

On metallic clusters squeezed in atomic cages

M. Apostol

 Department of Theoretical Physics,
 Institute of Atomic Physics, Magurele-Bucharest MG-6,
 POBox MG-35, Romania

Abstract

The stability of metallic clusters of sodium (Na) in the octahedral cages of Na -doped fullerenes Na_6C_{60} and $Na_{11}C_{60}$ is discussed within a Thomas-Fermi model. It is shown that the tetrahedral Na_4 -cluster in Na_6C_{60} has an electric charge $\sim +2.7$ (in electron charge units), while the body-centered cubic Na_9 -cluster in $Na_{11}C_{60}$ is almost electrically neutral.

The nature of the metallic clusters is currently receiving a great deal of interest.[1] Metallic clusters trapped in zeolites cages provide the opportunity of studying them by various magnetic resonance techniques,[2]–[4] and, in this respect, the nature of the chemical bonding, the distinction between metallic and covalent bondings and the degree of ionicity of the clusters are of utmost importance. Recently, the existence of Na -clusters in the octahedral cages of Na -doped C_{60} -fullerite has been suggested from X -ray analysis.[5]·[6] Similar clusters of calcium (Ca) in Ca -doped C_{60} has previously been pointed out.[7] Tetrahedral-shaped Na_4 -clusters seem to build up in the octahedral cages of the (face-centered cubic) fcc - Na_6C_{60} ,[5] with the Na atoms disposed alternately on the corners of a cube of side 2 \AA . Similarly, body-centered cubes of 9 sodium atoms (Na_9 -cluster) seem to occur in the octahedral cages of the fcc - $Na_{11}C_{60}$,[6] with the cube side 3.2 \AA . This is in contrast with the C_{60} -fullerite doped with heavier species, such as A_6C_{60} , $A = K, Rb, Cs$, where the alkali cations push through the fcc -structure of the host pristine C_{60} and distort it into a bcc -structure, while acquiring a conventional ionic character.[8] The stability and the chemical bonding of isolated, small-size alkali-clusters, like Na - and Li -clusters, have extensively been studied.[9]–[12] Recently, the formation of Na -clusters in Na_6C_{60} has been challenged, on computational grounds.[13] Here we present a Thomas-Fermi model of Na -clusters in Na_6C_{60} and $Na_{11}C_{60}$, discuss its stability and compute the distribution of electric charges and the degree of ionization of the clusters.

The main observation we start from is that the Na - Na distance in these Na -clusters is much shorter than the Na - Na distance 3.7 \AA in bulk metallic sodium, though slightly larger than twice the Na^+ -radius 1.15 \AA . Indeed, the Na - Na distance in the tetrahedral Na_4 -cluster in Na_6C_{60} [5] is $2\sqrt{2} \text{ \AA} = 2.82 \text{ \AA}$, while in the cubic Na_9 -cluster in $Na_{11}C_{60}$ [6] this distance (the shortest) is $3.2\sqrt{3}/2 \text{ \AA} = 2.75 \text{ \AA}$. This indicates that, in comparison with the bulk metallic sodium, the Na -clusters in doped C_{60} are squeezed (or compressed) in the octahedral cages provided by the neighbouring fullerene molecules. In the octahedral coordination of the fcc - C_{60} the fullerene molecules are placed at $\sim 7.1 \text{ \AA}$ from the coordination centre,[14]·[15] and, allowing for a radius of $\sim 3.5 \text{ \AA}$ of the fullerene molecule, one obtains an average radius $R_0 = 2 \text{ \AA}$ of the octahedral cage.[5]·[6] For the tetrahedral Na_4 -cluster, whose atoms are placed at $R = 2\sqrt{3}/2 \text{ \AA} = 1.73 \text{ \AA}$ from the coordination centre, this cage provides an average atomic radius of $2^{1/3} \text{ \AA}$, and an average inter-electron separation much smaller than the Bohr radius. This suggests that a Thomas-Fermi

model is suitable for describing the Na_4 -cluster. The confinement of the cluster in the octahedral cage is ensured by the electronic clouds of (carbon) C -atoms on the surface of the fullerene molecules, which, in order to be penetrated, require higher-energetical electrons. They act as very high potential barriers. The confinement of electrons in the much narrower tetrahedral sites of the $fcc-C_{60}$ (whose radius is estimated at $\sim 1.12 \text{ \AA}$ [7]) may certainly provide them with enough energy as to make them able of penetrating the confinement, which may explain the absence of clusters in these cages. Similar considerations apply for heavier-alkali atoms in the octahedral cages, and even for the Na_9 -cluster in $Na_{11}C_{60}$, whose atoms, placed at $R = 3.2\sqrt{3}/2 \text{ \AA} = 2.75 \text{ \AA}$, clearly trespassed the 2 \AA limit found above. However, the penetration of the electronic clouds of the C -atoms proceeds gradually, and, in the octahedral cages, the C -atoms provide another limit of about 4 \AA in the (111)-directions: it is the distance from the coordination centre to the octahedral faces passing through the centres of the fullerene molecules. We may take, tentatively, a mean value of these two limits (2 \AA and 4 \AA), and set up an average cage radius $R_0 \sim 3 \text{ \AA}$ for the Na_9 -cluster. This gives an average atomic radius $3^{\frac{1}{3}} \text{ \AA}$, which again justifies a Thomas-Fermi model for this Na_9 -cluster. It is worth-remarking at this point that the resistance the cage walls oppose to the penetrating electrons (which may also apply in the case of the zeolites cages) is an expression of the Pauli exclusion principle, which requires fastly-varying (in space) wavefunctions for the latter (and therefore higher energy) if they are going to penetrate into the space regions already occupied by atomic-core electrons. This confining effect of the cage boundaries on an atomic cluster may be formalized as an external field "pseudo-potential", much in the same manner as it has already been done for bulk metals.[16] It can easily be seen that these "pseudo-potentials" would vary strongly over short distances (as in the short-range parts of the inter-atomic Lennard-Jones or Born-Mayer potentials, for example), and their functional dependence on distance (which would depend, among others, on the number of confined electrons) will provide an effective cage radius R_0 for a given cluster, as we shall discuss below in more detail.

As it is well-known the Thomas-Fermi model is a quasi-classical theory of interacting electrons and atomic nuclei which assumes that the Fermi wvector k_F of the electrons, and the electron density n ,

$$n = \frac{1}{3\pi^2} k_F^3 \quad , \quad (1)$$

vary slowly in space. This is true (except for distances very close to the nuclei) due to the effective screening of the nuclear charges accomplished by the high-density electrons. We shall see that this assumption is a consistent one also in the present Thomas-Fermi model of clusters. Under this assumption the particular shape of the atomic cluster is no longer very relevant, so that we may introduce an additional simplification by assuming that the total charge z of the nuclei is uniformly distributed over a spherical shell of radius R , plus a central Na -nucleus of charge $+11$ (in electron charge units) in the case of the Na_9 -cluster. We denote by V the electrostatic potential created by this distribution of positive charges, and remark that its particular expression is not very important in subsequent calculations; the only requirement on the positive charge distribution is that of symmetry, from obvious reasons of stability, and the approximation made is that of radial symmetry. In the high-density limit the electron exchange interaction is a higher-order contribution (as well as other contributions to the electron interaction energy), and we may assume that an electrostatic potential φ is generated by the electron distribution, which does not depend on k_F . We may therefore set up the basic Thomas-Fermi relationship (in atomic units Bohr radius $a_H = \hbar^2/me^2 = 0.53 \text{ \AA}$, $e^2/a_H = 27.2 \text{ eV}$ and $\hbar = 1$)

$$\frac{1}{2} k_F^2 - \varphi - V - U = -\varphi_0 \quad , \quad (2)$$

where U is the potential well of the cage and φ_0 is the chemical potential; the latter should be constant in order to ensure the local equilibrium and equal to the "pseudo-potential" of the external field at the cage frontier R_0 , such as to prevent any flux of electrons pouring in and out of the cage. The variation of this external "pseudo-potential" over the distance R_0 may be taken as the depth U of the potential well. Using (1) and (2) we may rewrite the Poisson equation $\Delta\varphi = 4\pi n$ as

$$\Delta(\varphi + V + U - \varphi_0) = \frac{8\sqrt{2}}{3\pi}(\varphi + V + U - \varphi_0)^{\frac{3}{2}}, \quad (3)$$

everywhere except for $r = R$; introducing the reduced variables $x = r/R_0$ and

$$\varphi + V + U - \varphi_0 = \left(\frac{3\pi}{8\sqrt{2}R_0^2}\right)^2 \frac{\chi}{x} \quad (4)$$

we arrive at the Thomas-Fermi equation

$$x^{\frac{1}{2}}\chi'' = \chi^{\frac{3}{2}}, \quad (5)$$

for any x between 0 and 1 except for $x = a = R/R_0$. Since n is a continuous function φ and its two first derivatives must be continuous functions; it follows that the function χ has a slope discontinuity (but is itself continuous) exactly as the derivative of V has, *i.e.* at $x = a$; the magnitude of this slope jump will be obtained below by Gauss' law. It is therefore convenient to define $\chi_1(x) = \chi(x)$ for $0 < x < a$ and $\chi_2(x) = \chi(x)$ for $a < x < 1$, with the continuity condition

$$\chi_1(a) = \chi_2(a) \quad . \quad (6)$$

The number of electrons inside a sphere of radius x is easily obtained from (1) – (5) as

$$N(x) = 4\pi R_0^3 \int_0^x dx \cdot x^2 n = \frac{9\pi^2}{128R_0^3} \int_0^x dx [x\chi' - \chi] = \left\{ \begin{array}{l} \frac{9\pi^2}{128R_0^3} [x\chi_1' - \chi_1 + \chi_1(0)] \quad , \quad 0 < x < a \quad , \\ \frac{9\pi^2}{128R_0^3} \{x\chi_2' - \chi_2 + a[\chi_1'(a) - \chi_2'(a)] + \chi_1(0)\} \quad , \quad a < x < 1 \quad , \end{array} \right\} \quad (7)$$

and one remarks that it is continuous at $x = a$. The total number of electrons in the cage is obtained from (7) as

$$N = \frac{9\pi^2}{128R_0^3} \{ \chi_2'(1) - \chi_2(1) + a[\chi_1'(a) - \chi_2'(a)] + \chi_1(0) \} \quad . \quad (8)$$

By Gauss' law we get easily the net charge inside the sphere of radius x as

$$q(x) = \frac{9\pi^2}{128R_0^3}(\chi - x\chi') \quad , \quad (9)$$

whence, by using (7), we obtain the positive charge

$$q_{1+}(x) = \frac{9\pi^2}{128R_0^3}\chi_1(0) \quad (10)$$

inside the sphere of radius $x < a$. We remark that, if it exists, it is concentrated at $x = 0$. Obviously, for the Na_4 -cluster we should require

$$\chi_1(0) = 0 \quad , \quad (11)$$

while for the body-centered cubic Na_9 -cluster the corresponding boundary condition is

$$\frac{9\pi^2}{128R_0^3}\chi_1(0) = 11 . \quad (12)$$

The total charge inside the sphere of radius x , $a < x < 1$, given by (9) consists of z -positive charges distributed over the spherical shell of the cluster, a charge +11 at the centre, if the case, and $-N(x)$ electron charges; whence, by using (7), we get the magnitude

$$z = \frac{9\pi^2}{128R_0^3}a [\chi_1'(a) - \chi_2'(a)] \quad (13)$$

in the slope discontinuity of the function χ , as expected; (13) provides the third boundary condition for our problem, with $z = 44$ for the Na_4 -cluster and $z = 88$ for the Na_9 -cluster. The fourth boundary condition needed for the uniqueness of the solution of (5) is provided by the stability condition of the positive shell of the cluster. It is easy to get the electric self-field acting on the shell; in the absence of the central atom it is given by

$$E_s = z/2R^2 , \quad (14)$$

while in the case of the centered cluster we obtain

$$E_s = z/2R^2 + 11/R^2 . \quad (15)$$

The electric field on the shell due to the electrons is readily obtained as

$$E_e = -\frac{\partial\varphi}{\partial r} \Big|_{r=R} = \frac{9\pi^2}{128R_0^5} \frac{1}{a^2} [\chi_1(a) - a\chi_1'(a) - \chi_1(0)] \quad (16)$$

(or equivalently in terms of χ_2), and we remark that, in contrast to (14) and (15), it is negative, *i.e.* the electrons try to stabilize the exploding cluster shell. Using (13) we arrive easily to the equilibrium condition

$$2\chi_1(a) = a [\chi_1'(a) + \chi_2'(a)] \quad (17)$$

both for the non-centered and for the centered cluster. The equation (5) is solved numerically with the boundary conditions given by (6), (11)–(13) and (17), both for the Na_4 - and the Na_9 -cluster, and the results are described below. In each case we have been interested especially in the total charge

$$q = \frac{9\pi^2}{128R_0^3} [\chi_2(1) - \chi_2'(1)] \quad (18)$$

in the cage, as given by (9).

In the case of the Na_4 -cluster we have used $R = 1.73 \text{ \AA}$ and $R_0 = 2 \text{ \AA}$ ($a = R/R_0 = 0.86$), as suggested by the X -ray diffraction data.[5][7] The function χ is plotted *vs* x in Fig.1; it corresponds to a total charge $q = +2.72$, *i.e.* an average charge +0.68 per each Na -ion. The variation of the total charge in this case is also plotted *vs* R_0 in Fig.2. As we have discussed above, the numerical results obtained for the function χ are valid everywhere except for a range of about twice the Bohr radius around the position of the positive shell of charges, where the variation of χ/x is too large; even so, one can estimate that almost half of the electrons are located there, ensuring thus the screening of the positive charges. Another limitation of the present calculations occurs from the assumption of radial symmetry for the function χ . We may estimate the error introduced by this approximation as follows. Assuming the same variation of the electron density per unit

length in all directions the relative contribution of the angular part of the variation of the potential derivative with respect to the radial one is $\delta\varphi'_a/\delta\varphi'_r \sim \sqrt{\frac{4\pi}{s}}$, for a cluster consisting of s atoms; on the other hand, as these small variations are proportional to the variations of the distance we have $(\delta\varphi'_r)^2 + 2(\delta\varphi'_a)^2 = (\delta\varphi'_r)_0^2$, where the latter corresponds to the neglect of the angular part. As the variations of the potential derivatives are also proportional to the charge (from the Poisson equation), we find then easily that the relative error made in estimating the charge is at most $\sim 1 - \sqrt{1 + 8\pi/s}/(1 + 2\sqrt{4\pi/s})$. In the case of the Na_4 -cluster this amounts to $\sim 40\%$; one can see that the radial-symmetry approximation improves its accuracy for large s .

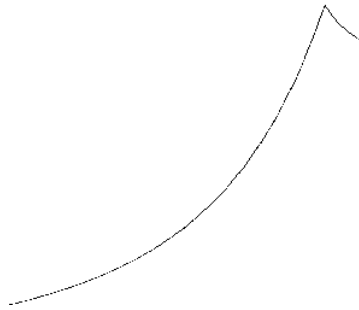


Figure 1: The function χ vs x for the Thomas-Fermi model of the Na_4 -cluster with $z = 44$, $R = 1.73 \text{ \AA}$ and $R_0 = 2 \text{ \AA}$, corresponding to a total charge $q = +2.72$.

Increasing the amount of negative charge on the cluster the position of the maximum value of χ in Fig.1 moves toward smaller values of x (smaller values of R), and it exhibits an opposite behaviour on increasing the degree of ionization. The variation of χ with respect to the cage radius R_0 brings into discussion the energy of the cluster. One can check easily that the density of the electronic kinetic energy is given by

$$\varepsilon_{kin} = \frac{1}{2\pi^2} \int_0^{k_F} dk \cdot k^4 = \frac{9(3\pi/32)^3}{10R_0^{10}} \cdot \frac{\chi^{\frac{5}{2}}}{x^{\frac{5}{2}}} \quad , \quad (19)$$

where (2) and (4) have been used; whence one can obtain straightforwardly the total kinetic energy of the electrons

$$\mathcal{E}_{kin} = \frac{3(3\pi/8)^4}{20R_0^7} \int_0^1 dx \cdot \frac{\chi^{\frac{5}{2}}}{x^{\frac{1}{2}}} \quad . \quad (20)$$

We obtain similarly the potential energy of the electrons

$$\mathcal{E}_{pot} = -\frac{(3\pi/8)^4}{4R_0^7} \int_0^1 dx \cdot \frac{\chi^{\frac{5}{2}}}{x^{\frac{1}{2}}} - N\varphi_0 \quad , \quad (21)$$

so that the electronic energy may be expressed as $\mathcal{E}_{el} = \mathcal{E}_1 - N\varphi_0$, where

$$\mathcal{E}_1 = -\frac{(3\pi/8)^4}{10R_0^7} \int_0^1 dx \cdot \frac{\chi^{\frac{5}{2}}}{x^{\frac{1}{2}}} \quad . \quad (22)$$

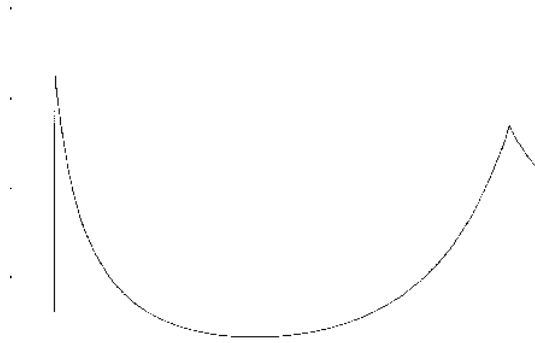


Figure 2: The total charge q vs the cage radius R_0 for the Na_4 -cluster with $R = 1.73 \text{ \AA}$.

The self-energy of the positive charges is given by $\mathcal{E}_s = \mathcal{E}_0 - zU$ for the non-centered cluster and $\mathcal{E}_s = \mathcal{E}_0 - (z + 11)U$ for the centered one, where $\mathcal{E}_0 = z^2/2R$ in the former case and $\mathcal{E}_0 = z^2/2R + 11z/R$ in the latter. On the other hand, expressing the interaction energy of the shell with the electrons in two distinct ways, namely, $z\varphi(R) = -\int d\mathbf{r} nV$, we get

$$U - \varphi_0 = \frac{9\pi^2}{128R_0^4}\chi_2'(1) . \quad (23)$$

Summing up all these contributions we obtain the total energy of the cluster as

$$\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{E}_2 - (2z - q)\varphi_0 , \quad (24)$$

where $\mathcal{E}_2 = -z(U - \varphi_0)$ as given above; in the case of the centered cluster we should replace z by $z + 11$ in (24). The numerical integration gives $\mathcal{E}_1 = -28$ and $\mathcal{E}_2 = -42$ for the Na_4 -cluster, while $\mathcal{E}_0 = 296$; the total energy, consisting of (24) and the energy of the electrons transferred to the cage walls, must be negative, in order the cluster be formed. For small values of the total charge of the cluster the latter contribution to the total energy is small, so that we may estimate that the energy E given by (24) must acquire negative values. Hence it follows that φ_0 must be of the order of $(296 - 28 - 42)/N \sim 2.6$ (for $N = 44$). On the other hand, φ_0 equals the external "pseudo-potential" at the cage frontier R_0 , as we have discussed before, whence one may have an estimation of the magnitude of this "pseudo-potential". One can see, therefore, that it acquires high values, as to ensure the confinement of the squeezed cluster within the R_0 range. In addition, as the present estimations are valid over a scale length larger than the Bohr radius, one can also see that the external "pseudo-potential" has a high variation over short distances. This illustrates again the gradual resistance developed by the inner-core electrons of the environment to the penetrating "pressure" of the confined cluster. The electron density varies also fastly over short distances at the frontier of the cage, in order to ensure the delimitation of the compressed cluster from its confining environment. The "pressure" exerted by the cluster electrons on their environment results in the deformation of the electronic clouds of the surrounding atoms. Having determined φ_0 by the external "pseudo-potential" at the cage frontier R_0 , the two remaining parameters R_0 and R will be obtained, within a complete theory, by minimizing the total energy of the cluster (given by (24)) and the electrons transferred to the cage walls. Of course, this requires first the computation of the "pseudo-potential".

From the discussion above one can see that the results of the computation are very sensitive to the values of R and R_0 ; this sensitivity may result in a higher inaccuracy for clusters consisting of a greater number of atoms. This can be seen in the case of the Na_9 -cluster, where, according to the experimental data suggested by the X -ray analysis,[6] we have used $R = 2.75 \text{ \AA}$ and $R_0 = 3.15 \text{ \AA}$ ($a = R/R_0 = 0.87$). The function χ is plotted *vs* x in Fig.3; it corresponds, within errors of $\pm 0.03 \text{ \AA}$ in R and R_0 , to a total charge of the cluster $q \sim \pm 1$. At this level of approximation we may conclude that the centered-cubic Na_9 -cluster is practically neutral. The dependence of the total charge q on the cage radius R_0 is also included in Fig.4 for this case. The same discussion regarding the screening and the value of the chemical potential φ_0 (~ 2.4) applies here as for the Na_4 -cluster. It is worth-noting that a similar calculation for a non-centered cubic cluster consisting of 8 atoms of Na , gives a total charge $q \sim +1$, for the same values of R and R_0 . Finally, noticing that the theory contains the charge z only in the product zR_0^3 (see, for example, (12), (13) and (18)) we can say that similar clusters formed by lithium may also form in the octahedral cages of the fullerite with a smaller size, or, equivalently, with a diminished cluster-size and ionization charge.

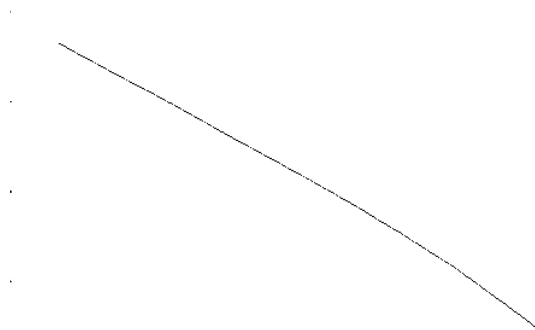


Figure 3: Same as in Fig.1 for the centered-cubic Na_9 -cluster with $z = 88$, $R = 2.75 \text{ \AA}$ and $R_0 = 3.15 \text{ \AA}$, and a vanishing total charge ($q \sim 0$).

In conclusion one may say that the calculations presented here indicate a metallic bonding of the Na_4 - and Na_{11} -clusters squeezed into the octahedral cages of the Na -fullerides. We emphasize that this squeezing is a central feature of the picture presented here, whose direct consequence is that of affecting all the electron states in the cluster; enough electronic energy may be gained in this way as to stabilize the cluster at lower values of R , as compared with R_0 . This is in contrast, at least for the Na_4 -cluster, with recent claims[13] that the Na -atoms in Na_6C_{60} are fully ionized and that the octahedral Na -ions are placed much further away from the coordination centre. These claims, based on numerical simulations within the local-density approximation, make use of a certain distinction between the valence and the core electrons, which might be inappropriate for the squeezed clusters. As we have seen from the present calculations, almost half of the electrons seem to be affected by the presence of the neighbouring atoms in the cluster, which indicates a drastic change in the inner electronic states of the isolated atoms. The metallic character of the alkali clusters in fullerides may be tested by various techniques, most notably by Raman and ^{23}Na -NMR spectroscopies.[17] In addition, it is worth-mentioning that the metallic clusters squeezed

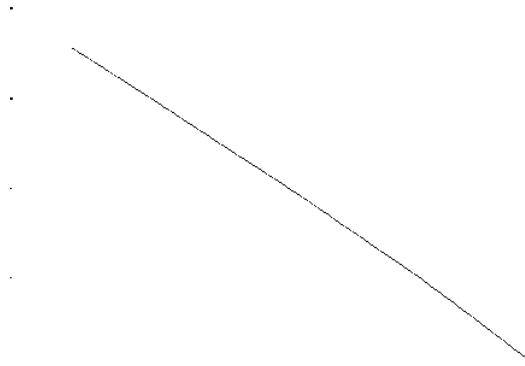


Figure 4: The total charge q vs the cage radius R_0 for the Na_9 -cluster with $R = 2.75 \text{ \AA}$.

in atomic cages may exhibit two types of collective modes, associated, one, with the vibrations of the positively-charged ions and, another, with the oscillations of the electron density. Preliminary calculations indicate that these two modes are in the range of the ultra-violet optical spectroscopy and the electron spectroscopy.

References

- [1] See, for example, the recent reviews by W. A. de Heer, *Revs. Mod. Phys.* **65** 611 (1993) and by M. Brack, *ibid.* 677 .
- [2] M. R. Harrison, P. P. Edwards, J. Klinowski and J. M. Thomas, *J. Solid State Chem.* **54** 330 (1984).
- [3] E. Trescos, F. Rachdi, L. C. de Menorval, F. Fajula, T. Nunes and G. Feio, *J. Phys. Chem.* **97** 11885 (1993).
- [4] A. Bifone, T. Pietrass, J. Kritzenberger, A. Pines and B. F. Chmelka, *Phys. Rev. Lett.* **74** 3277 (1995).
- [5] M. J. Rosseinsky, D. W. Murphy, R. M. Fleming, R. Tycko, A. P. Ramirez, T. Siegrist, G. Dabbagh and S. E. Barrett, *Nature* **356** 416 (1992).
- [6] T. Yildirim, O. Zhou, J. E. Fischer, N. Bykovetz, R. A Strongin, M. A. Cichy, A. B. Smith III, C. L. Lin and R. Jelinek, *Nature* **360** 568 (1992).
- [7] A. R. Kortan, N. Kopylov, S. Glmarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, F. A. Thiel and R. C. Haddon, *Nature* **355** 529 (1992).
- [8] O. Zhou, J. E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley, Jr., A. B. Smith III and D. E. Cox, *Nature* **351** 462 (1991).

-
- [9] I. Boustani, W. Pawestorf, P. Fantucci, V. Bonacic-Koutecky and J. Koutecky, *Phys. Rev.* **B35** 9437 (1987).
- [10] V. Bonacic-Koutecky, P. Fantucci and J. Koutecky, *Phys. Rev.* **B37** 4369 (1988).
- [11] U. Rothlisberger and W. Andreoni, *J. Chem. Phys.* **94** 8129 (1991).
- [12] M. R. Prince and R. W. Hall, *J. Phys. Chem.* **99** 8562 (1995).
- [13] W. Andreoni, P. Giannozzi and M. Parinello, *Phys. Rev. Lett.* **72** 848 (1994).
- [14] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S. M. Huang, R. Kaner, F. Diederich and K. Holczer, *Nature* **351** 632 (1991).
- [15] D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Tully and R. E. Walstedt, *J. Phys. Chem. Solids* **53** 1321 (1992).
- [16] J. R. Chelikowsky, *Phys. Rev.* **B21** 3074 (1980).
- [17] See, for example, Ref.15.