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OFF-CENTRE SITES IN ALKALI FULLERIDES

M. Apostol, C. Goze and F. Rachdi
Montpellier University II, GDPC-026, Montpellier 34095, France
and
M. Mehring
Stuttgart University, Stuttgart 70550, Germany

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It is shown that, under certain conditions, the octahedrally-coordinated alkali cation A in the A_3C_{60} fullerides may acquire off-centre positions, placed along the high-symmetry directions.

Keywords: A. fullerenes, C. crystal structure and symmetry.

RECENTLY, it has been suggested [1] that the alkali cation A in the A_3C_{60} fullerides might acquire off-centre equilibrium positions, as a result of its competing coordinations (tetrahedral and octahedral) in these compounds. The existence of the off-centre sites in alkali halides has long been indicated for substitutional impurities [2], as a consequence of the balance between the repulsion and the polarization forces, the latter having the tendency of reversing the potential curvature at the centre of the atomic configuration. Taking into account the interaction of the alkali cation with its nearest-neighbouring fullerenes, we show here, by direct calculation, that for a Lennard–Jones potential there exists a range of the potential parameters for which the alkali cation may be placed in the centre of the tetrahedral coordination, but off the centre of the octahedral one.

The structural unit we employ is the body-centered cube [3] shown in Fig. 1, with the side 7.1 Å taken as equal to unity; one can see in Fig. 1 the tetrahedrally-coordinated alkali cation A and an octahedrally-coordinated one, denoted by A′. The tetrahedral configuration is also shown in Fig. 2, where the coordinates of the atomic centres are given. We shall assume that the main contribution to the atomic interaction originates from the carbon atoms placed on the surface of the large fullerene molecule in the vicinity of the alkali cation; therefore, we shall consider only the interaction between the alkali cation and its nearest-neighbouring fullerenes. Within a first approximation, in order to see the effect qualitatively, we may describe this interaction by a Lennard–Jones potential [4, 5] $V_{LJ} = \sigma/2r^{12} - 1/r^6$, where r is the distance between the centres of the alkali cation and the fullerene molecule, and σ is a parameter. In addition, we shall be interested in the equilibrium positions of the alkali cations around the centre of each atomic configuration. Since the transferred electrons reside almost entirely on the fullerene sub-lattice one may consider, within a first approximation, that each alkali cation is embedded in a neutralizing electric cage, so that the Coulomb interaction brings only a constant contribution which does not affect the equilibrium positions; in view of our purpose we may, therefore, neglect the Coulomb interaction. In general, the attractive Coulomb interaction has a destabilizing effect on the positions of the alkali cations in any atomic configuration

Using the Lennard–Jones potential given above we can write straightforwardly the energy of the alkali cations A placed at $(x, y, z + 1/2\sqrt{3})$ around the centre of the tetrahedral coordination, and perform a second-order expansion; the result is given by

$$V = \frac{2^8}{3^3}\left(\frac{2^5}{3^3}\sigma - 1\right) + \frac{2^{10}}{3^4}\left(11\frac{2^6}{3^3}\sigma - 5\right)(x^2 + y^2 + z^2), \tag{1}$$

whence one can see that the equilibrium is reached at the centre of the tetrahedron for $\sigma > 5 \cdot 3^3/11 \cdot 2^6 = 0.19$. Actually, one can check that for $\sigma > 0.2$ this is the lowest minimum value of the potential. Similarly, one can write down the energy of the octahedral configuration

$$V = \frac{\sigma}{2}[(x+1)^2 + y^2 + z^2]^{-6} - [(x+1)^2 + y^2 + z^2]^{-3} + \frac{\sigma}{2}[(x-1)^2 + y^2 + z^2]^{-6} - [(x-1)^2 + y^2 + z^2]^{-3} + (x \leftrightarrow y) + (x \leftrightarrow z), \tag{2}$$

where the coordinate axes are taken along the sides of the cube and (x, y, z) label the position of the alkali cation around the centre of the octahedral coordination. After somewhat lengthy but straightforward calculations we obtain the fourth-order expansion

$$V = -V_0 - A(x^2 + y^2 + z^2) + B(x^4 + y^4 + z^4) + C(x^2y^2 + y^2z^2 + x^2z^2), \tag{3}$$

where

$$V_0 = 3(2 - \sigma), \qquad A = 6(5 - 11\sigma)$$
$$B = 3(469\sigma - 92), \quad C = 4(102 - 203\sigma). \tag{4}$$

We can see from equations (3) and (4) that the equilibrium is reached at the centre of the octahedron for $\sigma > 5/11 = 0.45$ $(A < 0)$. There exists, therefore, a range of values of the parameter σ, $0.19 < \sigma < 0.45$, wherein we may have on-centre tetrahedral sites but off-centre octahedral ones. In what follows we shall discuss the behaviour of the multiwell potential V given by (3) within this range of values of the parameter σ.

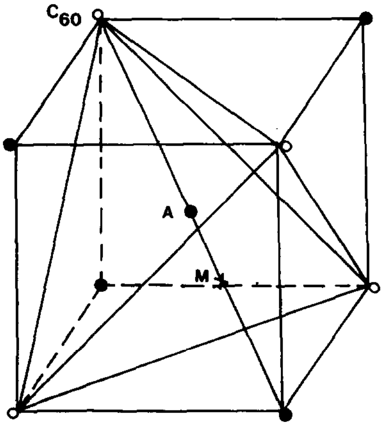

Fig. 1. The structural unit of A_3C_{60} referred to in the text, with the centres of the alkali cations A (tetrahedral) and A′ (octahedral) and the fullerene C_{60}; the side of the cube is taken as equal to unity and M denotes the centre of the equilateral triangle formed by the three C_{60} molecules.

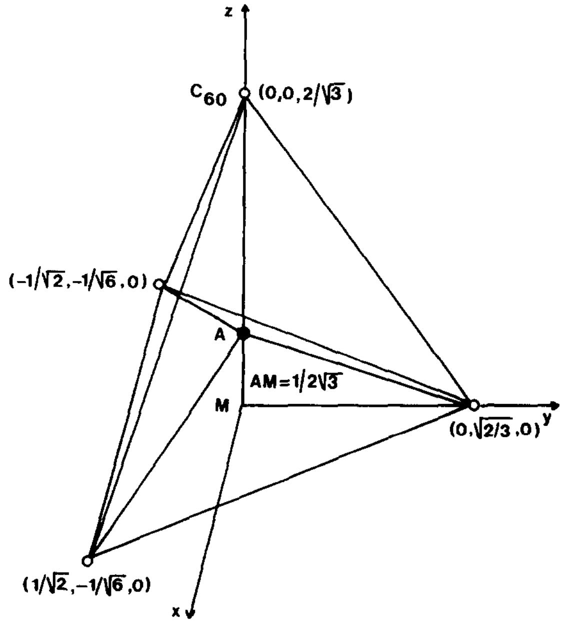

Fig. 2. The tetrahedral coordination of the alkali cation A.

The potential function V has a maximum $-V_0$ at the centre of the octahedron $x = y = z = 0$, and a set of minima lying on the high-symmetry directions of the cubic structural unit; in addition, for $\sigma = 0.26$ there exists a spherical surface of minima with the radius $r = (x^2 + y^2 + z^2)^{1/2} = 0.25$ [6]. The minima occurring along the (1 1 1)-type directions are placed at

$$r = \sqrt{3}x = 3\left(\frac{5 - 11\sigma}{595\sigma + 132}\right)^{1/2} \tag{5}$$

and their magnitude with respect to the maximum value $-V_0$ is given by

$$\Delta V_{111} = -27\frac{(5 - 11\sigma)^2}{595\sigma + 132}; \tag{6}$$

the minima placed along the (1 1 0)-type directions have the positions given by

$$r = \sqrt{2}x = \left(6\frac{5 - 11\sigma}{1001\sigma - 144}\right)^{1/2} \tag{7}$$

and the magnitude

$$\Delta V_{110} = -18\frac{(5 - 11\sigma)^2}{1001\sigma - 144}; \tag{8}$$

finally, the (1 0 0)-type minima do not exist for $0.19 < \sigma < 0.196$, and are placed beyond the validity limits of our expansion for σ slightly larger than 0.196; requiring their distance to the centre be less than unity, for example, we get $\sigma > 0.2$, in which case their positions are given by

$$r = x = \left(\frac{5 - 11\sigma}{469\sigma - 92}\right)^{1/2}, \tag{9}$$

and their magnitude

$$\Delta V_{100} = -3\frac{(5-11\sigma)^2}{469\sigma - 92}. \tag{10}$$

Comparing now the magnitudes of these minima we obtain readily that for $0.38 < \sigma < 0.45$ the preferred off-centre sites are those lying on the (1 1 1)-type directions, at distances [given by equation (5)] varying between $r = 0$ for $\sigma = 0.45$ and $r = 0.14$ for $\sigma = 0.38$. For values of σ below 0.38 the (1 1 0)-type minima start to prevail, and they are the favoured off-centre sites for $0.23 < \sigma < 0.38$ (except for $\sigma = 0.26$, where the spherical surface of minima appears, as mentioned above); their positions vary between $r = 0.14$ for $\sigma = 0.38$ and $r = 0.43$ for $\sigma = 0.23$. These minima occur again for $0.19 < \sigma < 0.2$ at $r = 0.55$ for $\sigma = 0.2$ and $r = 0.6$ for $\sigma = 0.19$. One can see that on decreasing σ one gradually obtains minima placed further and further away from the centre, where the validity limits of the series expansion are trespassed. The same happens for $0.2 < \sigma < 0.23$ where the (1 0 0)-type minima are energetically favoured, at distances $x = 0.43$ for $\sigma = 0.23$ and $x = 1$ for $\sigma = 0.2$. Clearly, these results indicate an instability of the alkali cation in the octahedral coordination for values of σ approaching 0.19 from above. For values of σ slightly below 0.45 we can definitely say that the off-centre octahedral sites are placed along the (1 1 1)-type directions, at distances from the centre given by equation (5) [7]. As a matter of fact, for values of σ slightly less than the octahedral instability threshold σ_0 the (1 1 1)-type minima compete with the minima placed along the (1 1 0)- and (1 0 0)-directions, in agreement with computations reported recently [8].

Although we have discarded the Coulomb interaction it is instructive to illustrate at this point its small effect. Assuming a $1/r$-type of Coulomb interaction it can be readily checked that it does not contribute to the second-order expansion of the potentials in both configurations, as expected for a cubic symmetry. It follows that the instability range found above for the parameter σ is unchanged by the Coulomb interaction, in the first-order approximation. Higher-order corrections can only slightly modify the numerical values given above for this instability range, but the overall picture is preserved.

A more realistic potential describing the interaction between the alkali cation and the fullerene molecule should take into account the large radius R of the latter; in the present units this radius is $R = 0.5$, corresponding to 3.5 Å. One may allow for such an affect by using a modified Lennard–Jones potential of the type

$$V_{LJ} = \frac{\sigma}{2}(r-\lambda)^{-12} - (r-\lambda)^{-6}, \tag{11}$$

where the parameter λ is less than R. We may estimate λ by assuming that equation (11) includes all the contributions of the carbon atoms lying on the spherical surface of the fullerene molecule inside the solid angle under which the latter is seen from a point situated at the distance r from its centre (where the alkali cation is placed) [9]. Doing so, we get for the both configurations $\lambda \cong 0.4$. Using equation (11) we can compute the second-order expansion

$$V = \text{const} + \tfrac{1}{2}V_2(x^2 + y^2 + z^2) \tag{12}$$

around the centre of both the tetrahedral and the octahedral configuration; the coefficient V_2 in equation (12) is given by

$$V_2 = \frac{2n}{d(d-\lambda)^{14}}[11d + 2\lambda)\sigma - (5d + 2\lambda)(d-\lambda)^6], \tag{13}$$

where n is the number of coordinating fullerenes and d is their distance to the configuration centre. In the tetrahedral case we have $n = 4$ and $d = \sqrt{3}/2$, while in the octahedral one we have $n = 6$ and $d = 1$. It can readily be checked that for $\lambda = 0$ in equation (13) we recover the second-order coefficients used previously in equation (1) and equation (3), respectively. From equation (13) one can see that the equilibrium is reached at the centre of the tetrahedral coordination for

$$\sigma > \sigma_T = (\sqrt{3}/2 - \lambda)^6 \frac{5\sqrt{3} + 4\lambda}{11\sqrt{3} + 4\lambda} \tag{14}$$

and at the centre of the octahedral one for

$$\sigma > \sigma_0 = (1-\lambda)^6 \frac{5 + 2\lambda}{11 + 2\lambda}, \tag{15}$$

and we can check that $\sigma_T < \sigma_o$ for $\lambda < 0.9$; this means that for our estimated $\lambda \cong 0.4$ there is again an octahedral instability range for the parameter σ. In general, one may expect such an instability for any other reasonable potential, the reason being that the tetrahedral coordination is more close packed than the octahedral one. For $\lambda = 0.4$ we get from equations (14) and (15) $\sigma_T = 0.005$ and $\sigma_o = 0.023$. Using the van der Waals radius of carbon [10] $r_c = 1.7$ Å and the ionic radius of rubydium [11] $r_{Rb} = 1.48$ Å we obtain (in the present units) $\sigma = 2\ (r_c + r_{Rb})^6 = 0.018$ (which coincides with the value obtained from [4]); therefore, one may say that the octahedral central site is unstable in Rb_3C_{60}. Since σ is close to σ_o this instability could be of the (1 1 1)-type, as

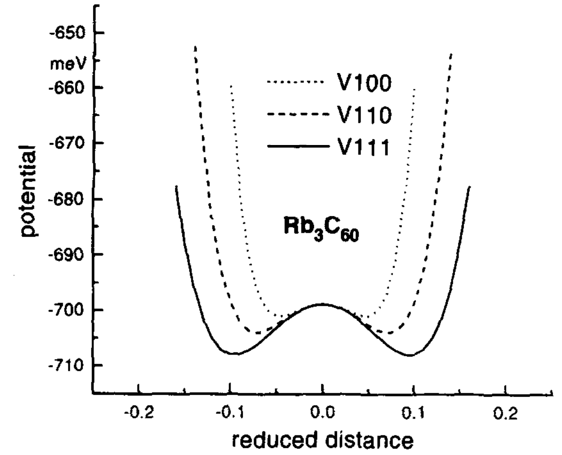

Fig. 3. The potential energy V of the Rb-cation around the centre of the octahedral coordination plotted along the high-symmetry directions vs the reduced distance to the centre (in units of 7.1 Å); the energy is computed by using the effective Lennard–Jones potential given by equation (11) with the strength 6.2 meV, $\sigma = 0.018$ and $\lambda = 0.4$.

discussed above. Using equations (5) and (6), as well as the Lennard–Jones potential parameters [4] (in our notations the strength of the Lennard-Jones potential between carbon and alkali cations is $\sim 5{-}7$ meV, as extracted from [4]), we find that the Rb-cation may be placed at distances ~ 0.5 Å from the octahedral centre, along the (1 1 1)-directions, the height of the potential barrier between two adjacent off-centre positions being about 10–30 meV. The potential energy of the Rb-cation around the centre of the octahedral coordination is plotted in Fig. 3 for the three high-symmetry directions vs the reduced distance to the centre. One can see from this figure the small values of the potential minima, and the preferred off-centre sites placed along the (1 1 1)-directions. However, as we have mentioned above, taking into account the uncertainty in the potential parameters, the approximations we have employed, as well as the competition between the off-centre sites placed along various directions, we can not say definitely where the small off-centre deviations are placed for the Rb-cations [12]. Similarly [4], we have $\sigma = 0.015$ for K, indicating again an instability, while $\sigma \cong 0.026$, for Cs, which suggests that the equilibrium positions would be central in both configurations in the latter case. It is also worth remarking that, according to the present model, off-centre instabilities may appear in the octahedral coordination of the AC_{60} fullerides, as previously suggested [13]. However, we emphasize that the small potential barriers between the adjacent off-centre sites placed around a normal site make the corresponding alkali cations be practically uniformly distributed around these normal sites, over the range of the off-centre distances.

In conclusion, we may say that within a simple model of nearest-neighbour interaction between the alkali cations and the surrounding fullerenes, described by a potential of the Lennard–Jones type, there may exist off-centre sites for the alkali cation in the octahedral coordination, along, at least, the (1 1 1)-type directions, while the corresponding equilibrium in the tetrahedral coordination is attained at the central positions. The existence of the off-centre sites for the alkali cation A in the A_3C_{60} fullerides might be relevant for the presence of the vacancies in these compounds, as suggested recently [14, 15]. In general, the disorder implied by the off-centre sites of the alkali cations may affect the conducting (and superconducting) properties of the alkali fullerides, including the ternary compounds $A_2A'C_{60}$, where A and A′ are two distinct alkali metals [16]. The jumps of the cations between various off-centre sites around the normal equilibrium positions will increase the diffusion in the X-ray and neutron scattering, and the associated disorder will give anomalies in the thermal properties of these compounds. Generally, one may expect off-centre sites and instabilities whenever there are distinct, competing coordinations and/or an imbalance between the ionic radii. The investigation of the off-centre sites in alkali fullerides and their implications on various physical properties are in progress and will be reported in a forthcoming paper.

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