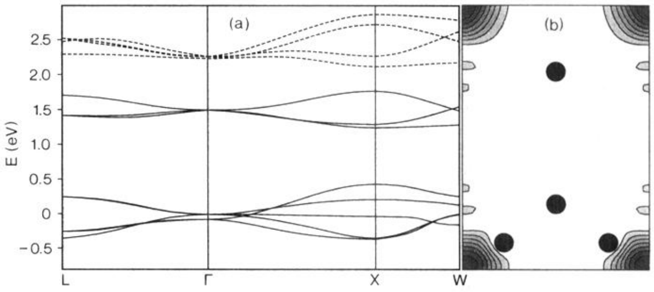

FIG. 3. Na_6C_{60} (a) band structure and (b) probability density of the O state at Γ on the (110) plane. Contours as in Figs. 2(b)–2(d).