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# COHESIVE ENERGY OF $K_nC_{60}$ DOPED SOLIDS

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We report cohesive energy calculations for doped $K_nC_{60}$ solids. Model calculations are presented for $K_1C_{60}$, $K_2C_{60}$, $K_3C_{60}$, $K_4C_{60}$ and $K_6C_{60}$. In this work, the $C_{60}$ molecule is modelled as a uniform spherical shell with appropriate surface density of carbon atoms, while the ionised alkali atoms, forming the cations are taken to be point charges. Part of the electrons freed by those ionised K atoms are 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. We also account for on-shell Coulomb repulsion between the electrons on the $C_{60}$ shell. With these assumptions the total cohesive energy is calculated taking into consideration vander Waals and screened Coulomb interaction between different ions. On minimising the energy thus calculated with respect to $x$, the fraction of electrons forming electron gas, we find that $x$ is zero *i.e.*, total charge transfer from cation to anion is favoured. Thus ionic character of $K$ doped $C_{60}$ solids is established on the basis of the model. Comparison of the total energy thus obtained has been made with other calculations. We also show the phase instability of $K_2C_{60}$ system.

**Keywords** : $K_nC_{60}$; Cohesive energy; Ionic solid, Bulk modulus; Structure.

## INTRODUCTION

Carbon has a variety of stable forms like diamond, graphite and nanotubes. Apart from this it has its own class of compounds known as organic compounds, which form the basis of life.

Carbon has also the tendency to form clusters of various sizes. These clusters may contain minimum of about 11 and a maximum of 114 carbon atoms [1]. The closed cage nearly spherical molecule, $C_{60}$—a cluster of 60 carbon atoms, and other related fullerene molecules have attracted a great deal of interest in recent years because of their unique structures and properties.

The 60 carbon atoms in a $C_{60}$ molecule are located at the vertices of a truncated icosahedron where all carbon sites are equivalent. A regular truncated icosahedron has 90 edges of equal length, 60 equivalent vertices, 20 hexagonal faces and 12 additional pentagonal faces to form a closed shell. The boundary between a hexagon and its neighbouring pentagon is a single $C–C$ bond and that between two hexagons is a double bond. The molecule is known to have a structure slightly deviating from the ideal truncated icosahedron, in that the single and double bonds have slightly different lengths *i.e.*, 1.45 and 1.4 Å, respectively [2]. While the bonding within a $C_{60}$ molecule is covalent (mixture of $sp^2$ and $sp^3$), the interfullerene bonding in the solid is recognised to be of vander Waals type, making the solid $C_{60}$ a loosely bound condensate. Hence, it is not surprising that the $C_{60}$ molecules condense into a 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. The free $C_{60}$ molecule in its ground state electronic configuration has a completely filled HOMO level. The LUMO is split into two three-fold degenerate levels which get filled as the bucky-ball is charged with more and more electrons. When the pure $C_{60}$ solid is doped with alkali metal (exohedral doping) $M_nC_{60}$ compounds are formed, where n can go up to 6 filling the above described levels [3]. The alkali metal doped $C_{60}$ solid has attracted a great deal of attention as $M_3C_{60}$ systems (M represents alkali metal) were found to be superconducting with $T_C$ around 30 K or larger. Subsequently, $M1_xM2_{3-x}C_{60}$ (M1, M2 being different alkali metals) systems were extensively studied as it was found that $T_C$ can be increased considerably with a suitable $M1$–$M2$ combination. For these reasons, a lot of interest in structure and stability of these compounds was generated.

We present model calculations for alkali metal doped $C_{60}$ solids to find their cohesive energy and the ionic state of $C_{60}$ molecule. Wide disparity in cohesive/ Madelung energy calculations [4–9] has made it an interesting problem. 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 [10–11]. Not only $K_3C_{60}$ but total charge transfer takes place in $K_6C_{60}$ also [12]. However, in view of on-shell Coulomb repulsion, this is even less likely. Therefore, it becomes pertinent to enquire the ionic state of $C_{60}$ molecule in alkali doped solids. We attempt to answer this question in the present paper. In doped $C_{60}$ solids, there is little overlap between molecular wave functions on neighbouring $C_{60}$, so the electrons are practically localised on $C_{60}$ shell. The alkali metal atoms are completely ionised. This leads one to believe that even in $K_4C_{60}$ and $K_6C_{60}$ systems such calculations may suffice. However, since the on-shell Coulomb repulsion is large for the $C_{60}$ molecule, as the charge on the anion is increased, the possibility of delocalisation develops. In the next section we describe the model used for our calculations. In Section 3 we describe numerical calculations. Results and discussion are presented in Section 4.

## MODEL AND CALCULATIONS

In this section we describe van der Waals and Coulomb interaction between various species. 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 at length.

### 2.1 Interactions between ions/atoms

To calculate the potential energy of a system, one needs to take into account various interactions between constituent ions/atoms of the solid. Among the doped $K_nC_{60}$, the structure of $C_{60}$ sublattice changes from FCC to BCC as n increases. For $n = 1 - 3$ the structure is found to be FCC and for $n = 4$ and 6, BCT and BCC, respectively [9]. The dopant alkali ions (denoted by M in the formulae) occupy interstitial positions 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.

The $C_{60}$ molecule, in our model, is taken to be completely rigid. This is justifiable since interactions within the solid are known to leave the bucky-ball undistorted [13]. 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 [13]:

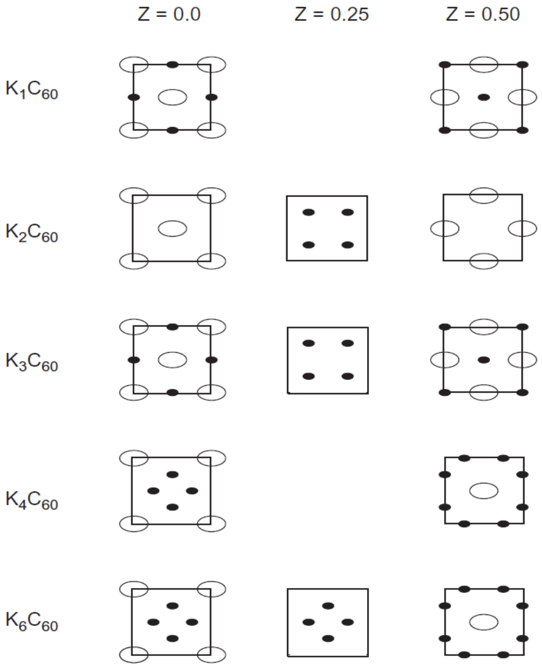

**Fig. 1. Unit cells of Potassium doped $C_{60}$ solids. The squares show various relevant cross-sections parallel to *x–y* plane. Open circles represent $C_{60}$ ions and solid circles are K ions.**

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

The first term in Eq. (1) is the attractive part, having its origin in van der Waals interaction, while the second term is the Born–Mayer repulsion. In $M_nC_{60}$ systems, however, the bonding is known to be mainly of the ionic type [2, 10–12]. 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 eight per unit cell, or octahedral ($O$), of which these are four per unit cell. They also get ionised, becoming $K^+$, while the $C_{60}$ molecules acquire the electrons and become anions. The extent of anion formation depends upon the electron affinity (EA) of $C_{60}$ and ionisation potential (EI) of the $M$ atom. This interstitial site filling goes on till the formula of the doped solid is $M_3C_{60}$. On induction of further alkali atoms into the matrix, the host lattice (of $C_{60}$ molecules) distorts to present a BCT structure [14] till the formula is $M_4C_{60}$. Further diffusion of $M$ into the lattice may be done till the system is $M_6C_{60}$ when the host lattice is BCC [15]. Although the system is not entirely insulating, the electron density around the large anion is sufficiently localised and an ionic type calculation is justified.

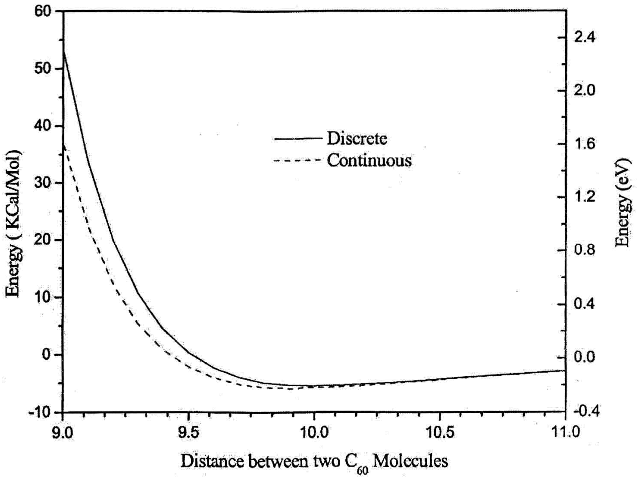

**Fig. 2. Variation of vander Waal's energy between two $C_{60}$ molecules in discrete and shell model. The distance between two $C_{60}$ molecules is in Å.**

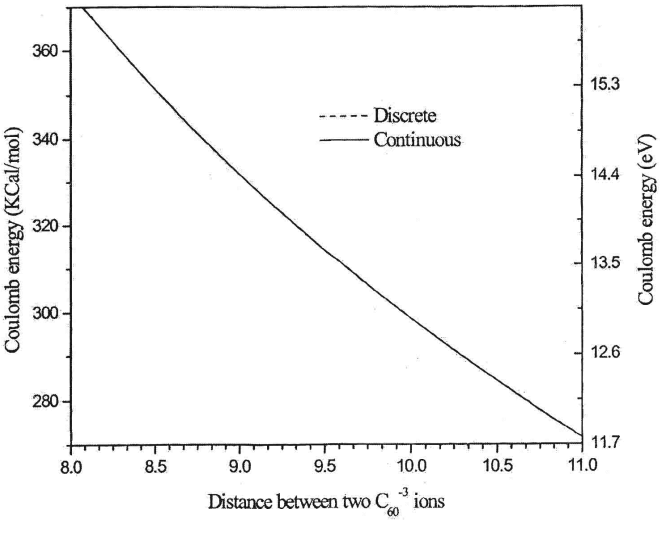

**Fig. 3 : Variation of Coulomb energy between two $C_{60}^{-3}$ molecules in discrete and continuous models. The distance between two $C_{60}^{-3}$ ions is in Å.**

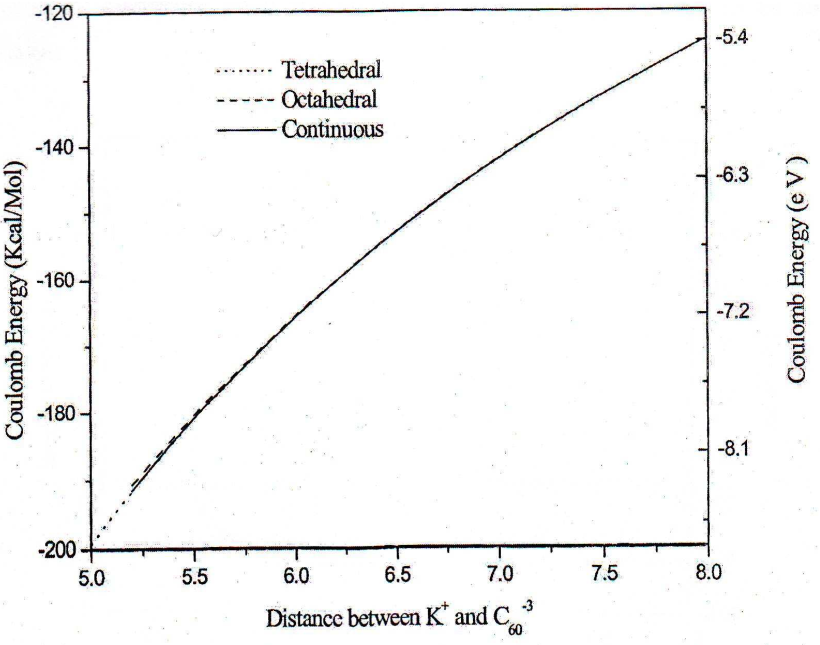

**Fig. 4 : Variation of Coulomb energy between $C_{60}^{-3}$ ion and $K^+$ in discrete and continuous model. The tetrahedral and octahedral in discrete model are not visible distinctly. The distance is in Å.**

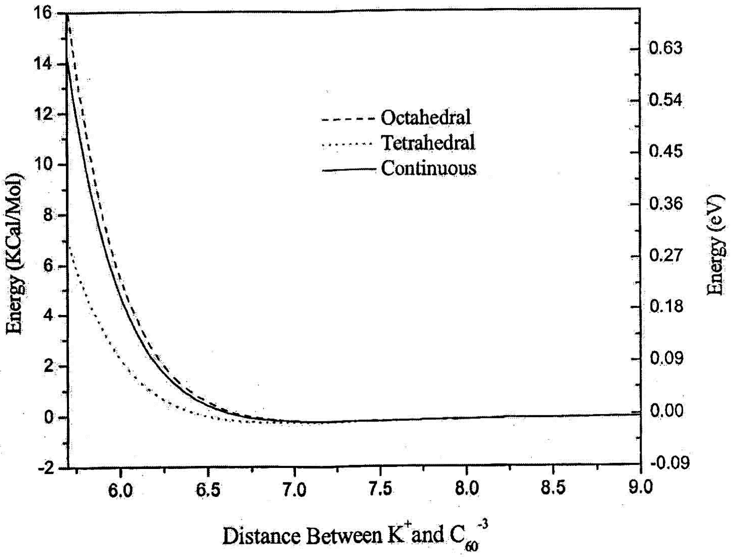

**Fig. 5 : Variation of vander Waals energy between $C_{60}^{-3}$ ion and $K^+$ in discrete and continuous model. The tetrahedral and octahedral refer to two different directions from which $K^+$ is approaching $C_{60}^{-3}$ as discussed in the text. The distance is in Å.**

The $C_{60}$ molecule, which acquires anything from 1 to 6 electrons in these systems, can be a heavily charged anion. This extra charge is expected to be distributed over the whole molecule. The *n* extra electrons may add to the electron clouds around the atom sites, or around single or double bond sites, and may even be non-uniformly distributed over the shell. However, we use a uniformly charged sphere model for Coulombic interactions of the anion. This approximation introduces very little error. The reason for this belief lies in comparison between the uniform charged sphere and discrete distribution (1/60th of electron) of charge on each of the 60 vertices of $C_{60}$ molecule. We have calculated the van der Waals and Coulomb energy between two $C_{60}^{-3}$ ions assuming discrete C atoms and charges at the vertices and compare with same energies in the smeared shell model. vander Waals interaction energy (Fig. 2) is found to be dependent on distribution of carbon atoms on bucky-ball at distances less than 9Å , whereas Coulomb interaction (Fig. 3) is same for discrete model and shell model. We have also made a similar comparison of the interactions between $C_{60}^{-3}$ and a point charge $M^+$. Fig. 4 shows the plot of Coulomb energy with $M^+$ placed along two directions *x*-axis (octahedral) and (1, 1, 1) (tetrahedral), keeping $C_{60}$ in ‘‘standard’’ orientation, and that with $C_{60}$ as a uniformly charged sphere. From this figure it is clear that discrete distribution of charge does not make substantial difference in Coulomb energy as compared to uniform charged sphere model. In case of van der Waals interaction (Fig. 5), discrete model differs from shell model, but only at distances less than 6.5Å. In doped $K_nC_{60}$ systems the equilibrium nearest neighbour distance between a $C_{60}$ molecule and $K^+$ is about 6Å. The vander Waal interaction energy in discrete model differ (by about 2 kcal/ mol for each pair of interacting ions at a distance of about 6Å) from shell model for tetrahedral direction of alkali metal dopant. While computing the total energy of formula unit ($M_3C_{60}$) one tetrahedral $M$–$C_{60}$ pair contribute so discrete model gives a difference of only 2 kcal/mol of total energy, which is about 330 kcal/mol and hence does not make a substantial difference. For octahedral direction no substantial difference in the vander Waals interaction energy has been seen when discrete and shell model are compared. Therefore, shell model which is simpler, is found to be more suitable.

The interaction between a $C_{60}$ anion and an alkali cation is predominantly of the Coulomb type or screened Coulomb type, screening depending upon the concentration of delocalised electrons. Apart from this, C-atoms on a $C_{60}$ molecule and the $M^+$ ion also interact via a 6-exp interaction (Eq. (1)). The parameters *A*, *B* and α for *C*-alkali interaction are chosen by us based on considerations described below. Two alkali cations also interact via Coulomb and van der Waals interactions, the latter being negligible.

Effects of on-shell Coulomb correlations (or Hubbard parameter U) and incomplete charge transfer from cation to anion are considered in a subsequent section.

### 2.2 Parameters of 6-exp interaction

The van der Waals interaction 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 interaction between *C* and alkali atoms are, however, not readily available. The interaction parameters [13] *A*, *B* and α are known for interactions between two carbon atoms (the *C*–*C* interaction). To find parameters for interaction between a *C*-atom and an alkali ion, we make use of alkali halide parameters [16]. For these pairs, we observe,

$$\propto \left(Z_1 Z_2\right)^{1/2} \quad \text{... (2a)}$$

and

$$\frac{B}{\left(Z_1 Z_2\right)^{\frac{1}{2}}} = 0.0165\times 10^{-8}\,\text{erg} = 2372.99\text{k cal/mole} \quad \text{... (2b)}$$

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

$$\frac{B}{\left(Z_1 Z_2\right)^{\frac{1}{2}}} \approx 0.0487\times 10^{-8}\,\text{erg} = 7000\text{k cal/mole} \quad \text{... (2c)}$$

which is at variance with the value (Eq. (2b)) for alkali halides. This is, however, not surprising since 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 $Z_{\text{eff}}$ we get B values for *K*–*C* interactions. For *K*–*K* interaction Eq. (2b) may be used directly.

If vander Waals radii of two ions are $r_1$ and $r_2$ then it is reasonable to expect the repulsive range parameter α to obey

$$\alpha \propto \frac{1}{r_1 + r_2} \quad \text{... (3a)}$$

Comparing again with the given α values for alkali halides, and using the known radii for these ions, we find

$$\alpha^{-1} \approx 0.11\left(r_1 + r_2\right) \quad \text{... (3b)}$$

Radius for *K* is 1.33 Å using which we obtain $\alpha_{KK}$. Kitaigorodsky has given $\alpha_{CC}$. We obtain $\alpha_{\text{KC}}$ as the harmonic mean of $\alpha_{\text{CC}}$ and $\alpha_{KK}$ in accordance with Eq. (3).

The 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 (see Appendix B)

$$A_{KC} \cong .8786\left(A_{KK} A_{CC}\right)^{1/2} \quad \text{... (3.9)}$$

In this way, we have estimated various parameters for *K*–*K* and *K*–*C* interactions. These parameters (*A*, *B*, and α) thus obtained for *K*–*K* and *K*–*C* interactions need further refinement. This is done by obtaining best fit to the experimental values of lattice parameters and bulk modulus of $K_3C_{60}$. The refined parameters are presented in Table 1. It may be mentioned that the parameters $A$, $B$, $\alpha$ for $K^+ - K^+$ interactions have no major role in the determination of cohesive energy of doped $C_{60}$ systems, as interactions between these small cations are dominated by Coulomb interaction.

**Table 1 : Interaction Parameters**

| Atom-Atom | A (kcal-Å$^6$/mol) | B (kcal/ mol) | $\alpha$ (A$^{-1}$) |
|---|---|---|---|
| C-C | 358 | 42000 | 3.58 |
| K-K | 171 | 49138 | 3.62 |
| K-C | 235 | 28370 | 3.50 |

## UNIFORM SPHERE APPROXIMATION

We have shown in Section 2.1, that orientation of $C_{60}$ molecule is mostly unimportant. One can then replace the $C_{60}$ molecule by a spherical shell [13], with 60 carbon atoms uniformly smeared over the shells. In order to do this for the 6-exp part of the potential of the interaction between two $C_{60}$ molecules; we integrate the potential (Eq. (1)) over the surface of two spheres. While integrating, $\vec{r}$ is the position vector of surface area element $ds$ from origin of ball $b$ and $\vec{r}$ is the position vector of surface area element $ds'$ of ball $b'$ from its own origin. $S$ and $S'$ are the surfaces of two balls of radius $R_B$. $\vec{R}$ is the position vector of the point alkali metal or ball $bb'$ from the centre of ball $b$ as the case may be:

$$U_{bb'}^{vdw} = \frac{(60)^2}{(4\pi R_B^2)^2}\int_S \int_{S'} V\left(\vec{R}+\vec{r}\,'-\vec{r}\right) ds\, ds',$$

$$U_{bb'}^{vdw}(R) = -(60)^2\left[\left(\frac{A}{R^6}\right)\frac{1-2(R_B/R^2)+8/3(R_B/R)^4}{\{1-(2R_B/R)^2\}^3} - B\exp(-\alpha R)\left(\frac{\sinh(\alpha R_B)}{\alpha R_B}\right)^2 \times\left\{1+\frac{2}{\alpha R}\left(1-\frac{\alpha R_B}{\tan h(\alpha R_B)}\right)\right\}\right] \quad \dots (5)$$

$R$ is the distance between the centres of the two bucky-balls, and $R_B$ is their radius. Similarly, the potential energy arising from van der Waals interaction between an alkali metal ion and a $C_{60}$ molecule separated by a distance $R$ is given by

$$U_{bK}^{vdw} = \frac{60}{4\pi R_B^2}\int_S V\left(\vec{R}-\vec{r}\right) ds,$$

$$U_{bK}^{vdw}(R) = \frac{60A}{r^6}\left[\frac{(1+(R_B/R)^2)}{(1-(R_B/R)^2)^4}\right]$$

$$+\frac{60B\exp(-\alpha R)}{R_B\alpha}\left[-\frac{R_B}{R}\cosh\,(R_B\,\alpha)+\left(1+\frac{1}{R\alpha}\right)\sinh\,(R_B\,\alpha)\right]$$

The vander Waals interaction between two alkali metal ions separated by distance $R$ is of the same form as Eq. (1).

$$U_{KK'}=-\frac{A}{R^6}-B\exp\left(-\alpha R\right) \qquad \text{... (6)}$$

## ENERGY IN CHARGE STATES

The $C_{60}$ molecule, on acquiring extra electrons, becomes a large anion. The energy required to put one additional electron, which goes in the LUMO, is generally accepted to be –2.65 eV (the measured electron affinity, $E_A$, of the $C_{60}$ molecule is 2.65 eV). Addition of still more electrons, however, involves 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

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

where $U$ is an average pair wise Coulomb repulsion parameter. To determine appropriate values of $E_A$ and $U$, we make use of data [17], giving energies of various charge states of $C_{60}$ anion. The data fits to $EA = -2.76$ eV and $U = 3$ eV. When the anion is a part of solid, $U$ gets modified to a value of 1.3 eV [18]. It is interesting to note that the energy required for a metallic sphere of radius 3.58 Å (same as that of $C_{60}$ molecule) to be charged with $n$ electrons is $\frac{n\left(n-1\right)}{r}$, which corresponds to $U \cong 4$ eV, not very different from the LDA calculations [17]. We use well established values of $E_A = 2.65$ eV and $U = 1.3$ eV in our calculations.

## MODEL FOR IONIC CHARACTER

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, incorporate in our model, the possibility of fractional charge state of the anion. Let $n - x$ be the charge (no. of electrons) on each $C_{60}$ shell. Then the total energy of anion and cation become, for the $M_nC_{60}$ System,

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

where $E_I$ denote the ionisation energy of the alkali atom $M$ (for $K$, $E_I = 4.34$ eV). Eq. (8) gives energy per $M_nC_{60}$ molecule excluding the interaction between the various charged species of ions.

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 $K^+$ sites, must exist in the *s*-band, although in formula (8) above, we have neglected the width of that band. A more pronounced role played by these *s*-electrons would, however, be to screen the Coulomb interaction between the ions. Thus the system is now supposed to consist of $C_{60}^{-(n-x)}$ and $K^+$ 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 well known that there is virtually no electronic charge density in the interior of the fullerene cage.

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

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

where *e* is the charge of electron. To obtain the screened Coulomb potential between the $K^+$ and $C_{60}^{-(n-x)}$ anion in the smeared out model, we perform the appropriate integration over the $C_{60}$ shell. The charge per carbon atom is – (*n* – *x*) *e*/60. The desired integral becomes

$$U_{bK}^{SC}=-\frac{60e^2}{4\pi R_B^2}\frac{n-x}{60}\int_s\frac{\exp\left(-\left(\vec{R}-\vec{r}\right)/\lambda\right)}{\vec{R}-\vec{r}}ds$$

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

where $\vec{R}$ is the position vector of the point $K^+$ cation or ball *b*' from the centre of ball *b* as the case may be. While integrating $\vec{r}$ is the position vector of surface area element *ds* from origin of ball *b* and $\vec{r}$ is the position vector of surface area element *ds'* of ball *b'* from the origin of ball *b'*. *S* and *S'* are the surfaces of two balls of radius $R_B$. Similarly, performing the integration over surface of two uniform spheres charged with (*n* – *x*) electrons, yields, for screened Coulomb potential between two $C_{60}^{-(n-x)}$ anions,

$$U_{bb'}^{SC}=\left(\frac{60}{4\pi R_B^2}\right)^2 e^2\left(\frac{n-x}{60}\right)^2\int_S\int_{S'}\frac{\exp\left(-\left(\vec{R}-\vec{r}+\vec{r}'\right)/\lambda\right)}{\vec{R}-\vec{r}+\vec{r}'}ds\,ds'$$

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

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.*,

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

where $n_0$ is the electron density and $\varepsilon_F$ is free-electron Fermi energy. This gives

$$\lambda^{-1} \cong 2.73\times10^{-10} n_0^{1/6}$$

The effective mass of the *s*-band is likely to be large. However, presently we use free electron mass in Eq. (12).

## NUMERICAL CALCULATIONS

Taking into account all interactions, we now proceed to calculate total cohesive energy and thus calculate bulk modulus for all $K_nC_{60}$ systems under consideration.

### 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. (5), (6), (8)–(11), we express the total potential energy of a monovalent atom-doped $C_{60}$ solid in the following form.

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

The summation is over all pairs of lattice points within the chosen volume. The summation over vander 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 straightforward sum; so we use Evjen's method [19] to calculate Coulomb contribution to the cohesive energy. The appropriate lattice sum of the Coulomb part (Appendix A) yields Madelung energy. We have calculated Madelung constant for each of the $M_nC_{60}$ structures used. This procedure for calculating Madelung constant yields correct values for NaCl and CsCl structures [20]. This method shows a good convergence of the Coulomb potential sum with few lattice distances. The screened Coulomb summation also converges nicely using Evjen's method with few lattice distances.

Thus the total energy Φ is expressed as a function of parameters, *x* (fraction of electron forming gas) and *a* (cubic lattice constant). For $K_4C_{60}$, which is the only non-cubic system out of those considered, it is a function of *x*, *a* and *c*. Equilibrium lattice constant $a_0$ (or $a_0$ and $c_0$ for $K_4C_{60}$) and *x* is obtained by minimising cohesive energy with respect to these parameters.

### 3.2 Bulk modulus

We plot (Fig. 6) 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 bulk modulus is calculated for x = 0 case (complete charge transfer to anion).

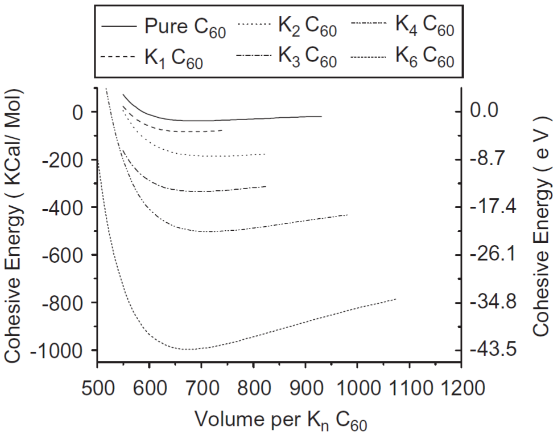

**Fig. 6. Variation of Total Cohesive energy with volume per $K_nC_{60}$ volume is in Å$^3$**

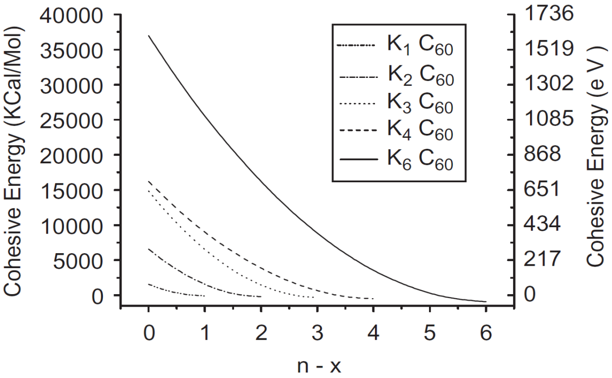

**Fig. 7 : Variation of cohesive energy with $n - x$ for $K_nC_{60}$ systems.**

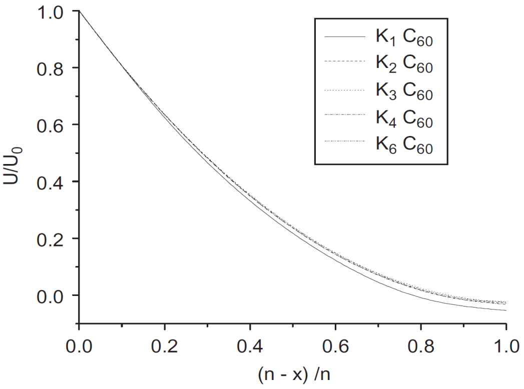

**Fig. 8 : Variation of $(n - x)/n$ with $U = U_0$. Here $U_0$ is energy of the system at $x$ equal to $n$ *i.e.*, no charge placed on $C_{60}$.**

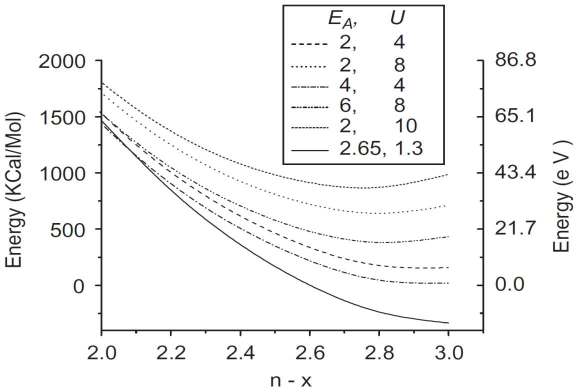

**Fig. 9. The comparison of total energy of $K_3C_{60}$ w.r.t different values of electron affinity (EA) and on shell Coulomb repulsion (U) for $n$–$x$ varying from 2.0 to 3.0. The solid line represents the realistic cas**

## RESULTS AND DISCUSSION

We first establish that shell model for $C_{60}$ molecule in doped $C_{60}$ solids is justified to calculate cohesive energy of these systems. As discussed in Sections 2.1 and 2.3 as far as Coulomb part of cohesive energy is concerned (Figs. 3 and 4), shell approximation is as good as discrete model. van der Waals part of cohesive energy certainly determines the orientation of $C_{60}$ in the solid if distances are short, as shown in Figs. 2 and 5. But in all $K_nC_{60}$ systems nearest distances are larger than what becomes important for discrete model. Shell model is simple and sufficiently accurate as well, so one can proceed with shell model. We look into the possibility of fractional charge transfer on $C_{60}$ molecule. We assume, in $K_nC_{60}$ system, only $n - x$ electrons transferred on each $C_{60}$ molecule, with $x$ electrons contributing to a free-electron gas. We have calculated the equilibrium fraction of charge ($n - x$) transferred to $C_{60}$ molecule. The variation of cohesive energy with $n - x$ is shown in Figs. 7 and 8. 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 Eq. (13) electron affinity ($E_A$) and on-shell Coulomb repulsion ($U$) are assumed to be constant. In order to further study the possibility of fractional charge transfer in similar systems, we have repeated these cohesive energy calculations with several different sets of value of parameters $E_A$ and $U$. We present the calculations for $K_3C_{60}$ system. In Fig. 9 different curves show the variation of cohesive energy with fraction ($3 - x$) of charge on $C_{60}$ molecule at constant $E_A$ and $U$. From these curves it is clear that there is a possibility of ($3 - x$) to be a fraction, *i.e.*, for minimum of the curve lie at non-zero $x$, but this happens only for large values of on-shell Coulomb repulsion ($U$). However, for these cases the total energy becomes positive and hence system is not stable. Again complete charge transfer or full ionic character has been supported. Establishing full ionic character of all $K_nC_{60}$ systems, we proceed to calculate cohesive energy. We find lattice constant ($a_0$) and bulk modulus. Fig. 6 shows variation of total cohesive energy with respect to volume per $K_nC_{60}$. Our calculations show that $K_1C_{60}$ (NaCl structure) is more stable than $K_1C_{60}$ (CsCl) which is supported by literature [2]. We have summarised our results in Tables 2 and 3. We have compared (Table 4) our results with band calculations [8] of Oshiyama et al., Martin and Troullier [6] and those of Friedberg [5]. Our calculations are in good agreement with Friedberg [5] for $K_1C_{60}$, $K_2C_{60}$ and $K_3C_{60}$. Encouraged from this we have predicted Madelung part of cohesive energy for $K_4C_{60}$ and $K_6C_{60}$ systems also. Bulk modulus for $K_3C_{60}$ is also in good agreement with band calculations. From Table 2 and Fig. 6 we observe that volume per $K_nC_{60}$ is not a monotonically increasing quantity with n. One would expect it to be so because as more and more interstitials are created in the lattice it is expected to dilate more and more.

Some remarks may be made here about the phase stability of different $K_nC_{60}$ structures on the basis of cohesive energies. From Table 4 we see that if we add cohesive energies of $K_1C_{60}$ and $K_3C_{60}$ we get an amount (17.97), which exceeds twice that of cohesive energy of $K_2C_{60}$. Thus, $K_2C_{60}$ would tend to separate into $K_1C_{60}$ and $K_3C_{60}$. This observation holds for all the columns in Table 4 except Oshiyama's calculations. Indeed this observation/result is correct because $K_2C_{60}$, although used for theoretical calculations, has not been found to be a stable system [21]. Same could be said about $K_3C_{60}$ separating into $K_2C_{60}$ and $K_4C_{60}$; but here the host lattices for $n$ = 2 and 4 are different (FCC and BCT, respectively); so phase separation does not take place (would be extremely difficult to achieve by range order).

**Table 2 : Bulk properties of $K_nC_{60}$ solids**

| **$K_nC_{60}$ ($n$)** | **Our Calculations** | | **Experimental** | | **Bulk Modulus (GPa)** | |
|---|---|---|---|---|---|---|
| | **Lattice Constant (Å)** | **Volume per $C_{60}$ (Å$^3$)** | **Lattice Constant (Å)** | **Volume per $C_{60}$ (Å$^3$)** | **Our calculations** | **Others** |
| 1 | 13.94 | 677.2 | 14.07 [21] | 696.3 | 18.4 | |
| 2 | 14.24 | 722.0 | | | 16.2 | |
| 3 | 14.11 | 702.3 | 14.240 [22] | 721.9 | 23.9 | 28 [8] |
| 4 | (a) 11.6 (c) 10.6 | 713.2 | 11.886 [23]<br>10.774 [23] | 764.7 | 31.8 | |
| 6 | 11.06 | 676.5 | 11.385 [15] | 738.8 | 61.0 | |

**Table 3 : Cohesive energy of $K_nC_{60}$ solids**

| **$K_nC_{60}$ ($n$)** | **Cohesive Energy - Lattice sum (eV)** | | **Electronic Energy Ionization (ev)** | | **Total Cohesive Energy = Cohesive Energy + Electronic Energy** | |
|---|---|---|---|---|---|---|
| | **Our Calculations** | **Friedberg [5]** | **Our Calculations** | **Friedberg [5]** | **Our Calculations** | **Friedberg [5]** |
| 1 (Octahedral) | – 5.32 | – 3.54 | 1.69 | 3.09 | – 3.63 | – 0.46 |
| 2 | – 12.76 | – 11.79 | 4.68 | 6.18 | – 8.08 | – 5.61 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3 | – 23.31 | – 22.41 | 8.97 | 9.27 | – 14.34 | – 13.14 |
| 4 | – 36.37 | | 14.56 | 12.36 | – 21.81 | |
| 6 | – 72.89 | | 29.64 | 18.54 | – 43.25 | |

**Table 4 : Comparison of cohesive energy of $K_nC_{60}$ solids**

| $K_nC_{60}$ (*n*) | **Our Calculations (e V)** | **Oshiyama et al [8] (LDA) (eV)** | **Friedberg [5] eV** | **Martins [6] (LD Pseudopotential) (eV)** |
|---|---|---|---|---|
| 1 (Octahedral) | – 3.63 | – 10.1 | – 0.46 | – 1.4 |
| 2 | – 8.08 | – 19.3 | – 5.61 | – 2.8 |
| 3 | – 14.34 | – 24.2 | – 13.14 | – 5.1 |
| 4 | – 21.81 | | | |
| 6 | – 43.25 | | | |

## CONCLUSION

This paper describes a model for binding energy of doped $C_{60}$ solids assuming formation of partially ionic $M_nC_{60}$. The calculation and result presented rule out the possibility of partial ionic character, clearly indicating a full ionic formation of $M_nC_{60}$. The results are in agreement with other calculations/experiments. We, thus, find that the uniformly smeared shell model describes well the structure of doped $C_{60}$ solids.

## ACKNOWLEDGEMENT

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**Appendix A. Evjen’s method of lattice sum applied to $M_nC_{60}$ lattices**

Let $e_i$ and $e_j$ be the charges on the *i*th and the *j*th ions of the lattice, respectively. If $r_{ij}$ is the distance between the two ions, then the electrostatic energy of the crystal will be

$$U = \frac{1}{2}\sum_{i,j} e_i e_j / r_{ij} \qquad \text{... (1)}$$

If the summation over j is independent of i, i.e., all ions are similarly situated w.r.t. like and unlike ions (e.g., in NaCl), then the summation taken over all *i, j* is

$$U = \frac{1}{2} N \sum_{j} e_i e_j / r_{ij} \qquad \text{... (2)}$$

where *N* is total number of ions. We can then write the electrostatic energy as

$$U = Ne^2 M / r_0 \quad \text{... (3)}$$

where $r_0$ is the nearest-neighbour distance in the lattice, and $M$ is the Madelung constant.

In $K_nC_{60}$ systems, when $n > 1$, all lattice points are not equivalent. Therefore, Eq. (2) is not valid. Let us consider a general case where there are three types of ions/lattice points $A$, $B$ and $C$. Let one unit cell contains $x$ formula units of the compound. Further, suppose that $l$, $m$ and $n$ are the number of type $A$, $B$ and $C$ ions, respectively, in each unit cell. Let the summation be carried over $y$ unit cells. Now we choose an ion one by one of each type and sum over rest of the lattice and we get

$$U_A = q_A \sum_i q_i / r_{Ai} \quad \text{... (4)}$$

$$U_B = q_B \sum_i q_i / r_{Bi} \quad \text{... (5)}$$

$$U_C = q_C \sum_i q_i / r_{Ci} \quad \text{... (6)}$$

where $r_{Ai}$ is the distances of $i$th ion (having $q_i$ electrons) from ion $A$ (having $q_A$ electrons). Replacing $A$ by $B$ and $C$, one gets corresponding quantities for $B$ and $C$. Now electrostatic energy per unit cell is

$$U_{CELL} = \frac{1}{2}\left(1 \times U_A + m \times U_B + n \times U_C\right) \quad \text{... (7)}$$

Multiplying Eq. (6) by $y$, we have

$$U = y \times x \times U_{ABC} \quad \text{... (8)}$$

where $U_{ABC}$ is electrostatic energy per formula unit. If $N = y \times x$, we have

$$U_{ABC} = U / N = M \quad \text{... (9)}$$

$U_{ABC}$ with unit lattice constant is the desired Madelung constant.

The summation involved in Eqs. (4)–(6) requires specific method. The common methods for calculation of lattice sums are Ewald’s and Evjen’s methods. We have used Evjen’s method [19]. One constructs a neutral closed volume enclosed by a surface, such as a cube. Then the size of this closed volume is increased successively and the Madelung constant compared with the previous value. In our systems a unit cell or a group of unit cells may be considered as the closed area for summation. We start with the volume enclosed by eight unit cells placed together so as to get a cube of dimensions $2a \times 2a \times 2a$, where $a$ is the lattice constant. We have calculated Madelung constant of NaCl before applying it to $K_nC_{60}$ systems. Here, Madelung constant is w.r.t. lattice constant (a) instead of nearest-neighbour distance, so that the electrostatic energy (UE) per formula unit is

$$U_E = M \times e^2 / a \quad \text{... (10)}$$

From Table 5, it is clear that our calculated Madelung constant for NaCl and $K_3C_{60}$ is in excellent agreement with the standard value.

**Table 5 : Madelung Constants of alkali doped $C_{60}$ structures**

| System | Madelung Constant *M* | | | Other authors |
|---|---|---|---|---|
| | Summation Volume | | | |
| | 2 × 2 × 2 | 4 × 4 × 4 | 6 × 6 × 6 | |
| NaCl and $K_1C_{60}$ | 3.46700 | 3.49503 | 3.49603 | 3.49512 [9] |
| $K_2C_{60}$ | 11.6422 | 11.6365 | 11.6406 | |
| $K_3C_{60}$ | 22.0690 | 22.1230 | 22.1313 | 22.08 [24] |
| $K_4C_{60}$ | 28.9947 | 29.1563 | 29.1592 | |
| $K_6C_{60}$ | 56.1524 | 46.4728 | 56.4626 | |

The problem of weak convergence of Coulomb summation has been effectively countered. Summing over just a few lattice vectors gives a very good estimate.

**Appendix B. Estimation of *vdW* interaction parameters**

The formula for estimation of *vdW* interaction between too many electron atoms, based on second-order perturbation theory, has been given by Pauling and Wilson [26], based on a method suggested by Landau. By this treatment, the interaction energy between two atoms *X* and *Y* separated by a distance *R*, is given by

$$U_{XY}(R) = -\frac{6n_X n_Y e^4 \overline{Z_X^2}\,\overline{Z_Y^2}}{R^6(I_X + I_Y)} \equiv -\frac{A_{XY}}{R^6} \qquad \text{... (1)}$$

where $n$ is the number of effective electrons; $\overline{Z^2}$ for a spherical atom may be taken as $\frac{1}{3}\overline{r^2}$, $\overline{r^2}$ being the mean square radial distance of the electrons from the nucleus; $I$ is an energy of the order of first ionisation potential. The interaction energy for same interacting atoms, $X$, say, is

$$U_{XX}(R) = -\frac{3n^2{}_X e^4(\overline{Z_X^2})}{R^6 I_X} \equiv -\frac{A_{XX}}{R^6} \qquad \text{... (2)}$$

Using above two relations, we get

$$A_{XX}A_{YY} = \frac{A_{XY}^2(I_X + I_Y)^2}{4I_X I_Y} \qquad \text{... (3)}$$

or

$$A_{XY} = \frac{2}{\sqrt{2 + \frac{I_X}{I_Y} + \frac{1_Y}{I_X}}}(A_{XX}A_{YY})^{1/2} \qquad \text{... (4)}$$

From the tables [16] ionisation energies for *C* atom and $K^+$ ion are, 11.26 and 31.81 eV respectively. For *C* and $K^+$ we have

$$A_{CK^+} = 0.8786(A_{CC}A_{K^+K^+})^{1/2} \qquad \text{... (5)}$$

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