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BULK PROPERTIES OF M_nC_{60} DOPED SOLIDS

S. CHANDRA, K. RANJAN AND V.K. JINDAL
Department of Physics, Panjab University, Chandigarh – 160014, India

The model calculations are presented for potassium, rubidium and cesium doped C_{60} solids formed by exohedral doping in pure C_{60} solid. The molecular formula is M_nC_{60}, M is the alkali metal (K, Rb and Cs) and n takes integer values 1, 3, 4 and 6. The C_{60} molecule is modelled as a uniform spherical shell having surface density of carbon atoms. Part of the electrons released by ionized alkali atoms distributed on the C_{60} molecule making it an anion, while the rest (say x) are assumed to form a delocalised electron gas. This electron gas screens the Coulomb interaction between the various anion and cations. With these assumptions, the total cohesive energy is calculated taking into consideration Van der Waals and screened Coulomb interaction between different ions. We found that the total charge transfer from cation to anion is favoured. Thus ionic character of alkali doped C_{60} solids is established on the basis of the model. The lattice constant, cohesive energy and Bulk modulus for these systems are in good agreement with other calculation or experimental observations. We make some remarks on phase stability of these solids.

Keywords: K_nC_{60}, Rb_nC_{60}, Cs_nC_{60}, Coulomb potential, Lattice constant, Cohesive energy, Bulk modulus

INTRODUCTION

The C_{60} molecule is a cluster of 60 carbon atoms, in which carbon atoms are located at the equivalent vertices of truncated icosahedron. The interaction between two C_{60} molecules is purely van der Waals type. The C_{60} molecules condense into an *fcc* solid, similar to the inert gas atoms. Because of the large size of fullerene molecules, the interstitial cavities in a C_{60} lattice are large too, and can accommodate various guest species. When the pure C_{60} solid is doped with alkali metal M_nC_{60} compounds are formed, where n can go up to six [1].

The model calculations for alkali metal doped C_{60} solids to find their cohesive energy and the ionic state of C_{60} molecule have been presented. Wide disparity in cohesive/Madelung energy calculations has made it an interesting problem [2-7]. In fact Schulte and Bohm have objected to the possibility of complete transfer of charge and thus to the formation of K_3C_{60} as an ionic solid. But various experiments have verified K_3C_{60} as a stable ionic system [8-9]. Not only K_3C_{60} but total charge transfer takes place in K_6C_{60} also [10]. The calculations for K, Rb and Cs doped C_{60} solids to inquire the ionic state of C_{60} molecule and other bulk properties been performed. The atomic size of rubidium and cesium is comparable to that of potassium, so the structure of Rb and Cs doped solids is almost the same.

MODEL AND CALCULATIONS

In our model, we consider van der Waals and Coulomb type interactions as the interaction between various constituents of these solids. The structure of doped C_{60} solids, determination of van der Waals parameters, electron affinity of C_{60} and on shell Coulomb repulsion have been discussed.

To calculate the potential energy of a system, one needs to take into account various interactions between constituent ions/atoms and the structural configuration. Among the doped M_nC_{60} (M denotes alkali metal–*K*, *Rb* and *Cs*), the structure of C_{60} sublattice changes from *fcc* to *bcc* as n increases. For n =1 to 3, the structure is found to be *fcc* and for n = 4 and 6, body centerd tetragonal (*bct*) and body centred cubic (*bcc*) respectively[7]. The dopant alkali ions occupy interstitial positions tetrahedral and octahedral in these C_{60} lattices. The unit cell of each of these is shown in Fig. 1. In our calculations, these experimentally observed structures enter as input in lattice sums.

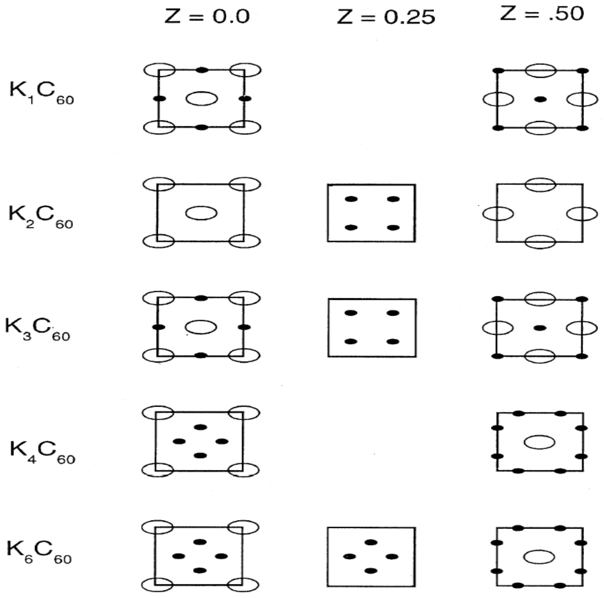

Fig. 1. Unit cells of alkali doped C_{60} Solids. The squares show various relevent cross-sections parallel to *x-y* plane. Open circles represent C_{60} ions and solid circles are alkali ions.

In the pure C_{60} solid, the intermolecular (C_{60}–C_{60}) interaction is described well by a *C–C* potential of 6-exp form given by Kitaigorodsky [11].

$$(r) = -\frac{A}{r^6} + B\exp(-\alpha r) \qquad \text{... (1)}$$

We have shown that the C_{60} molecule can be replaced by a spherical shell, with 60 carbon atoms uniformly smeared over the shells. This will make computation easy. The 6-exp part of the potential of the interaction potential is integrated over the surface of two C_{60} molecules to get:

$$U^{vdw}(R) = -(60)^2 \times \left[\begin{array}{l} \left(\dfrac{A}{R^6}\right) \dfrac{1-2(R_B/R)^2 + 8/3(R_B/R)^4}{\left\{1-(2R_B/R)^2\right\}^3} \\ -B\exp(-\alpha R)\left(\dfrac{\sinh(\alpha R_B)}{\alpha R_B}\right)^2 \left\{1+\dfrac{2}{\alpha R}\left(1-\dfrac{\alpha R_B}{\tanh(\alpha R_B)}\right)\right\} \end{array} \right] \quad \text{... (2)}$$

where R is the distance between the centers of the two bucky-balls, and R_B is their radius. The numerical value used in our calculations is 3.55 Å. Similarly, the potential energy arising from vander Waals interaction between an alkali metal ion and a C_{60} molecule separated by a distance r is given by :

$$U^{vdw}(r) = -\frac{60A}{r^6}\left[\frac{\left(1+\left(\dfrac{R_B}{R}\right)^2\right)}{\left(1-\left(\dfrac{R_B}{R}\right)^2\right)^4}\right] + \frac{60.B.\exp(-\alpha R)}{R_B\alpha}\left[-\frac{R_B}{R}\cosh(R_B\alpha) + \left(1+\frac{1}{r\alpha}\right)\sinh(R_B\alpha)\right] \text{... (3)}$$

The vander Waals interactions between two alkali metal ions is of the same form as Eq. (1).

The vander Waals interactions between two carbon atoms are widely used in literature and whether one is using 6-exp or 6-12 potential, the parameters are readily available. Those for interactions between C and alkali atoms are, however, not readily available. To find parameters for interaction between a C-atom and an alkali ion, we make use of alkali halide parameters [11-12]. For these pairs, we observe,

$$\frac{B}{(Z_1Z_2)^{1/2}} \approx 0.0165\times10^{-8}\,\text{erg} = 2372.99\,\text{k cal/mole} \quad \text{... (4a)}$$

where Z is the number of electrons in the interacting anion/cation/atom. However, for carbon, $Z = 6$ and if we consider the value of parameter B given by Kitaigorodsky for C–C interaction, we find:

$$\frac{B}{(Z_1Z_2)^{1/2}} \approx 0.0487\times10^{-8}\,\text{erg} = 7000\,\text{k cal/mole} \quad \text{... (4b)}$$

which is at variance with the value (Eq. 4a) for alkali halides. This is because electron distribution in a C-atom is quite different from an alkali or halide ion (where it is inert gas configuration). On the other hand, C atoms can be presumed to be like alkali or halide ions for this purpose, provided we attribute an effective charge, $Z_{\text{eff}} = 17.7$ to them. Using this Z_{eff} we get *B* values for *K-C* interactions. For *K-K* interaction, Eq. 4(a) may be used directly.

Second parameter is α. The relation between radii of two ions are r_1 and r_2 and repulsive range parameter α is:

$$\alpha \propto \frac{1}{r_1 + r_2} \quad \text{... (5a)}$$

For alkali halides, using the known radii and values of α for these ions, we find:

$$\alpha^{-1} \approx 0.11(r_1 + r_2) \quad \text{... (5b)}$$

Radii for *Rb* and *Cs* are 1.52 and 1.67 Å respectively using which we obtain α_{MM} [13]. We obtain α_{MC} as the harmonic mean of α_{CC} and α_{MM} in accordance with Eq. (3).

The third parameter *A* is not that important because madelung energy dominates Van der Waals interaction energy. For completeness we determined *A* for *K-C* interaction as the one giving best fit to lattice constant data with *B* and α fixed as obtained above. Finally *K-K* interaction parameter *A* is fixed from the criterion [14]:

$$A_{MC} \cong .8776\left(A_{MM} A_{CC}\right)^{1/2} \quad \text{... (6)}$$

In this way, we have estimated various parameters for *M-M* and *M-C* interactions and are given in Table 1. It may be mentioned that the parameters *A*, *B*, α for $M^+\!-\!M^+$ interactions have no major role in the determination of cohesive energy of doped C_{60} systems, as interactions between these cations are dominated by Coulomb interaction.

Table 1 : Interaction parameter

Atom-Atom	**A (kcal-Å/mole) [Ref. 6]**	**B (kcal/mole)**	**α (Å^{-1})**
C–C	358	42000	3.58
K–K	171	49138	3.62
K–C	235	28370	3.50
Rb–Rb	233	76628	3.43
Rb–C	458	31283	3.32
Cs–Cs	495	114942	3.04
Cs–C	680	38314	3.12

When alkali atoms are diffused into the pure solid C_{60} (*fcc* lattice), they start taking up positions at the interstitial void sites-tetrahedral (*T*), of which these are 8 per unit cell, or octahedral (*O*), of which these are 4 per unit cell. They also get ionized, becoming M^+, while the C_{60} molecules acquire the electrons becoming anions. The C_{60} molecule, on acquiring extra electrons, becomes a large anion. The energy required to put one additional electron, which goes in the lowest unoccupied molecular orbital (LUMO), is generally accepted to be –2.65 eV [15].

Addition of still more electrons, however, involve Coulomb repulsion between them. Thus, the energy required to add m electrons on a C_{60} molecule may be taken to be of the form:

$$E_m = mE_A + U\frac{m(m-1)}{2} \qquad \text{... (7)}$$

where U is an average pairwise Coulomb repulsion parameter.

We use values of $E_A = -2.65$ eV and $U = 1.3$ eV in our calculations [16].

In the system under consideration, m in Eq. (7) can go up to 6 so the Coulomb energy of the anion can become large. It may be energetically favourable for the solid to retain part of charge (out of n electrons in M_nC_{60}) in the vicinity of the cation *i.e.,* in the *s*-band. Thus, there is distinct possibility of incomplete charge transfer. We therefore look for the possibility of fractional charge state of the anion in our model. Let $n - x$ be the charge (number of electrons) on each C_{60} shell. Then, the total energy of anion and cation becomes, for the M_nC_{60} System:

$$\Phi_{ion} = (n-x)E_A + U\frac{(n-x)(n-x-1)}{2} + (n-x)E_1 \qquad \text{... (8)}$$

where $E_{\text{I denote}}$ the ionisation energy of the alkali atom M. Eq. (8) gives energy per M_nC_{60} molecule excluding the interaction between the various charged species of ions.

Hence, the inter-ionic interaction must be of the screened Coulomb type rather than pure Coulomb, where the screening is due to the electrons present in the *s*-band (x electrons per cation). These x electrons still localised around the M^+ sites, must exist in the *s*-band. The system is now supposed to consist of C_{60} $(n - x)$ and M_+ ions with x electrons per C_{60} forming a free-electron gas. While determining the electron density of this electron gas, the volume of the C_{60} molecules is excluded, as it is quite large and well known that there is virtually no electronic charge density in the interior of the fullerene cage.

The screened Coulomb potential between two M^+ cation is that between two point charges *i.e.,*

$$U_{KK}^{SC}(R) = \left(e^2/R\right)\exp(-R/\lambda) \qquad \text{... (9)}$$

The screened Coulomb potential between the M^+ and $C_{60}^{-(n-x)}$ anion in our model is obtained by the appropriate integration over the C_{60} shell and obtain:

$$U_{MM}^{SC}(R) = -\frac{e^2(n-x)}{R}\exp(-R/\lambda)\left\{\sinh(R_B/\lambda)/(R_B/\lambda)\right\} \qquad \text{... (10)}$$

where R is the distance between the point M^+ cation and centre of spherical C_{60} anion.

Similarly, performing the integration over the surfaces of two bucky balls ($C_{60}^{-(n-x)}$) having $(n - x)$ electrons on its surface, for screened Coulomb potential, we get:

$$U_{BM}^{SC}(R) = \frac{e^2(n-x)^2}{R}\exp(-R/\lambda)\left\{\sinh(R_B/\lambda)/(R_B/\lambda)\right\}^2 \qquad \text{... (11)}$$

These expressions are obtained assuming that the screening is due to a gas of free electrons, where λ, the screening length is, of the free electron gas, *i.e.*,

$$\lambda^{-1} = \left(6\pi n_0 \, e^2 / \varepsilon_F\right)^{-1/2} \qquad \text{... (12a)}$$

where n_0 is the electron density and ε_F is free-electron Fermi energy. This gives:

$$\lambda^{-1} \cong 2.73 n_0^{1/6} \qquad \text{... (12b)}$$

NUMERICAL CALCULATIONS

Taking into account all the interactions, the total cohesive energy and bulk modulus for all M_nC_{60} systems under consideration have been calculated.

3.1 Cohesive energy

The intermolecular contribution to total potential energy Φ can be obtained by carrying out the lattice sums, knowing the positions of the ions/atoms in the lattice. Combining Eqs. 2, 3, and 8-11, we express the total potential energy of a monovalent atom-doped C_{60} solid in the following form:

$$\Phi = \frac{1}{2} \sum_{l,k,l',k'} \left[U_{lkl'k}^{vdW} + U_{lk,l'k'}^{SC} \right] + \Phi_{ion} \qquad \text{... (13)}$$

The summation is over all pairs of lattice points within the chosen volume. The summation over van der Waals term in Eq. (13) is simple and converges after a few lattice distances taken into account. The screened Coulomb term is however not convergent if we make a straight forward sum; so we use Evjen's method to calculate Coulomb contribution to the cohesive energy [17]. Thus, the total energy Φ is expressed as a function of parameters, x (fraction of electron forming gas) and a (cubic lattice constant). For M_4C_{60}, which is the only non-cubic system out of those considered, it is a function of x, a and c. The equilibrium lattice constant a_0 (or a_0 and c_0 for M_4C_{60}) and x is obtained by minimizing cohesive energy with respect to all these parameters.

3.2 Bulk modulus

We plot cohesive energy as a function of volume and find the second derivative of the curves at their minima (equilibrium). This is used to evaluate bulk modulus, which is given by:

$$B = \left[V \frac{\partial^2 U}{\partial V^2} \right]_{V=V_0} \qquad \text{... (14)}$$

The lattice constant, cohesive energy and bulk modulus correspond to complete charge transfer to anion. Hence, all these doped C_{60} solids are ionic solids.

RESULTS AND DISCUSSION

First of all we look into the possibility of fractional charge transfer on C_{60} molecule so that we can decide what interaction is appropriate for consideration. We assume, only $n - x$ electrons transferred on each C_{60} molecule, with x electrons contributing to a free electron gas. We calculate cohesive energy with different values of charge ($n - x$) transferred to C_{60} molecule keeping other parameters constant. The variation of cohesive energy with n-x is shown in Fig. 2. The cohesive energy is maximum negative (maximum cohesion) for vanishing x, which implies complete charge transfer to C_{60} molecule in all K_nC_{60} systems. In case of rubidium and cesium, doped solids interaction parameters are changed. The Coulomb contribution to the cohesive energy remain unchanged, so one can consider these systems as ionic also. From this analysis, the complete charge transfer or full ionic character in M_nC_{60} solids has been established.

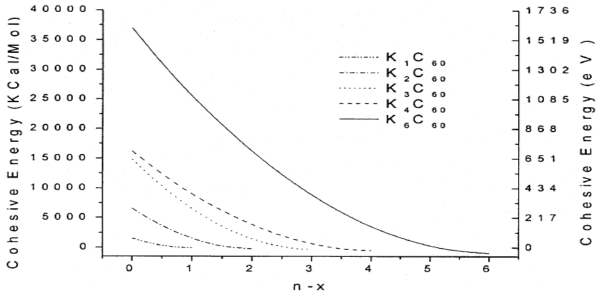

Fig. 2. Total cohesive energy versus *n-x* for K_nC_{60} systems[14]

Once the cohesive energy has been calculated, we also calculate lattice constant (a_0) and bulk modulus. Figures 3 and 4 show the variation of total cohesive energy with respect to volume per Rb_nC_{60} in the vicinity of minima. The detailed calculations for K_nC_{60} solids have been reported in our earlier work. In Cs_nC_{60} solids, we do observe well defined minima in cohesive energy as seen in Rb_nC_{60} systems. It is worthwhile to mention that there are two curves in Fig. 3, which correspond two possible configurations of Rb_1C_{60}. The lower one corresponds to octahedral doping site of Rb and another one to alternate tetrahedral site. From this, it is clear that octahedral Rb_1C_{60} (lower curve) is more stable than tetrahedral Rb_1C_{60}, which is in agreement with experimental results [18]. K_1C_{60} and Cs_1C_{60} also favour the same structural configuration. We have summarized our results in Table 2.

Looking at lattice constant values of all systems under consideration in Table 2, our calculations are in good agreement with others [19-20]. However, *fcc* structure of Cs_3C_{60} is not stable. Cohesive energy has been compared for *K* doped systems with Friedberg *et al.* [21].

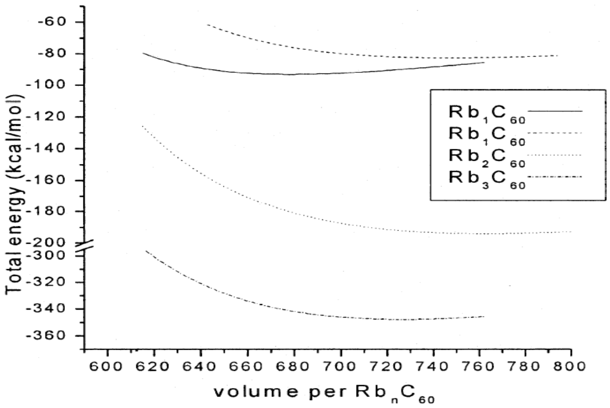

Fig. 3. Variation of total cohesive energy with volume per Rb_1C_{60}, Rb_2C_{60} and Rb_3C_{60}. Volume is in Å^3

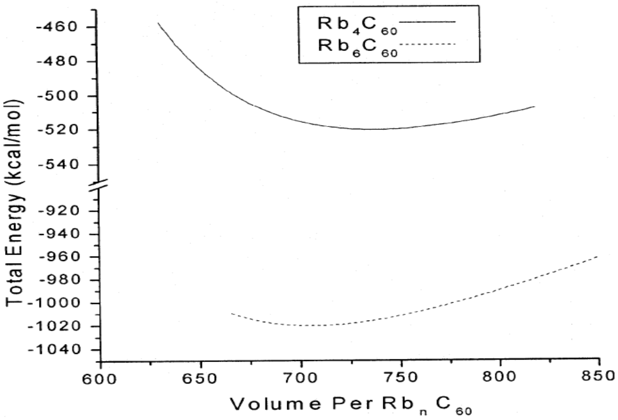

Fig. 4 : Variation of total cohesive energy with volume per Rb_4C_{60} and Rb_6C_{60}.Volume is in Å^3

The data for Rb and Cs doped systems is not available in the literature. According to band calculations[6], bulk modulus for K_3C_{60} is 28 GPa, which is in good agreement with present calculations. From Table 2, it is observed that M_3C_{60} compounds have larger equilibrium value of lattice constant, compared to other systems with same alkali metal M. In obtaining the equilibrium value of lattice constant minimization of total energy has been done, which has various components. It seems for M_3C_{60} repulsion due to electron transfer from M atoms is marginally larger compared to other systems. From Table 2 and Figs 3 and 4, we observe that volume per M_nC_{60} not a monotonically increasing quantity with n.

Table 2 : Bulk properties of M_nC_{60} solids

	Lattice constant(Å) M=K, Rb and Cs						Cohesive energy (eV)				Bulk modulus (GPa)		
	K		Rb		Cs		K		Rb	Cs	K	Rb	Cs
n	Present work	Others	Present work	Others	Present work	Others	Present work	Others	Present work	Present work	Present work	Present work	Present work
1	13.94	14.07[17]	13.94	14.08[17]	140	14.12[17]	-3.63	-0.46[3]	-3.85	-4.07	18.4	18.8	16.7
2	14.24		14.50		15.18		-8.08	-5.61[3]	-8.05	-7.70	16.2	12.4	7.5

3	14.11	14.26[18]	14.27	14.384[18]	14.86		-14.34	-13.14[3]	-14.55	-14.10	23.9	20.7	14.2
4	11.6*	11.89[19]	11.6	11.962[19]	12.0	12.057[19]	-21.81		-21.87	-21.22	31.8	28.2	20.0
5	10.6$	10.77[19]	11.0	11.022[19]	11.5	11.443[19]							
6	11.06	11.39[20]	11.06	11.548[7]	11.61	11.790[7]	-43.25		-43.21	-41.75	61.0	52.5	38.2

CONCLUSION

Some remarks may be made here about the phase stability of different M_nC_{60} structures on the basis of cohesive energies. From Table 2, we see that the sum of cohesive energies of M_1C_{60} and M_3C_{60} exceeds twice that of cohesive energy of M_2C_{60}. Thus, M_2C_{60} would tend to separate into M_1C_{60} and M_3C_{60}. Therefore, M_2C_{60} is an unstable system from our (cohesive energy analysis) point of view. In the literature, no experimental data is available for M_2C_{60} solids. It seems this phase for these alkali metal (*K*, *Rb* and *Cs*) doped solids has not been observed. Specifically, K_2C_{60} system has not been found to be a stable system[22], which is in agreement with our theoretical prediction on the basis of cohesive energy. The bulk modulus of M_2C_{60} solids is less than M_1C_{60} and M_3C_{60}. It means in the same host lattice, M_2C_{60} separates into M_1C_{60} and M_3C_{60}, which are more rigid and have more cohesion. Same could be said about M_3C_{60} separating into M_2C_{60} and M_4C_{60}; but here the host lattices are different. It is clear that these systems are ionic, so Coulomb contribution to cohesive energy dominate. From Table 2, it can be seen that the cohesive energy is almost independent of alkali atom type for particular M_nC_{60} solid. As more and more alkali metal atoms are doped in C_{60} the cohesion increases and solid becomes more and more incompressible. However, it decreases with increase in the size of alkali atom (*K* to *Cs*) for a particular value of *n* in M_nC_{60}, which means as the size of alkali metal increases the system become more compressible. Therefore, ionic type calculations with shell model describe well structure, bulk properties and ionic character of alkali doped C_{60} solids.

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