A lattice-gas model for alkali-metal fullerides: face-centred-cubic structure

A lattice-gas model for alkali-metal fullerides: face-centred-cubic structure

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Abstract. A lattice-gas model is suggested for describing the ordering phenomena in alkali-metal fullerides of face-centred-cubic structure assuming that the electric charge of alkali ions residing in either octahedral or tetrahedral sites is completely screened by the first-neighbour C_{60} molecules. This approximation allows us to derive an effective ion–ion interaction. The van der Waals interaction between the ion and C_{60} molecule is characterized by introducing an additional site energy at the tetrahedral sites. This model is investigated by using a three-sublattice mean-field approximation and a simple cluster-variation method. The analysis shows a large variety of phase diagrams as the site energy parameter is changed.

1. Introduction

Since the discovery of superconductivity in several alkali-metal fullerides [1–3] a large variety of $A_x C_{60}$ intercalation compounds have been prepared and investigated (for recent reviews see the papers [4, 5]). In the face-centred-cubic (FCC) structure of pristine C_{60} the molecules are bonded via van der Waals interaction. In this structure the tetrahedral and octahedral interstitial spaces are sufficiently large to accommodate alkali atoms without significant distortion of the lattice.

Because of the charge transfer the electrostatic energy plays an important role in the formation of different ordered structures, as well as in the distortion of the host lattice for large alkali concentration ($x > 3$). Fleming *et al* [6] have determined the electrostatic energies for $Rb_x C_{60}$ compounds assuming point charges for the Rb^+ ions, and the contribution of the C_{60}^{x-} ion is expressed as the minimum Coulomb repulsion of x point charges on a sphere of radius R, with R taken to be the C_{60} nucleon radius of 3.5 Å. In the calculation of electrostatic energies Rabe *et al* [7] have assumed a uniformly charged spherical shell with the same radius for the C_{60}^{x-} ion.

In the present work we introduce a simple lattice-gas model to study the ordering phenomena in alkali fullerides. In this model the interstitial sites may be empty or occupied by one type of alkali ion. In agreement with the large size of fullerenes, here we assume that an A^+ alkali ion is completely screened by uniformly distributing its transferred charge on the first-neighbour C_{60} molecules. For example, the alkali ion residing at a tetrahedral (octahedral) site is surrounded by four (six) C_{60} molecules with charges of $-e/4$ ($-e/6$). In other words, each intercalated alkali atom transfers charges to its neighbouring C_{60} molecules independently of the position of the remaining A^+. This simplification makes the derivation of an effective pair interaction possible, which is evidently a short-range one. The difference

between the sizes of tetrahedral and octahedral voids is considered by introducing extra site energy related to the van der Waals interactions. This site energy parameter depends on the radius of the intercalated particle; consequently it is characteristic of the type of alkali atom. In the knowledge of the effective interactions (and site energy) characterized by a few parameters we are able to study the ordering within the framework of the lattice-gas (Ising) formalism. Using a simple mean-field analysis and cluster-variation method we have evaluated a series of phase diagrams by varying the site energy (ionic radius) parameter.

The above formalism can describe the ordered structures observed in alkali fullerides with FCC structure. Namely, in pristine C_{60} all of the interstitial sites are empty, whereas in the superconducting compounds with nominal composition A_3C_{60} both the octahedral and tetrahedral sites are occupied by alkali ions [8, 1, 2, 3]. Only the octahedral sites are occupied in AC_{60}, forming NaCl structure for A = Rb and Cs [9]. Filling of the tetrahedral sites results in the CaF_2 structure observed by Rosseinsky *et al* [10] in the Na_xC_{60} system. According to our analysis the above phases are found to be stable if one takes the total energy of the charged C_{60} molecule into consideration as discussed later on.

The early experimental investigations of the alkali intercalated fullerides are summarized by Zhu *et al* [11] in a provisional phase diagram. Recently, Poirier and Weaver [12] and Winkler and Kuzmany [13] proposed a phase diagram for the K_xC_{60} system showing a eutectoid transformation from the homogeneous KC_{60} state to the composition of C_{60} and K_3C_{60} phases [12]. Our calculation confirms the existence of such a phase diagram for a narrow range of parameters.

The above model explains adequately the formation of different intercalated structures. Our purpose is not to argue that the present description gives the correct lattice-gas model for a given A_xC_{60} system but rather to emphasize some general features highlighted by this approach because the model is adaptable for other metal–C_{60} systems. By this means the present model provides a framework for classifying these systems. In this paper we restrict ourselves to the systems corresponding to A_xC_{60} with rigid FCC structure. In the present description the phenomena related to the orientational ordering are neglected. Both the interaction between two C_{60} molecules and the electronic structure are simplified; therefore the present model cannot describe the chain formation discovered very recently by Chauvet *et al* [14].

2. The model

The electronic structure calculations for alkali fullerides have indicated that the higher-lying s bands of the metal are unoccupied and the electrons fill the empty t_{1u} states of the C_{60} molecule, so the alkali atoms are ionized and their valence electrons are accepted by the fullerene molecule forming a negative ion [15, 16]. In such a situation the Coulomb interaction makes the most important contribution to the energy of the system. Several authors have already studied the effect of the Madelung energy on the charge-transfer solids [17], binary [18] and pseudobinary alloys [19] and intercalated graphite compounds [20].

Statistical physics is able to give an adequate description of the Ising systems with short-range interaction but many problems arise in handling the infinite-range Coulomb interaction. An effective way of eliminating this problem is to construct a renormalized short-range interaction. In our treatment a series of pair interactions that converges well is derived in order to avoid the difficulties arising from the long-range-order interactions among the ions.

Calculations taking into account the polarizability of the fullerene molecules in the host lattice have suggested that the energy of two charged C_{60} molecules in the intercalated solid

can be well described as the interaction between two point charges in a dielectric medium characterized by ε [21].

The charge of the alkali atoms has been taken to be e and the charge of the C_{60} is related to the occupation of the nearest-neighbour interstitial sites. The charge distribution may easily be described in the lattice-gas formalism introducing the site occupation variables η_i which take the value 1 if the ith interstitial site is occupied and take the value 0 if this site is empty. Within this formalism the charge at site i is evidently $q_i = e\eta_i$ and the charge transferred to the αth C_{60} molecule can be written as

$$Q_\alpha = -e \sum_{j \in N_\alpha} c_j \eta_j \tag{1}$$

where N_α means the set of first-neighbour tetrahedral and octahedral interstitial sites around the αth C_{60} molecule and c_j denotes the portion of charge transferred from the alkali atom residing at the jth site to each nearest-neighbour C_{60} molecule. More precisely, $c_j = 1/6$ for octahedral and 1/4 for tetrahedral sites. Such a choice provides for each alkali ion to be completely neutralized by its first-neighbour C_{60} molecules. The model assumes that the transferred charge accompanies the alkali ions when hopping from site to site. This charge distribution evidently satisfies the requirement of the neutrality of the crystal.

The energy of the system can be given in the following form:

$$E = \frac{1}{2\varepsilon} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} + \frac{1}{2\varepsilon} \sum_{\alpha \neq \beta} \frac{Q_\alpha Q_\beta}{r_{\alpha\beta}} + \sum_{i,\alpha} \frac{q_i Q_\alpha}{\varepsilon r_{i\alpha}} + \sum_\alpha E_{int}(Q_\alpha) \tag{2}$$

where $E_{int}(Q_\alpha)$ is the intramolecular energy, and the Greek and Latin indices run over the C_{60} sites and interstitial sites of the FCC lattice respectively. Substituting in the charges from (1), the Coulomb energy can be expressed as

$$E_C = \frac{e^2}{2\varepsilon} \sum_{i \neq j} \frac{1}{r_{ij}} \eta_i \eta_j - \frac{e^2}{\varepsilon} \sum_{i,\alpha} \sum_{j \in N_\alpha} \frac{c_j}{r_{i\alpha}} \eta_i \eta_j + \frac{e^2}{2\varepsilon} \sum_{\alpha \neq \beta} \sum_{j \in N_\alpha} \sum_{k \in N_\beta} \frac{c_j c_k}{r_{\alpha\beta}} \eta_j \eta_k . \tag{3}$$

On exchanging the order of the summations, the energy can be separated into the contributions of on-site and pair interactions, namely

$$E_C = \sum_i \epsilon_i' \eta_i + \frac{1}{2} \sum_{ij} V_{ij}' \eta_i \eta_j \tag{4}$$

where

$$\epsilon_i' = \frac{e^2}{2\varepsilon} \sum_{(\alpha,\beta) \in N_i, \alpha \neq \beta} \frac{c_i^2}{r_{\alpha\beta}} - \frac{e^2}{\varepsilon} \sum_{\alpha \in N_i} \frac{c_j}{r_{i\alpha}} \tag{5}$$

$$V_{ij}' = \frac{e^2}{\varepsilon r_{ij}} + \frac{e^2}{\varepsilon} \sum_{\alpha \in N_i} \sum_{\beta \in N_j} c_i c_j \frac{(1 - \delta_{\alpha\beta})}{r_{\alpha\beta}} - \frac{e^2}{\varepsilon} \sum_{\alpha \in N_j} \frac{c_j}{r_{i\alpha}} - \frac{e^2}{\varepsilon} \sum_{\alpha \in N_i} \frac{c_i}{r_{j\alpha}} \tag{6}$$

and N_i denotes the set of first-neighbour C_{60} positions around interstitial site i.

The magnitude of V_{ij}' decreases rapidly with the distance between sites i and j. Equation (6) expresses the Coulomb interaction between two clusters formed by the ith and jth alkali ions as the central site and their nearest-neighbour C_{60} molecules. Since the clusters are neutral and the systems have cubic symmetry, the monopole, dipole and quadrupole terms vanish. So there are only higher-order multipole interactions between two sites.

In order to evaluate the intramolecular energy a series of semi-empirical unrestricted Hartree–Fock (UHF) calculations have been performed using the parametrization according

to the modified neglect of differential overlap (MNDO) approximation [22] for up to a sixfold ionized single C_{60}^{x-} molecule where the characteristic bond lengths of the system were kept constant: $r_1 = 1.400$ Å and $r_2 = 1.440$ Å. The total energy of the charged molecule as a function of the number of excess electrons can be fitted quite well with a parabola given by

$$E_{tot} = A + Bx + Cx^2 \qquad (7)$$

where x is the number of extra electrons on the molecule and $A = -7635.02$ eV, $B = -4.71926$ eV, and $C = 1.6262$ eV. Such an almost perfect parabolic behaviour does not hold for other fullerenes with lower symmetry.

The quadratic energy dependence of the isolated molecule on the excess charges allows us to introduce an effective radius for the C_{60} molecule having a value of $R = 0.312a$ where the lattice constant a is given by experiment [8]. From previous calculations [21, 23, 24] $R \approx 4.8$ Å can be obtained. The differences between the present and the cited calculations are due to the different choices of the equilibrium bond lengths. Since the C_{60} molecule is embedded in the crystal lattice the energy of the single molecule is modified by the surrounding media. Supposing a dielectric screening mechanism one can apply the Onsager–Kirkwood theory of the electrostatic solvation [25] for estimating the effect of the lattice:

$$E_{int} = E_0 - \frac{1}{2}\left(\left(1 - \frac{1}{\varepsilon}\right)\frac{Q^2}{r_0} + 2\frac{\varepsilon - 1}{2\varepsilon + 1}\frac{\mu^2}{r_0^3} + \cdots\right) \qquad (8)$$

where r_0 is the radius of the cavity into which the molecule is embedded. Since the dipole moment μ of the charged C_{60} is zero, choosing the effective radius as the radius of the cavity, the intramolecular energy can be written as

$$E_{int} = A + Bx + \frac{e^2 x^2}{2\varepsilon R}. \qquad (9)$$

The first term gives a constant contribution to the total energy and the linear term shifts the on-site energies. Both effects may be transformed out by rescaling the energy. The quadratic term gives a V_{ij}''-contribution to the pair interaction between those alkali ions which transfer some charge to the same C_{60} molecule, i.e.,

$$V_{ij}'' = \frac{2}{\varepsilon}\sum_\alpha c_i c_j C \qquad (10)$$

where $\alpha \in N_i \cap N_j$. Obviously, this contribution vanishes when r_{ij} exceeds a threshold value. Furthermore, the energy of C_{60}^{x-} increases the site energies too with

$$\epsilon_i'' = \frac{1}{\varepsilon}\sum_{\alpha \in N_i} c_i^2 C. \qquad (11)$$

The contribution of the van der Waals interaction to the site energy is distinct for the tetrahedral and octahedral sites and depends on the size of the alkali ion. To characterize this contribution we introduce an additional site energy, i.e.,

$$\epsilon_i = \begin{cases} \epsilon_o & \text{for octahedral sites} \\ \epsilon_t + \delta E_t & \text{for tetrahedral sites} \end{cases} \qquad (12)$$

where δE_t is considered as the difference between the two types of site and is expected to be positive for large alkali ions. In this expression the sum of ϵ_i' and ϵ_i'' is indicated by ϵ_o and ϵ_t for the octahedral and tetrahedral sites, respectively. The numerical calculations give $\epsilon_o = -1.178\,17e^2/\varepsilon a$ and $\epsilon_t = -1.37843e^2/\varepsilon a$ (where $e^2/a \approx 1$ eV), i.e. the tetrahedral sites are primarily occupied for $\delta E_t = 0$.

We are now in a position to express the total energy of the system within the lattice-gas formalism. The following Hamiltonian defines the energy for any configuration of alkali ions described by the variables η_i:

$$H = \sum_i \epsilon_i \eta_i + \frac{1}{2} \sum_{ij} V_{ij} \eta_i \eta_j \tag{13}$$

where $V_{ij} = V'_{ij} + V''_{ij}$, and ϵ_i, V'_{ij}, V''_{ij} are defined above by equations (12), (6) and (10).
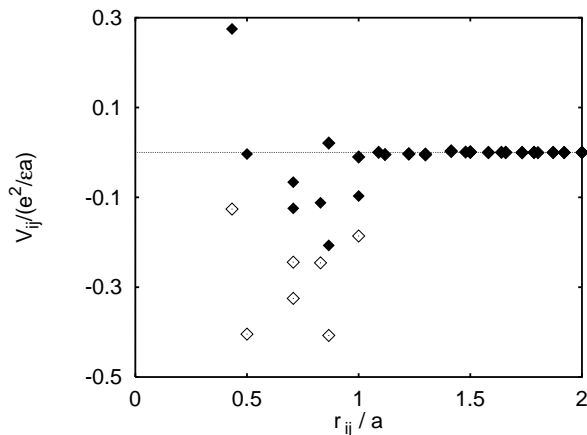
**Figure 1.** The effective pair interaction as a function of ion–ion distance. Open diamonds represent the pure coulombic interaction (V'_{ij}); closed diamonds refer to the full interaction (V_{ij}) including the energy of the charged C_{60} molecule.

The effective pair interactions V_{ij} versus r_{ij}/a are shown in figure 1. V_{ij} has different values for the same distances; in other words, the pair interaction depends on the orientation of the pair for some values of r_{ij}. Figure 1 demonstrates clearly that V_{ij} becomes extremely weak if $r_{ij} > a$. The attractive contributions of the effective pair interaction (for $a/2 < r_{ij} \leqslant a$) indicate the stability of alkali-intercalated fullerides at large alkali concentrations.

As a comparison V'_{ij} is also plotted in figure 1. The striking difference between V_{ij} and V'_{ij} indicates the important role of the electronic energy of C_{60}^{x-} ions; this will be investigated in detail in the subsequent sections.

3. Ground states

The electrostatic energies of some ordered structures have already been investigated [6, 7]. Now we concentrate on analysing such FCC structures which may be described by introducing three sublattices as demonstrated in figure 2. The sites of each sublattice form a FCC structure equivalent to the cage lattice. For later convenience the sublattices are labelled 0 for octahedral and 1 or 2 for tetrahedral sites. In the three-sublattice formalism the states are characterized by a vector consisting of sublattice occupations. For example, the state $(\sigma_0, \sigma_1, \sigma_2)$ denotes an alkali distribution where the sites of sublattice ν are occupied with a probability σ_ν. In general $0 \leqslant \sigma_\nu \leqslant 1$; however, $\sigma_\nu = 0$ or 1 for ordered structures. These ordered states are well known in crystallography. For example, the states (1, 0, 0), (0, 1, 1), and (1, 1, 1) are equivalent to the NaCl, CaF_2, and BiF_3 structures.
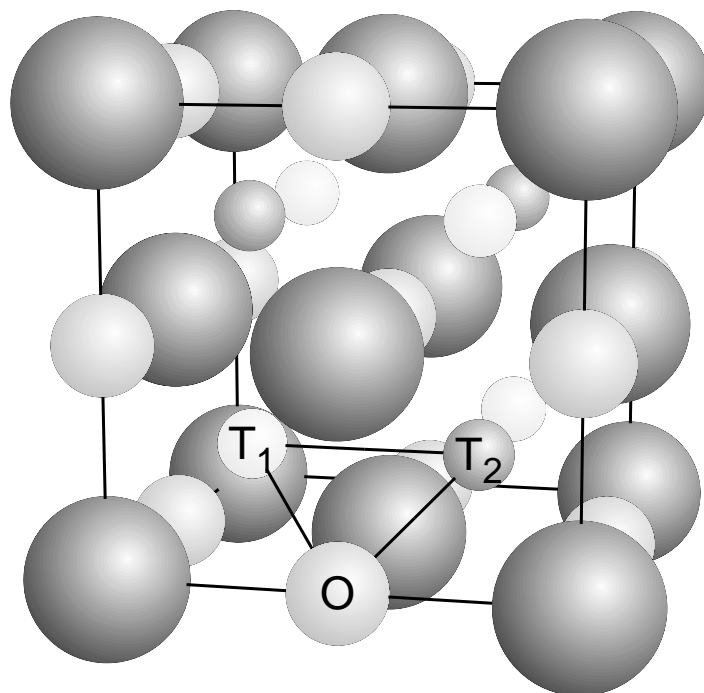
Figure 2. The arrangement of octahedral (medium-size spheres) and the two tetrahedral (dark and light small spheres) interstitial sites in an FCC lattice formed by C_{60} molecules (large spheres). The triangle represents the basic cluster of our CVM approximation.

One can easily see that according to the present model the C_{60} molecules are uniformly charged for the ordered states defined above. Consequently, the electrostatic energies are equivalent to the Madelung energies determined previously [6, 7]. In agreement with expectation the energies of ordered states are equivalent to those predicted by Rabe *et al* [7] when choosing $R = 3.5$ Å. In the above model, however, we have chosen larger R as detailed in the previous section.

In order to study the stability of the ground states we introduce the chemical potential μ which controls the alkali content (x) in the system. The stable state as a function of μ is determined by the minimum of the Gibbs potential per C_{60} defined as

$$\mathcal{G}_0 = \mathcal{H}_0 - \mu x \tag{14}$$

where the index 0 refers to zero temperature and $\mathcal{H}_0$ denotes the total energy per C_{60}. A simple numerical calculation gives the stable state as a function of μ and δE_t. The results are summarized in figure 3. This map shows that the alkali content increases with the chemical potential for a fixed δE_t. The present model suggests three stable ground states $((0, 0, 0), (1, 0, 0),$ and $(1, 1, 1))$ if $\delta E_t > 1.0106 e^2/\varepsilon a$. There is a region of δE_t when the $(0, 0, 0)$ state transforms directly to $(1, 1, 1)$ for increasing μ as is suggested theoretically by Fleming *et al* [6]. If $\delta E_t < 0.1406 e^2/\varepsilon a$, then the $(0, 1, 1)$ state is stable. This behaviour is a consequence of the fact that δE_t does not give an energy contribution to the states $(0, 0, 0)$ and $(1, 0, 0)$; however, it shifts the energy of the states $(0, 1, 1)$ and $(1, 1, 1)$ by the same value.

We have evaluated the energies of several ordered states related to a different sublattice
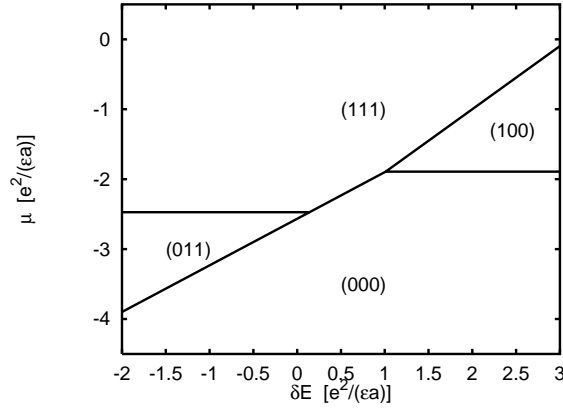
Figure 3. Ground states of $A_x C_{60}$ as a function of chemical potential μ and δE_t.

division of the tetrahedral sites. In order to determine the ground states of the systems both the octahedral and tetrahedral (FCC) lattices have been decomposed into four simple cubic lattices and the energies of all the possible ordered structures on the 12 sublattices have been calculated. In comparison with previous results we obtained higher energies for all the states distinguishable from the former ones. This investigation confirms the above sublattice division thereby providing a framework for later analysis.

4. Mean-field approximation

In this section the thermodynamic properties of the lattice-gas model defined by the Hamiltonian (13) are investigated by using a three-sublattice mean-field approximation. It is assumed that the interstitial points are occupied by an alkali ion with the same probability σ_ν within the sublattice $\nu = 0, 1, 2$.

By means of the mean-field approximation the energy per C_{60} molecule may easily be expressed in terms of the variables σ_ν as

$$\mathcal{H} = \sum_\nu \epsilon_\nu \sigma_\nu + \frac{1}{2} \sum_{\nu,\tau} J_{\nu\tau} \sigma_\nu \sigma_\tau \tag{15}$$

where the coupling constants $J_{\nu\tau}$ contain all the interactions between an alkali ion in sublattice ν and those ions residing in sublattice τ, i.e.,

$$J_{\nu\tau} = \sum_{j \in S_\nu} V_{ij} \qquad (i \in S_\tau) \tag{16}$$

where S_ν denotes the set of sites belonging to sublattice ν. The tensor of coupling constants is symmetric—that is, $J_{\nu\tau} = J_{\tau\nu}$. Furthermore, $J_{01} = J_{02}$ and $J_{11} = J_{22}$ because of the equivalence of the tetrahedral sublattices. Consequently, we have only four different coupling constants characteristic of the model in the mean-field approximation. Their values may be determined by straightforward numerical calculation which gives

$$J_{00} = -1.428\,79 \frac{e^2}{\varepsilon a} \qquad J_{01} = -0.290\,00 \frac{e^2}{\varepsilon a}$$

$$J_{11} = -1.603\,86 \frac{e^2}{\varepsilon a} \qquad J_{12} = -0.865\,60 \frac{e^2}{\varepsilon a} \tag{17}$$

if $R/a = 0.312$. Notice that all the $J_{\nu\eta}$ are negative, i.e., the attractive forces dominate the short-range repulsion (see figure 1).

The thermodynamic properties of the system are determined by the minimization of the Gibbs potential

$$\mathcal{G} = \mathcal{H} - T\mathcal{S} - \mu \sum_{\nu} \sigma_{\nu} \tag{18}$$

with respect to σ_{ν} for fixed temperature T and chemical potential μ. In the above expression the configurational entropy per C_{60} is given as

$$\mathcal{S} = -k_B \sum_{\nu} [\sigma_{\nu} \log \sigma_{\nu} + (1 - \sigma_{\nu}) \log(1 - \sigma_{\nu})] \tag{19}$$

where k_B is the Boltzmann constant.

5. The cluster-variation method

The cluster-variation methods (CVM) are successfully used for deriving phase diagrams with sufficient accuracy [27]. Two basic difficulties emerge when adapting this technique to the present lattice-gas model. On the one hand, the interstitial sites form a non-Bravais lattice; on the other hand, instead of the usual first- (and second-) neighbour interaction(s) there are a lot of parameters V_{ij} characteristic of the interaction between sites i and j. Here we suggest the application of a simple version of the CVM to increase the accuracy of the three-sublattice mean-field approximation.

First we introduce a set of variables $t(\eta_0, \eta_1, \eta_2)$ to denote the probability of a configuration (η_0, η_1, η_2) on three neighbouring sites where η_{ν} refers to the occupation of the site belonging to sublattice ν. The position of such a three-point cluster is indicated by a triangle in figure 2. The probability of a configuration on a part of this triangle may be easily expressed by the values of t. For example, the probabilities for pair and single-site configurations are given as

$$p_{01}(\eta_0, \eta_1) = \sum_{\eta_2} t(\eta_0, \eta_1, \eta_2) \qquad s_0(\eta_0) = \sum_{\eta_1, \eta_2} t(\eta_0, \eta_1, \eta_2)$$

$$p_{02}(\eta_0, \eta_2) = \sum_{\eta_1} t(\eta_0, \eta_1, \eta_2) \qquad s_1(\eta_1) = \sum_{\eta_0, \eta_2} t(\eta_0, \eta_1, \eta_2) \tag{20}$$

$$p_{12}(\eta_1, \eta_2) = \sum_{\eta_0} t(\eta_0, \eta_1, \eta_2) \qquad s_2(\eta_2) = \sum_{\eta_0, \eta_1} t(\eta_0, \eta_1, \eta_2).$$

The values of s_{ν} are directly related to the sublattice occupations σ_{ν} introduced previously, namely $s_{\nu}(1) = \sigma_{\nu}$ and $s_{\nu}(0) = 1 - \sigma_{\nu}$.

The contribution of the first- and second-neighbour interactions to the system energy is expressed by the variables $p_{\nu\tau}(1, 1)$ and only the remaining terms are approximated on the basis of mean-field theory. That is, now the energy per C_{60} molecule is given as

$$\mathcal{H}^{(CVM)} = 4V(1)[p_{01}(1, 1) + p_{02}(1, 1)] + 6V(2)p_{12}(1, 1)$$

$$+ \frac{1}{2} \sum_{\nu,\tau} J'_{\nu\tau} s_{\nu}(1)s_{\tau}(1) + \sum_{\nu} \epsilon_{\nu} s_{\nu}(1) \tag{21}$$

where $V(1) = 0.274\,59e^2/\varepsilon a$ and $V(2) = -0.003\,86e^2/\varepsilon a$ denotes the interactions V_{ij} at the shortest and second shortest distances, and $J'_{\nu\eta}$ is equivalent to $J_{\nu\eta}$ defined by equation (16) except that the coupling constants should be reduced by the contributions of $V(1)$ and $V(2)$:

$$J'_{01} = J_{01} - 4V(1) \qquad J'_{12} = J_{12} - 6V(2). \tag{22}$$

Here we restrict ourselves to demonstrating how the entropy may be derived on the analogy of a pair approximation developed by Bethe [28]. The non-Bravais lattice of interstitial sites may be built up by repeating periodically the triangle of an octahedral and two tetrahedral sites as prescribed by the primitive cell of the FCC structure. This construction makes it clear that each triangle is surrounded by twelve triangles with the same orientation. According to the pair approximation the entropy is expressed by the probability of pair configurations [28, 29]. In the present situation the probability of a configuration on a pair of triangles is approximated as a product of $t(\eta_0, \eta_1, \eta_2)$ variables. The calculation leads to the following formula:

$$\mathcal{S}^{CVM} = -6k_B \sum_{\eta_0, \eta_1, \eta_2} t(\eta_0, \eta_1, \eta_2) \log t(\eta_0, \eta_1, \eta_2)$$
$$+ k_B \sum_{\nu < \tau} x_{\nu\eta} \sum_{\eta_\nu, \eta_\tau} p_{\nu\tau}(\eta_\nu, \eta_\tau) \log p_{01}(\eta_\nu, \eta_\tau) + k_B \sum_{\nu} y_\nu \sum_{\eta_\nu} s_\nu(\eta_\nu) \log s_\nu(\eta_\nu)$$

$$(23)$$

where $x_{01} = x_{02} = y_1 = y_2 = 2$ and $x_{12} = y_0 = 1$.

Substituting equations (21) and (23) into (18) one obtains the Gibbs potential as a function of the variables $t(\eta_0, \eta_1, \eta_2)$. As is well known, $\mathcal{G}$ reaches its minimum at the equilibrium values of these variables. In fact we have seven independent variables because the eighth configuration probability is determined by the condition of normalization. The numerical treatment is similar to those followed in mean-field approximation. The only difference is that instead of the three σ_ν-variables we now have seven parameters with respect to which we have to minimize the Gibbs potential.

All of the phase diagrams have been recalculated by using this technique. The differences between the results of mean-field approximation and the CVM are not relevant, as demonstrated in the subsequent section.

6. Results

The results of the numerical calculations are summarized in temperature–composition $(T–x)$ phase diagrams for different values of δE_t. The alkali concentration is related to sublattice occupations $(x = \sum \sigma_\nu)$ determined directly by the numerical procedure.
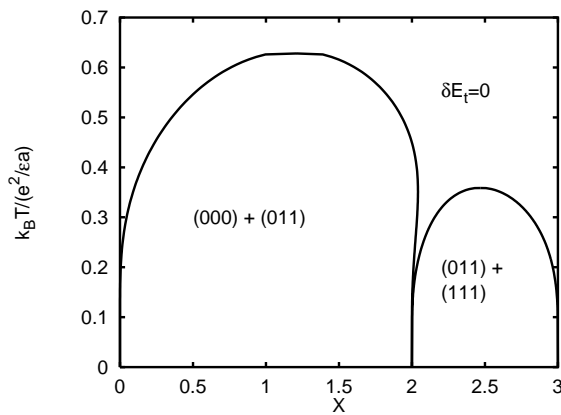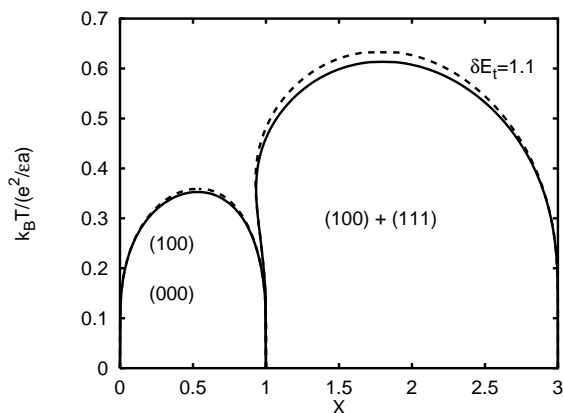

Figure 4. The phase diagram for $\delta E_t = 0$ in the mean-field approximation.

In agreement with the ground-state analysis, figure 4 illustrates that only the (0, 0, 0), (0, 1, 1), and (1, 1, 1) phases are stable at low temperatures for $\delta E_t = 0$. For intermediate compositions the system segregates into two phases as indicated in the figure. It is emphasized that in the high-temperature phase the tetrahedral and octahedral sites are occupied with different probabilities. More precisely, the tetrahedral sites are preferred to the octahedral ones for $\delta E_t < 0.1402$. For example, if the temperature is decreased for a fixed concentration $x = 2$ the present model suggests a continuous ordering process observed for the CaF_2-type superionic conductors [26].
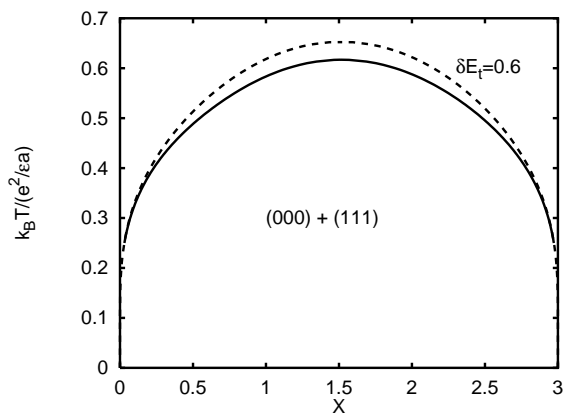
Figure 5. A comparison of phase diagrams suggested by mean-field approximation (the dashed line) and the CVM (the solid line) for $\delta E_t = 0.6e^2/\varepsilon a$.

Figure 5 shows the simplest phase diagram characteristic to the present model for $0.1402 < \delta E_t/(e^2/a) < 1.0106$. In this case the disordered state decomposes into high- and low-concentration regions corresponding to the (0, 0, 0) and (1, 1, 1) states in the zero-temperature limit.

Figure 6. The phase diagram for $\delta E_t = 1.1e^2/\varepsilon a$ determined by mean-field approximation (the dashed line) and the CVM (the solid line).

As mentioned above the energy of both the (0, 1, 1) and (1, 1, 1) phases increases with δE_t; meanwhile the energy of the phases (0, 0, 0) and (1, 0, 0) remains unchanged.

As a result the (1, 0, 0) phase appears in the phase diagrams for $\delta E_t > 1.0106 e^2/\varepsilon a$ as demonstrated in figure 6. Notice that the CVM suggests lower transition temperatures in comparison with mean-field results. In general we can say that the difference is only a few per cent for $R/a = 0.312$; however, it becomes larger for smaller R when the short-range interactions are more repulsive.
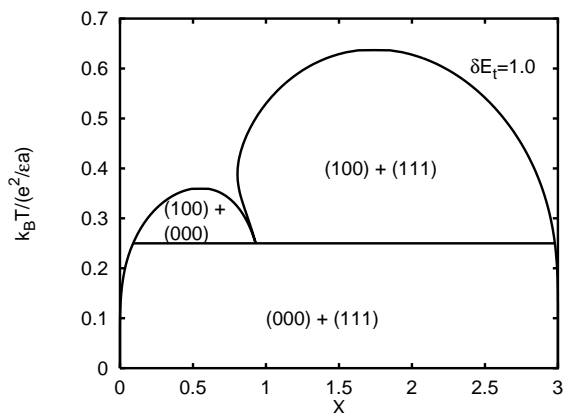
Figure 7. Mean-field analysis of the lattice-gas model suggests a eutectoid phase transition for $\delta E_t = e^2/\varepsilon a$.

Slightly below the stability threshold value one can observe a eutectoid transition as plotted in figure 7. This phase diagram is similar to those suggested by Poirier and Weaver [12] and Winkler and Kuzmany [13] for the $K_x C_{60}$ system for $x < 3$. With x-ray photoemission and Raman spectroscopy they observed a reversible transformation from KC_{60} to a mixed phase of C_{60} and $K_3 C_{60}$ at the eutectoid temperature ($T_{eut} = 150 \pm 10$ °C). For $\delta E_t = e^2/\varepsilon a$ the present approach predicts $k_B T_{eut} = 0.250 e^2/\varepsilon a$.

It is emphasized that in the above phase diagrams the two tetrahedral sublattices are occupied with the same probability, implying the union of these sublattices. However, some modification of the model parameters results in the appearance of the (0, 1, 0) and (1, 1, 0) states. This is the situation when accepting the spherical-shell model suggested by Rabe *et al* [7] with the radius of the C_{60} molecule ($R = 3.5$ Å). Unfortunately the rigorous analysis of all of the possible diagrams as a function of R and δE_t goes beyond the scope of the present paper.

7. Summary and conclusions

We have developed a lattice-gas model for investigating the formation of different alkali-intercalated fullerides with FCC structure. In this (Ising-type) model the tetrahedral and octahedral interstitial sites of the cage lattice are empty or singly occupied by one type of alkali ion. It is assumed that the Coulomb interaction between two alkali ions is screened out by distributing their s electrons uniformly on their nearest-neighbour C_{60} molecules. This plausible assumption results in a short-range interaction which is very convenient for the lattice-gas formalism. For ordered structures this model reproduces the electrostatic energies found by previous authors [6, 7].

Besides the electrostatic energy the model takes into account the electronic energy of C_{60}^{x-} ions as well as the van der Waals interaction between an alkali ion and a C_{60} molecule. A

series of quantum chemical calculations show that the total energy of a charged C_{60} molecule has a term proportional to the square of its charge. This non-linear contribution mediates an interaction between those alkali ions which transfer electrons to the same C_{60} molecule. This contribution is equivalent to the electrostatic energy of a charged spherical shell with radius R. The site energy (δE_t) characteristic of the extra van der Waals interaction at the smaller (tetrahedral) interstitial voids makes a distinction between the different types of alkali atom. Without this term the tetrahedral sites are preferred in the system as observed for A = Li and Na. This energy contribution increases with the size of the alkali atom and the octahedral sites are primarily occupied when δE_t exceeds a threshold value.

The thermodynamic properties of this model are investigated by using a three-sublattice mean-field approximation and the CVM. The general features are illustrated via a series of phase diagrams. These diagrams illuminate the effect of the size of the alkali ion on the ordering processes.

Choosing the dielectric constant to be $\varepsilon \approx 4$ [21] the maxima of the predicted ordering temperatures agree qualitatively with those expected on the basis of recent experiments. There are more reliable data on the phase separation temperature observed in the $K_x C_{60}$ system. The present model can describe such types of phase diagram (see figure 7) for a very narrow range of δE_t in agreement with the fact that this feature has not been observed for other fullerides [30]. When applying pressure in order to contract the lattice, the varying model parameters can cause a sharp variation of the eutectic temperature.

The generalization of the present description for alkaline-earth (or other) metals is straightforward. If the intercalated atoms have z valence electrons we should substitute a new energy unit, $(ze)^2/\varepsilon a$, for $e^2/\varepsilon a$ and find a suitable δE_t expressed in this unit. Due to using the enhanced energy unit the $A_2 C_{60}$ composition can appear over a wider range of δE_t. At the same time the variation of the lattice constant modifies the ratio R/a and can lead to some change in the phase diagrams.

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