PHYSICAL REVIEW B VOLUME 52, NUMBER 21 1 DECEMBER 1995-I

Off-center sites in some lightly intercalated alkali-metal fullerides

C. Goze, M. Apostol, and F. Rachdi*
Université Montpellier II, Groupe de Dynamique des Phases Condensées 026, Montpellier 34095, France

M. Mehring
Stuttgart University, Stuttgart 70550, Germany

(Received 9 May 1995; revised manuscript received 1 August 1995)

It is shown that the alkali cations A in the A_nC_{60}, $n=1,2,3$ alkali fullerides may acquire off-center sites in the octahedral coordination, placed along the (111) directions, while those in the tetrahedral coordination remain in the central positions of equilibrium.

It was suggested recently,[1-3] from the analysis of the x-ray and neutron scattering data that the alkali cations A in some fcc-alkali fullerides AC_{60} and A_3C_{60} may acquire off-center sites, as a result of the two competing (tetrahedral and octahedral) coordinations existing in these compounds. Similar off-center sites have already been indicated[4,5] in other alkali fullerides, with a higher content of alkali cations, as, for example, A_4C_{60} and A_6C_{60}, where the alkali cations may form clusters of regular geometrical shapes. While for these latter compounds the existence of the off-center sites might be expected, as they may accommodate more alkali cations, the off-center sites in the lightly intercalated alkali fullerides A_nC_{60}, $n=1,2,3$, which are addressed in this paper, may appear as being a little surprising. Actually, the existence of the off-center sites has long been indicated[6] for small-size substitutional impurities in the alkali halides, as a consequence of the balance between the repulsive and the polarization forces, the latter having the tendency of destabilizing the central equilibrium. We show in this paper that in the case of the alkali fullerides there may appear off-center sites even for medium-size alkali cations, like K, the reason being the imbalance in the coordination sizes and/or in the atomic (ionic) radii. Specifically, we show herein that the octahedrally coordinated alkali cations in some fcc-alkali fullerides A_nC_{60}, with $n=1,2,3$, may acquire off-center sites, placed along the (111) directions, while those in the tetrahedral coordination remain in the central positions of equilibrium. The general reason for the existence of the off-center sites has recently been illustrated[7] by a model calculation for a general crystalline structure of the type of the A_3C_{60} structure, using pointlike atoms (ions) as sources of the potentials, as well as an approximate, effective interatomic potential.

Although the crystalline structure of the fcc-alkali fullerides is widely known[8,9] we have included in Figs. 1 and 2 the structural elements we employ here. The structural unit shown in Fig. 1 is the body-centered cube with the side ~7.1 Å which represents 1/8 of the standard unit cell of the fcc structure. One can see in Fig. 1 the tetrahedrally coordinated alkali cation A (which is missing in AC_{60}), as well as one of the octahedrally coordinated alkali cation, denoted A' (which is missing in A_2C_{60}). The tetrahedral coordination is also shown in Fig. 2, where the coordinates of the centers of the alkali cation and the neighboring fullerene molecules are given, in units of 7.1 Å. On looking at Figs. 1 and 2 one should bear in mind the large radius $R=3.5$ Å of the C_{60} molecule.

Generally, the interatomic (ionic) potentials in solids consist of a repulsive part at short distances and an attractive part at long distances, coming from the repulsion between the electronic orbitals, polarization, Coulomb forces, dipole-dipole interaction, etc. Since the mass of the fullerenes is much larger than the mass of the alkali cations, we shall consider the positions of the former as being rigid. The relaxation of the fullerenes being, therefore, absent, the corresponding dipole-dipole interaction between the nearest neighbors (which plays an important role for the substitutional impurities in the alkali halides[10]) vanishes. Further on, leaving aside for the moment the Coulomb potential, we may also consider that the main contribution to the (short-range) interatomic interaction energy of the alkali cation comes from its interaction with the carbon atoms placed on the spherical surface of the nearest-neighboring fullerene molecules inside the solid angles under which the latter are seen from the position of the alkali cation. We shall show below that including the contribution of all the carbon atoms on the fullerene molecules changes little these short-range potentials. The polarization of the carbon atoms and the alkali cations produces the well-known van der Waals forces, which we include in our potential as the $1/r^6$ term. As regards the repulsion interaction we shall use the $1/r^{12}$ power law, instead of other functional forms, as for example, the exponential law in the Born-Mayer potential. While the former is more suitable for the proximity interaction between two distinct electronic orbitals, the latter accounts better for the interpenetrating clouds of electrons, as in ionic salts. In the case of the alkali-doped fullerides the transferred electrons are spread over the large size of the fullerene molecules (being shared by 60 carbon atoms in each fullerene molecule), as well as they are distributed to the conducting bands, so that there remain little of interpenetrating electronic clouds around carbon atoms and alkali cations, at least for not too small distances. Therefore, it seems more suitable

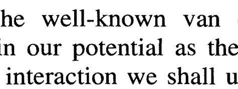

FIG. 1. The structural unit of the fcc-alkali fullerides used in the present work, with the centers of the alkali cations A and A' and the fullerenes C_{60}; the side of the cube is 7.1 Å.

0163-1829/95/52(21)/15031(4)/$06.00

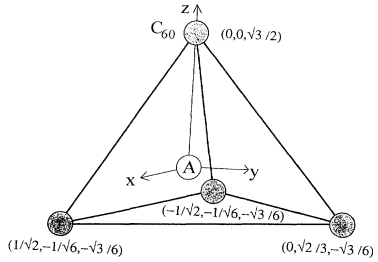

FIG. 2. The tetrahedral coordination of the alkali cation A.

to use in this case a (12-6)-power-law Lennard-Jones potential

$$V_{\mathrm{LJ}}(r)=\varepsilon(\sigma^6/2r^{12}-1/r^6) \tag{1}$$

for the carbon-alkali cation interaction. In this respect the alkali fullerides might be better referred to as intercalated molecular solids instead of ionic compounds, though the terminology in this case is largely a matter of convention. Indeed, the interatomic potentials are semiphenomenological potentials, and they would not differ too much from each other over a reasonably small range of distances around the equilibrium positions (and we emphasize that our calculations are only valid over such distances) providing the parameters in these potentials are properly fitted to the relevant experimental data of the lattice constants and the bulk compressibility moduli. The existence of the off-center sites does not depend essentially on the particular choice of the functional dependence on distance of the interatomic potentials, its origin residing, as we have said above, in the imbalance between the coordination sizes and/or atomic (ionic) radii. The estimation of the parameters of the interatomic potentials, however, must take into account the existence of the off-center sites, whenever these might be relevant, leading, therefore, to a self-consistent general picture of both the off-center sites and the potential parameters.

The Lennard-Jones potentials of the type given by (1), between both carbon-carbon and carbon-alkali cation pairs, have recently been used[11–14] in discussing the properties of the alkali fullerides. The available potential parameters σ and ε for medium-size alkali cations are listed in Table I. Difficulties seem to have been encountered in deriving these parameters for small-size alkali cations; our suggestion is that these difficulties might be related exactly to the existence of rather far-lying off-center sites for these cations, as we shall see below. The values corresponding to $A=\mathrm{K}$ and Rb are taken from Ref. 11. The values of the parameter σ coincide with those given by the semiempirical formula $\sigma=2^{1/6}(r_C+r_A)$, corresponding to $V_{\mathrm{LJ}}=0$, where $r_C=1.7$ Å is the van der Waals radius of carbon[15] and r_A is the ionic radius of the alkali cation. This formula was used for obtaining the other values of the parameter σ in Table I, with the ionic radii $r_{\mathrm{Li}}=0.69$ Å, $r_{\mathrm{Na}}=1.02$ Å, $r_{\mathrm{Cs}}=1.70$ Å ($r_{\mathrm{K}}=1.38$ Å, $r_{\mathrm{Rb}}=1.49$ Å).[1]

In order to get the interaction potential between the alkali cation and the fullerene molecule we sum the Lennard-Jones potentials $V_{\mathrm{LJ}}(r_i)$ given by (1), where r_i is the carbon-alkali cation distance, over all the carbon atoms i lying on the spherical surface of the fullerene molecule inside the solid angle under which this molecule is seen from the position of the alkali cation.[16] The contribution of the other atoms, lying further away from the alkali cation, is neglected, including the carbon atoms on the opposite side of the fullerene molecule; both the long distances and the screening effects concur in rendering the effects of these contributions negligibly small. In general, one may expect a small attractive interaction from the far-sitting atoms, which adds to the destabilizing effects. Furthermore, the summation over the carbon atoms lying inside the solid angle Ω defined above may be replaced by an integral average,

TABLE I. The parameters σ and ε of the Lennard-Jones potential (1) between the alkali cation A and the carbon atom, and the distance d of the off-center sites placed along the (111) directions to the center of the octahedral coordination.

A	Li	Na	K	Rb	Cs
σ[Å]	2.68	3.05	3.46	3.58	3.82
ε[eV Å^6]	-	-	69.7	84.3	-
d[Å]	1.7	1	0.3	0	0

$$V(r)=\sum_{i\in\Omega}V_{\mathrm{LJ}}(r_i)=\frac{60}{4\pi R^2}\,2\pi R^2\int_0^{\theta_0}d\theta \times\sin\theta\; V_{\mathrm{LJ}}(\sqrt{r^2+R^2-2rR\cos\theta}), \tag{2}$$

where R is the radius of the C_{60} fullerene molecule, r is the distance between the centers of the alkali cation and the fullerene molecule, and $\cos\theta_0=R/r$. Doing so we neglect the small irregularities due to the nonuniform distribution of the carbon atoms on the fullerene molecule, as well as the orientational effects.[12,14] Performing the integral in (2) we get the interaction potential

$$V(r)=\frac{3\varepsilon\sigma^6}{2rR}\left[\frac{1}{(r-R)^{10}}-\frac{1}{(r^2-R^2)^5}\right]-\frac{15\varepsilon}{2rR}\left[\frac{1}{(r-R)^4}-\frac{1}{(r^2-R^2)^2}\right] \tag{3}$$

between the alkali cation and the fullerene molecule.[17] For comparison we give here the potential

$$U(r)=\frac{3\varepsilon\sigma^6}{2rR}\left[\frac{1}{(r-R)^{10}}-\frac{1}{(r+R)^{10}}\right]-\frac{15\varepsilon}{2rR}\left[\frac{1}{(r-R)^4}-\frac{1}{(r+R)^4}\right], \tag{4}$$

obtained by integrating in (2) over the whole sphere of the fullerene molecule; one can check easily that the numerical values of the two potentials are close to each other around the equilibrium positions of the alkali cations. Indeed, the potentials $V(r)$ and $U(r)$ are plotted versus the distance r from the center of the fullerene molecule in Fig. 3 for the K cation ($\varepsilon=69.7$ eV Å^6, $\sigma=3.46$ Å), and one can see that the difference between these two potentials is up to ~12% around the center of the configuration, $r=7.1$ Å. In addition, one can see also that the two potentials have almost the same shape (i.e., almost the same derivative), and their minima have almost the same position, which indicates that the equilibrium positions of the alkali cations are not affected signifi-

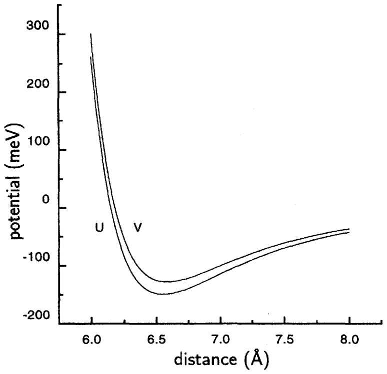

FIG. 3. The potentials V and U, as given by (3) and, respectively, (4), between a fullerene molecule and the K-alkali cation ($\varepsilon=69.7$ eV Å^6, $\sigma=3.46$ Å), plotted vs distance around the center of the octahedral coordination (7.1 Å).

cantly if one works with one or the other of these potentials. However, we prefer to employ the potential $V(r)$ instead of $U(r)$ for two reasons. First, the parameters of the Lennard-Jones potential are not reliable for large distances, as the distances included in the potential $U(r)$ (as they are not for very short distances, as well); second, the potential $U(r)$ brings an additional attractive contribution, as one can see in Fig. 3, and we wish to overestimate the conditions of central equilibrium of the alkali cations; i.e., our off-center results presented below should be considered as minimal.

The potential energies of the alkali cation in the tetrahedral and octahedral coordinations, denoted by V_T and, respectively, V_O, are obtained by summing the potentials given by (3) over the nearest-neighboring fullerene molecules. The four nearest-neighboring fullerene molecules of the alkali cation in the tetrahedral coordination are shown in Fig. 2, together with the coordinates of their centers. For the octahedrally coordinated alkali cation A' shown in Fig. 1 there are six nearest-neighboring fullerene molecules, placed along the (100) directions. A min-max computing program has been used for finding the minima of the functions $V_{T,O}$, and their positions with respect to the coordination center. The results are given in Table I and Fig. 4. It was found that the lowest minimum value of the potential energy V_T in the tetrahedral coordination is always at the coordination center, providing $\sigma>\sigma_T=2.64$ Å, while in the octahedral coordination the minimum is central for $\sigma>\sigma_O=3.51$ Å. There exists, therefore, an instability range for the parameter σ, $\sigma_T<\sigma<\sigma_O$, for which one may have off-center sites in the octahedral coordination and on-center equilibrium positions in the tetrahedral coordination, in agreement with the results reported previously.[7] The positions of the off-center sites in the octahedral coordination have further on been investigated for this instability range of the parameter σ, and it has been found that they lie along the (111) directions; their distances to the center have been computed, and are given by the solid line in Fig. 4; their values for the alkali cations are also included in the last row of Table I. One can see from Fig. 4 that, while Rb and Cs may occupy on-center sites in both tetrahedral and octahedral coordinations, the remaining of the alkali cations have a central equilibrium position in the tetrahedral coordination and off-center equilibrium sites, placed along the (111) directions, in the octahedral coordination. The height of the potential barrier between two adjacent off-center sites of the K cation is about 3 meV. In Fig. 5 we have plotted the curves of the potential energy of K around the octahedral center along the three high-symmetry directions versus distance. One can see from this figure the small potential differences between the off-center sites and the coordination center, as well as the sizable extent of the off-center distances. As a result of the uncertainty in the potential $V(r)$, as discussed above, we may expect a downward shift of the curves given in Fig. 5 of about 12% at most. We emphasize that, due to the small values of the potential barriers between the adjacent off-center sites around a normal site, the corresponding alkali cations are practically uniformly distributed around the normal site, within the range of the off-center distances. The Rb cation has a special position, as it lies close to the octahedral instability limit in Fig. 4. Taking into account the uncertainty in the potential parameters and the fact that our potential (3) overestimates the central stability we cannot say definitely that the Rb cation occupies a central equilibrium position in the octahedral coordination. For example, replacing the lattice parameter 7.1 Å by 7.2 Å we obtain a slightly off-center equilibrium position for Rb. As a matter of fact, for values of

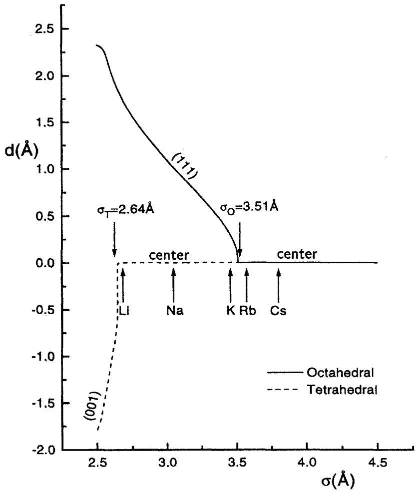

FIG. 4. The distance to the center d vs the parameter σ for the off-center sites in the octahedral coordination (solid line) and in the tetrahedral coordination (dashed line).

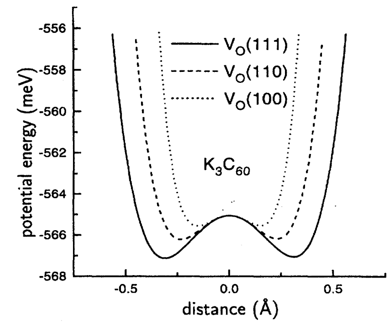

FIG. 5. The potential energy V_O of K along the high-symmetry directions around the octahedral center vs distance. As discussed in the text the curves may be shifted downward up to ~12%.

σ close to σ_O there exist also minima of the energy V_O along the (110) and (100) directions, which compete with the minima along the (111) directions (as one can see from Fig. 5), so that the latter are no longer very well defined in this case.[18,19] Particularly interesting is also the Li cation, which exhibits a large instability, close to the tetrahedral instability threshold. We emphasize that this only indicates the possibility of cluster formation in the case of the fullerides highly doped with small-size alkali cations (as suggested recently[4,5]), the complete investigation of the existence of these clusters requiring the inclusion of the interatomic potentials between the cluster members. A similar problem may also appear for some fullerides with a lower content of small-size alkali cations, the structure of these compounds being still controversial, to a certain extent. We also mention here that in the case of far-lying off-center sites the effect of renormalizing the potential parameters may be important for establishing the final self-consistent equilibrium positions. The off-center sites have also been investigated in the tetrahedral coordination for values of σ slightly less than σ_T; it was found that they are placed along the (001) directions (in the reference frame of Fig. 2), and their distance to the center is represented by the dashed line shown in Fig. 4. We remark also on the steep dependence on σ of the positions of the off-center sites in both coordinations for values of σ close to σ_T and σ_O.

We turn now to examine the effects of the Coulomb interaction. In the first approximation one may consider the alkali cations as embedded in a neutralizing cage of uniformly distributed electric charge, due to the fact that the electrons are almost completely transferred to the fullerenes sublattice; consequently, the Coulomb interaction would only bring a constant contribution to the potential energy of the alkali cations which will not affect their equilibrium positions (though being the main contribution to the cohesive energy). Second, if one assumes a $1/r$-Coulomb interaction as coming from the transferred charge, it is easy to see that the second-order expansion of the potential energy around the coordination center is not affected by this Coulomb interaction (except for a constant term), as one may expect in a cubic symmetry. Indeed, assuming that the nearest-neighboring fullerene molecules are the source of a Coulomb potential of the form $-ne^2/r$ where n is the number of electrons transferred to a fullerene molecule and e is the electron charge, we obtain the following series expansions of the potential energies V_T and V_O around the coordination centers:

$$V_T = A_T + B_T(x^2+y^2+z^2) + \cdots, \tag{5}$$

where

$$\begin{aligned} A_T &= (1.63\times10^{-5}\sigma^6 - 0.0261)\varepsilon - 9.36n \ \ (\mathrm{eV}), \\ B_T &= (4.28\times10^{-5}\sigma^6 - 0.0130)\varepsilon, \end{aligned} \tag{6}$$

and

$$\begin{aligned} V_O = {} & A_O + B_O(x^2+y^2+z^2) + C_O(x^4+y^4+z^4) \\ & + D_O(x^2y^2+y^2z^2+x^2z^2) + \cdots, \end{aligned} \tag{7}$$

where

$$\begin{aligned} A_O &= (9.86\times10^{-7}\sigma^6 - 0.0095)\varepsilon - 12.17n \ \ (\mathrm{eV}), \\ B_O &= (1.40\times10^{-6}\sigma^6 - 0.0026)\varepsilon, \\ C_O &= (1.67\times10^{-6}\sigma^6 - 0.001)\varepsilon - 0.0028n, \\ D_O &= (-7.96\times10^{-7}\sigma^6 + 0.0009)\varepsilon + 0.0084n. \end{aligned} \tag{8}$$

One can see from the above equations that the second-order coefficients $B_{T,O}$ in the power expansions are not affected by the presence of the Coulomb interaction; in addition, one can check that the central equilibrium is reached for $B_{T,O}>0$, which yield $\sigma>\sigma_T=2.6$ Å, slightly less than the value of $\sigma_T=2.64$ Å found before, and $\sigma>\sigma_O=3.51$ Å, which is identical with the σ_O value obtained without the Coulomb interaction. One may, therefore, conclude that the Coulomb interaction will only bring minor changes in the picture of the off-center sites shown in Fig. 4, at least for those off-center sites lying close to the coordination centers.

In conclusion, one may say that the octahedrally coordinated alkali cations in some fcc-alkali fullerides may acquire off-center sites placed along the (111) directions, while their equilibrium positions in the tetrahedral coordination remain central. The existence of the off-center sites in the alkali fullerides might be relevant for the structural analysis of these compounds, as well as for the processes related to the distribution of the electron density. The disorder associated with the presence of the off-center sites may affect the conducting (and superconducting) properties of the alkali fullerides, as well as their thermal properties.

---

*To whom correspondence should be sent.

[1] D. W. Murphy *et al.*, J. Phys. Chem. Solids **53**, 1321 (1992).

[2] Q. Zhu *et al.*, Phys. Rev. B **47**, 13 948 (1993).

[3] W. I. F. David (unpublished).

[4] M. J. Rosseinsky *et al.*, Nature **356**, 416 (1992).

[5] T. Yildirim *et al.*, Nature **360**, 568 (1992).

[6] J. A. D. Matthew, Solid State Commun. **3**, 365 (1965).

[7] M. Apostol, C. Goze, F. Rachdi, and M. Mehring (unpublished).

[8] P. W. Stephens *et al.*, Nature **351**, 632 (1991).

[9] P. W. Stephens *et al.*, Phys. Rev. B **45**, 543 (1992).

[10] See, for example, R. Smoluchowski, in *Magnetic Resonance and Radiofrequency Spectroscopy*, edited by P. Averbuch (North-Holland, Amsterdam, 1969), p. 120.

[11] E. J. Mele, in *Chemical Physics of Intercalation II*, edited by P. Bernier *et al.*, Vol. 305 of NATO Advanced Study Institute, Series B: Physics (Plenum, New York, 1993), p. 93.

[12] T. Yildirim, *et al.*, Phys. Rev. B **48**, 12 262 (1993).

[13] J. P. Lu *et al.*, Phys. Rev Lett. **68**, 1551 (1992).

[14] T. Yildirim and A. B. Harris, Phys. Rev. B **46**, 7878 (1992).

[15] A. Bondi, J. Phys. Chem. **68**, 441 (1964).

[16] A similar potential between pairs of carbon-carbon atoms has been introduced in the study of the fullerene solids by L. A. Girifalco, J. Phys. Chem. **95**, 5370 (1991).

[17] An effective Lennard-Jones potential $V(r) = (30\varepsilon/\pi)[\sigma^6/2(r-\lambda)^{12} - 1/(r-\lambda)^6]$, which has been used in Ref. 7, can be obtained from (3) for $\lambda=0.4$ and r close to the central positions of the alkali cations.

[18] W. Andreoni *et al.*, Phys. Rev. B **51**, 2087 (1995).

[19] J. E. Fischer (unpublished).

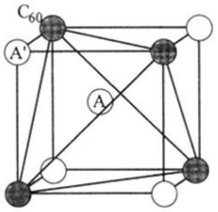

FIG. 1. The structural unit of the fcc-alkali fullerides used in the present work, with the centers of the alkali cations A and A' and the fullerenes C_{60}; the side of the cube is 7.1 Å.

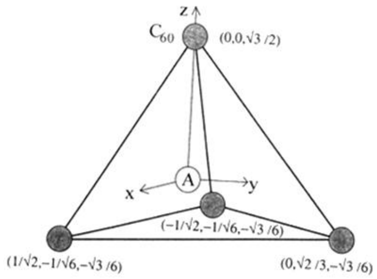

FIG. 2. The tetrahedral coordination of the alkali cation A.