

Test of a simple model of the intermolecular potential of C_{60} on the series of K_nC_{60} , $0 < n \leq 6$, crystals

Cite as: J. Chem. Phys. **102**, 8132 (1995); <https://doi.org/10.1063/1.469224>

Submitted: 20 January 1994 . Accepted: 09 February 1995 . Published Online: 04 June 1998

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Test of a simple model of the intermolecular potential of C_{60} on the series of K_nC_{60} , $0 < n \leq 6$, crystals

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(Received 20 January 1994; accepted 9 February 1995)

We perform a further test of a simple atom-atom model of the intermolecular potential of C_{60} by applying it to the alkali-metal doped crystals K_nC_{60} , $0 < n \leq 6$. The model consists in an icosahedron of 12 Lennard-Jones interaction sites and no further refinement of its LJ parameters is performed. The electrostatic interactions due to the charges transferred by K atoms are taken into account. Several static and dynamical properties, at room temperature and zero pressure, are calculated by constant-pressure molecular dynamics methods. Comparison with available experimental data shows that the icosahedron model plus an accumulative charge at each interaction site, gives good results for $n \leq 4$, but further improvement is needed for $n = 6$. © 1995 American Institute of Physics.

I. INTRODUCTION

In a recent paper¹ we proposed a simplified atom-atom intermolecular potential model for the condensed phases of C_{60} . Here, we test this model by calculating the crystal structures and dynamical properties of the series of K_nC_{60} crystals, $0 \leq n \leq 6$. As the phase diagram of these compounds exhibits a rich variety of crystalline phases, depending on the kind and location of interstitial atoms and the orientational molecular disorder,² these calculations are a further and stringent test for any proposed intermolecular potential model of C_{60} .

At room temperature, pure C_{60} packs in a fcc structure, with the molecules performing diffusive reorientational motion.³ By decreasing the temperature, a first order phase transition to a simple cubic Pa3 structure is found at 250 K. In this phase, and above 90 K, the molecules perform thermal jumps between nonequivalent orientations around the crystalline site symmetry axes C_3 . At 90 K a glass transition, due to the "freezing in" of the molecular motion, is observed.³⁻⁷

In the fcc lattice of C_{60} crystals there are two types of interstices that can be occupied by atoms: the octahedral sites at $(\pm 1/2, 0, 0)$ and the tetrahedral sites at $(\pm 1/4, \pm 1/4, \pm 1/4)$. In the high temperature phase of KC_{60} crystals, the K atom is located at the octahedral sites,⁸ the K_2C_{60} phase is unstable and segregates in crystals with $n = 0, 1$, and 3, and in K_3C_{60} crystals both types of sites are fully occupied.² The packing fraction of the fcc structure is 0.74 and it can support a nominal composition K_nC_{60} , with $0 \leq n \leq 3$. To include more interstitial atoms the stable structure is now the bcc, with a packing fraction 0.68. The number of interstitial sites increases from three to six in the bcc crystal, all of them equivalent, with distorted tetrahedral symmetry. K_4C_{60} packs in a body centered tetragonal unit cell, which is a small distortion of a bcc lattice.^{9,10} K_5C_{60} is unstable, similar to

K_2C_{60} , and K_6C_{60} packs in a bcc structure.^{11,12} The absorption of potassium atoms saturates at the stoichiometric composition $n = 6$, and further doping segregates out.² The phase diagram of Rb_nC_{60} is quite similar to that of K_nC_{60} but for smaller alkali-metals there are large differences in the allowed stoichiometric compositions.^{2,13} Figure 1 shows the two possible lattices of C_{60} molecules, fcc and bcc, and the interstices that can be filled up in each case.

Alkali-doped A_nC_{60} ($A = K, Rb, Cs$) crystals are highly ionic compounds, of large cohesive energies,¹⁴ in which up to $n = 6$ electrons are completely transferred to C_{60} .^{2,15} In this paper we study the limits of an ionic intermolecular potential model in describing the structural and dynamical properties of the whole series: K_nC_{60} , $0 \leq n \leq 6$. We assume complete charge transfer from the potassium atoms to C_{60} , with a homogeneous distribution on all sites, and perform classical constant pressure MD simulations of this series of ionic crystals. Comparison with available experimental data shows that many structural and dynamical properties can be reproduced in this way, as was pointed out by several authors.^{6,15-17} This is due to the strong electrostatic interactions, which overwhelm the usual van der Waals and multipolar electrostatic interactions of uncharged molecules.

Cheng and Klein¹⁷ performed constant pressure classical molecular dynamics (MD) simulations of the K_nC_{60} ($n = 3, 6$) doped crystals at room temperature and zero pressure, obtaining good agreement with available experimental data. They also found that fcc crystals have the lowest configurational energy for $n \leq 3$ and the bcc ones for $n > 3$. Their intermolecular potential model is of the nonbonded atom-atom type, with 60 LJ interaction centers at the C atoms. The charge transferred by alkali atoms is located on the molecular surface, equally distributed among the 60 C atoms. In these crystals the charge distribution of the isolated molecule can be neglected, even when it is necessary for pure C_{60} crystals, to attain the low temperature cubic unit cell and the experimental molecular orientation.^{5-7,18,19} This intermolecu-

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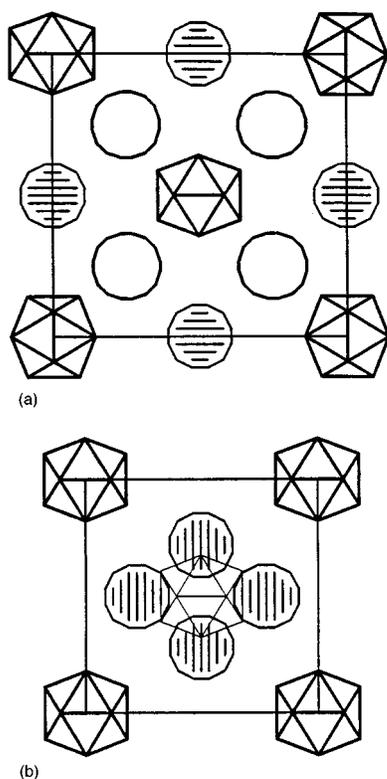


FIG. 1. fcc and bcc structures of potassium doped C_{60} crystals with an icosahedron model for C_{60} molecules, the calculated molecular orientations for each stoichiometric composition are given in the text: (a) fcc unit cell, white circles indicate interstices of octagonal symmetry, shaded circles those of tetrahedral symmetry; (b) bcc unit cell, all interstices are equivalent.

lar potential model was successfully used, afterwards, in several calculations: in Refs. 6 and 7 the temperature of the order–disorder reorientational transition of K_3C_{60} crystals is estimated with the Ising model and in Ref. 20 the lattice vibrational density of states of K_3C_{60} is calculated in the harmonic approximation, in accord with experimental data.

Nevertheless, this detailed molecular model consists of 60 charged LJ sites and this high number of interaction centers makes very expensive and lengthy the simulation of the condensed phases of pure and doped C_{60} crystals, making it difficult to study the whole doped series and the effect of different initial lattice configurations or of the applied periodic boundary conditions. Moreover, there are other problems that also need a large number of molecules to be resolved, like an accurate calculation of the lattice vibrational density of states and a study of the disorder in samples of K_xC_{60} , $x \neq$ integer, where phase segregation between several stoichiometric crystals is found.^{2,8}

Due to this fact and taking into account the high point group symmetry (I_h) of C_{60} , we proposed a simplified model of the intermolecular potential for the condensed phases of C_{60} .¹ This model consists in an icosahedron of 12 LJ interaction sites, with their ϵ and σ LJ parameters adjusted so as to fit the experimental data on packing energy and crystal structure of pure C_{60} . The reduction in the number of interaction centers makes affordable the above mentioned calculations. This model reproduces the properties of the high temperature cubic plastic phase and shows an order–disorder

phase transition to a low temperature cubic Pa3 phase. It gives a qualitative pattern of the C_{60} phase diagram and the calculated unit cell parameters and energies are in accord with experimental data. It fails in reproducing the temperature of the phase transition (which is calculated too low) and the experimental molecular orientation at low temperatures.¹ Nevertheless, due to its extreme simplicity and the qualitative agreement attained for C_{60} ¹ and C_{70} ²¹ crystals, it is worthwhile to perform a further test of this model with the series of alkali-doped C_{60} crystals.

In Sec. II we present the intermolecular potential model, in Sec. III the performed calculations, in Sec. IV the obtained results, in Sec. V a discussion of the molecular model for C_{60}^{-n} and in Sec. VI the conclusions.

II. THE INTERMOLECULAR POTENTIAL MODEL

The simplified intermolecular potential model for C_{60} is of the nonbonded atom–atom type.¹ As a first approximation to the real intermolecular potential of C_{60} , we replaced the molecule of 60 C atoms by an icosahedron of 12 LJ interaction sites, both belong to the point group symmetry I_h . The icosahedron has a reduced radius of 2.546 Å (that of C_{60} is 3.55 Å). This value was obtained¹ by taking into account that in alkali-doped crystals there is complete charge transfer from the alkali atoms to the C_{60} molecule. As these charges are located at the molecular surface, the generated molecular multipolar moments Q_{6m} (the first ones different from zero, except the total charge Q_0) of the real molecule are equal to those generated by the icosahedron if the latter has a reduced radius. The LJ parameters ($\epsilon=0.75$ kJ/mol, $\sigma=6.20$ Å) of the 12 sites model were afterwards adjusted so as to fit the experimental unit cell parameters and heat of sublimation of pure C_{60} crystals.¹

In our MD simulations of K_nC_{60} crystals we use the icosahedron model of Ref. 1, plus the n charges transferred by the K atoms, equally distributed among the 12 sites. For K atoms we use the LJ model ($\epsilon=0.044$ kJ/mol and $\sigma=4.686$ Å) of Ref. 17. The cross rules are applied for the cross-site interactions.

III. CALCULATIONS

The calculations were performed with a classical constant-pressure MD algorithm, which is useful to analyze the stability of the proposed crystal structures, by allowing structural transformations. As for any algorithm that searches configurations of minimum energy, the system can be located in secondary minima (metastable phases). Due to this problem, and the time scale of this type of calculations, some crystals were studied with different initial configurations, to confirm the most stable structure at $T=300$ K and $P=0$ kbar.

The MD algorithm is fully explained in Refs. 22 and 23. The molecules are considered as rigid bodies, the motion of the centers of mass is integrated with a third-order predictor–corrector algorithm, and their reorientational motion is followed using quaternions and four-order algorithm. In our calculations the molecular inertial moment is rescaled to its real value, to correct for the reduced size of our molecular model.

TABLE I. Unit cell parameters and configurational energies calculated for the series K_nC_{60} , $0 \leq n \leq 6$. Units: T (K); P (kbar); $a, b, c, \alpha, \beta, \gamma$ unit cell parameters (Å, deg); V cell mean molar volume (10^3 m^3). In each case, the first lines give the calculated values and the last one the available experimental data.

	T	P	Uconf	a	b	c	α	β	γ	V cell
C_{60} ^a	300(10)	0.0(2)	-190.7(2)	14.09(6)			90.0(2)			fcc 42.1
Expt. ^b	300(10)	0.0(2)		14.17			90.0(2)			fcc 42.8
K_1C_{60}	300(10)	0.4(3)	-268.0(4)	14.02(1)			90.0(2)			fcc 41.5
Expt. ^c	473	0		14.07			90			fcc 41.9
K_2C_{60}	309(6)	0.6(2)	-394.1(3)	10.25(2)	10.54(2)	16.34(2)	90.	90.	120.	hcp 46.1
	295(9)	0.5(2)	-399.3(2)	14.69(5)			90.0(2)			fcc 47.7
K_3C_{60}	294(7)	0.0(2)	-552.3(5)	14.44(4)			90.0(2)			fcc 45.3
Expt. ^{d,e}	300	0	-496	14.24(1)			90			fcc 43.5
K_4C_{60}	302(11)	0.0(5)	-697.0(5)	11.94(3)	11.97(7)	10.51(2)	90.0(3)			bct 45.1
Expt. ^f	300	0		11.88		10.77	90			bct 45.7
K_5C_{60}	306(8)	0.0(3)	-835(1)	14.93(3)			90.1(2)			fcc 50.1
K_5C_{60}	300(3)	0.3(5)	-846(5)							52.3
K_6C_{60}	316(7)	0.0(5)	-974.0(2)	22.94			90			bcc 45.3
K_6C_{60}	320(13)	0.0(5)	-997.1(2)	10.20			65.5			trigonal 50.6
Expt. ^{g,h}	300	0	-956	11.39			90			bcc 44.5

^aReference 1.

^bReference 3.

^cReference 8.

^dReference 24.

^eMeasured heats of formation in Ref. 14.

^fReference 10.

^gReference 11.

The studied samples consist of 54 and up to 256 C_{60} molecules. The cutoff radius for intermolecular interactions is of 18 to 21 Å in the real space, and correction terms due to the truncated tails of the potentials are taken into account. The electrostatic interactions are handled with the Ewald's sums method.

The time step is of 0.0025 to 0.005 ps, and typically the systems were equilibrated for 10 000 time steps and measured in the next 10 000 time steps.

IV. RESULTS

A. KC_{60}

X-ray diffraction and differential scanning calorimetry measurements⁸ revealed the unusual thermal stability of the AC_{60} crystals ($A=K, Rb, \text{ or } Cs$) at high temperatures. Above 433 K KC_{60} packs in a rocksalt structure in which only the octahedral sites are occupied by K^+ ions and the C_{60} molecules show orientational disorder, as in pure C_{60} crystals.

In our MD simulation this structure is stable and shows a contraction of the unit cell, relative to pure C_{60} , due to the strong electrostatic interaction of C_{60}^- with K^+ ions. Table I shows the calculated configurational energy and unit cell parameters.

The C_{60} molecules show a continuous reorientational motion, to achieve, in an average over time, the local site symmetry. The calculated reorientational time is $\tau_2=7$ ps. As in pure C_{60} crystals,¹ the orientational distribution is not uniform and it gives a measure of the potential well in which the molecules are moving. The calculated vibrational density of

states (VDS) shows a band at $\sim 60 \text{ cm}^{-1}$ for the K displacements and nonzero values at zero frequencies for the diffusive molecular reorientational motion.

Taking into account that the icosahedron model gives, for pure C_{60} , an order-disordered phase transition at ~ 120 K,¹ while it is observed at 240 K,³ we can see that this simulation is reproducing the stable cubic high temperature phase of KC_{60} .²

B. K_2C_{60}

The experimental data implies that this phase is not stable. Nevertheless, we performed two MD simulations on initial fcc arrays of C_{60} molecules with different initial location for the K atoms.

One of the samples remain fcc, with the K atoms located at tetrahedral sites. The molecular orientation is similar to that found in K_3C_{60} crystals: the molecules are oriented with three of their C2 axes along the C4 crystalline axes and exhibit a static disorder between the two possible orientations (merohedral disorder).²⁴

The second sample transformed to a hcp structure with a slightly higher configurational energy than the first system. This sample is in a plastic phase: the molecules reorientate continuously, with a characteristic time $\tau_2 \sim 14$ ps. The a and b unit cell axes (Table I) are larger than in the ideal hcp, due to the regular location of K atoms at interstitial sites.

Comparison of the free energy of these systems with those of KC_{60} and K_3C_{60} could define whether these structures are stables or if there is segregation into K_3C_{60} and C_{60} crystals. These quantities can be estimated following the ap-

proach of Refs. 10 and 25, where the relative stability of the various A_nC_{60} phases is established by electrostatic calculations. Using these data no stable structure is calculated for K_2C_{60} crystals: the contribution of our calculated van der Waals terms to the total energy do not change the above mentioned results of Refs. 10 and 25.

C. K_3C_{60}

The crystal structure of K_3C_{60} was measured by x-ray diffraction at room temperature.²⁴ It belongs to the $Fm\bar{3}m$ space group and consists in a fcc lattice of C_{60} molecules with K atoms occupying all octahedral and tetrahedral interstitial sites. The molecules are oriented with hexagonal faces along $[1,1,1]$ directions and show a static disorder between two possible orientations, related to each other by a 90° rotation around a crystallographic $[100]$ axis or by a 44.5° rotation around $[111]$ axes [Fig. 1(a)].

In our MD measurement of 50 ps we observed no molecular reorientations, in accord with measured NMR reorientational times of $\approx 10^{-9}$ seg.^{9,26,27} The molecules show merohedral disorder, but not the orientational pattern suggested in Refs. 28 and 29.

The calculated vibrational density of states follows the general pattern of Ref. 20, although the rotational modes are calculated at 17 cm^{-1} , too low by comparison with experimental data ($\sim 30\text{ cm}^{-1}$).³⁰ This frequency depends on the size of the tetrahedral ion²⁷ and our low value implies that further improvement of the repulsive term of our potential model is needed. The molecular VDS spans the range from 10 to 60 cm^{-1} and the vibrational modes of the K atoms show two distinct peaks (at ~ 40 and $\sim 100\text{ cm}^{-1}$) due to, respectively, the K atoms at tetrahedral and octahedral sites. The band at $\sim 100\text{ cm}^{-1}$ is in accord with neutron²⁰ and Raman measurements.³¹

D. K_4C_{60}

The crystal structure of K_4C_{60} is body centered tetragonal (bct), space group $I4/mmm$,¹⁰ similar to that of Rb_4C_{60} .⁹ The alkali atoms are located at $(\pm 0.23, 0.5, 0)$ sites, with four K atoms in the basal plane ($a=b>c$) and two atoms in the planes ac and bc , at $\hat{c}=1/2$. This structure can be obtained from the bcc one of K_6C_{60} by removing two alkali atoms on the vertical faces.

Two MD samples, with initial fcc and bcc arrays of C_{60} molecules, transform in a bct structure. Table I shows the unit cell parameters. The K atoms in the ab plane are located at $(\pm 0.5, \pm 0.2, 0)$ and those in the ac and bc planes at $(\pm 0.3, 0, 0.5)$ and $(0, \pm 0.3, 0.5)$. All C_{60} molecules have one of its C_5 axes oriented along the crystallographic axis c and the molecules reorientate continuously around it, with a decay time $\tau_2=11$ ps.

E. K_5C_{60}

The experimental evidence implies that, at this stoichiometric composition, there is segregation in bct plus bcc structures.² Nevertheless, we studied two samples, with an initial fcc and bcc arrays of C_{60} molecules.

The initial fcc array is very stable. Surprisingly, all molecules have the orientation measured in the low temperature Pa3 phase of pure C_{60} , which consists in a 98 deg. counterclockwise rotation around the corresponding crystalline C3 axis, starting from a F3m initial orientation.³

The bcc array is unstable and the MD box distorts to a tetragonal symmetry ($a_{MD}=b_{MD}<c_{MD}$, $\alpha\approx\beta\approx\gamma\approx 90$ deg). Table I shows the calculated configurational energy, which is lower than that of the first sample.

As for K_2C_{60} , free energy estimations following the approach of Ref. 8 imply that it is more probable a segregation in K_4C_{60} and K_6C_{60} phases.

F. K_6C_{60}

X-ray powder measurements of K_6C_{60} crystals were reported in Refs. 11 and 12. The structure belongs to the $Im\bar{3}$ space group and consists in a bcc array of C_{60} molecules, with four K atoms in each face of the bcc unit cell, at positions $(0.5, 0.27, 0)$ [Fig. 1(b)]. The C_{60} molecules are orientationally ordered with one of their C_2 axes parallel to a crystallographic axes, all molecules show a parallel orientation. In this crystalline structure there are three nonequivalents sites for the 60 C atoms, instead of one as in the isolated molecule.

A MD simulation of the experimental bcc array turned out to be unstable and evolved towards a structure that depends on the initial array and sample size. These systems are very sluggish and the final arrays resemble the patterns found for the transition-metals oxides.³² Therefore and to find out the structure of minimum configurational energy, several calculations were performed, starting from bcc, fcc, and hcp arrays.

The unique bcc array that could be stabilized was one that doubles the experimental bcc unit cell along the three axes ($Z=8$), with the molecular orientations alternating in a 90 deg rotation about the $[100]$ axis.

The structure of minimum configurational energy turned out to be trigonal, and therefore this potential model fails in reproducing the experimental unit cell.^{11,12} The calculated structure resembles the experimental data: The molecules are orientationally ordered and parallel, with one molecular C_2 axis pointing along the main diagonal of the trigonal lattice. Table I shows the calculated structures and energies.

Using trigonal coordinates, the unit cell angles $\alpha=\beta=\gamma$ take a value of 60 deg in a fcc unit cell and of 70.53 deg in the bcc case. Our calculated value of $\alpha\approx 65$ deg shows that the expected structural transformation, upon doping, is incompletely reproduced by this potential model.

V. THE INTERMOLECULAR POTENTIAL MODEL FOR C_{60}^{-n}

Our calculations show that a simple icosahedron model gives a good picture of the intermolecular interactions for K_nC_{60} , $n\leq 4$. Nevertheless, the proposed model is a very rough approximation of the real intermolecular potential, and there are several reasons for its failure at high values of n . Here, we discuss each term of this semiempirical model.

A. Electrostatic interactions

First of all, if we assume that the charge transferred by the alkali atoms is homogeneously distributed on the molecule surface (π molecular orbital), these results could imply that the icosahedron do not simulate well enough the molecular multipolar moments of the real molecule. This problem is enhanced for increasing values of molecular charge, and for $n=5,6$ it should be necessary to simulate also molecular multipolar moments higher than Q_{6m} .

On the other hand, the assumption that the charges transferred by K atoms are homogeneously distributed on the molecule surface is also an oversimplified model. It does not take into account that upon condensation, the molecule adapts to the crystalline site symmetry, lowering its isolated point group symmetry by cage distortions or by an effective average introduced by merohedral or dynamical disorder.

Considering the last point, our model seems to be adequate for $n \leq 3$. X-ray measurements indicate that there is almost no distortion of the C_{60} cage in K_3C_{60} crystals²⁴ and that the molecule adapts to the site symmetry by orientational disorder. There is no experimental data for cage deformation in K_4C_{60} crystals, but we calculate a plastic phase and, due to its orientational disorder, it should not be necessary a molecular distortion in the crystal.

Erwin *et al.*³³ performed a first principles electronic structure calculations for crystalline K_6C_{60} and proposed a nonuniform distribution for the 6 electrons on the π band, that preserves the crystal site symmetry and minimizes the Madelung energy. The molecule distorts to attain the site symmetry T_h (the maximum common subgroup of the cubic group O_h and the icosahedral group I_h), by a molecular elongation along the three crystallographic axes, with the excess charge accumulating at the C atoms that are nearer to K atoms.^{33,34} Following this suggestion we tested a molecular model in which the six electrons are located at the molecular surface, along the three crystallographic axes (on three molecular C_2 axes). Again, a trigonal unit cell is calculated more stable.

Here, we have studied two very different charge distribution models, obtaining similar results for K_6C_{60} crystals. In fact, the results obtained in this work, for all K_nC_{60} crystals, do not differ too much from those obtained by locating n electrons at the molecular origin.³⁵ For C_{60}^{-n} ion the first multipolar moments different from zero are Q_0 , Q_{6m} , Q_{10m} . Taking into account that the electrostatic interaction series is of the form $Q_i Q_j / r^{(i+j+1)}$, it can be seen that the leading term is, by far, the total charge-total charge interaction. Due to these facts, it seems improbable that a more detailed electrostatic model could substantially change these results.

B. van der Waals interactions

The remaining terms of this semiempirical intermolecular potential are the van der Waals terms, that here were simulated with a site-site (12-6) LJ potential. There are several reasons that imply, most probably, that the repulsive term of our icosahedron model needs further improvement.

On one hand, in K_3C_{60} crystals we calculate a too low librational frequency. In Ref. 27 it is shown that when the

size of the alkali ion (A) is greater than the size of the tetrahedral site, the energy of the librational band increases, implying that the repulsive term of the C_{60} -A interaction is the main factor that determines the orientational potential. As the LJ potential for K atoms gives good results when used with a detailed model of C_{60} ,¹⁸ it is our repulsive model of C_{60} that needs further improvement.

On the other hand, there is ample evidence that (12-6) LJ systems pack in fcc or hcp structures.³⁶ In fact, it is known that particles interacting with a repulsive potential of the form $V(r) = \epsilon(\sigma/r)^n$ pack in a fcc structure if $n > 7$. For softer potentials ($n \leq 7$) the system shows a phase transition, by increasing the temperature, to a bcc phase before melting.³⁷ This behavior is typical of metals.³⁷

There is a strong analogy between the series A_nC_{60} and interstitial solid solutions of metals, in which atoms of much smaller radius can be dissolved and the solutions have always the structure of the solvent.³⁸ Pursuing the analogy, C_{60} can be considered as a transition metal atom because the electrons transferred by the alkali atoms remain tightly bound to C_{60} . In Refs. 39 and 40 the total energy of bcc and hcp structures relative to fcc in a transition metal is calculated as a function of the number of valence electrons. There is a striking similarity between the behavior of A_nC_{60} series upon doping and that of transition metals with increasing number of valence electrons, the structural trends are totally similar in both systems. Whether this analogy is real or casual, it is useful for a comparison of the analytical forms of the intermolecular potential used in both cases. In particular, in Ref. 41 a potential interaction model conveniently similar to the LJ form is suggested: $V(r) = \epsilon_1(a/r)^n - \epsilon_2(a/r)^m$, where a is the unit cell parameter.

VI. CONCLUSIONS

The main aim of this study was to obtain a qualitative idea of the C_{60}^{-n} interactions in the phase diagram of K_nC_{60} crystals, $n \leq 6$, as it is not always possible to perform this study with detailed intermolecular potential models.^{5,6,17,19} In this paper we studied a simple model of the intermolecular potential for the C_{60}^{-n} ion, obtaining good results for the static and dynamical properties of K_nC_{60} crystals, with $n \leq 4$. Unfortunately, it is inaccurate for $n=6$ and in the preceding section we have discussed several possible reasons for its failure.

It is also clear that the electrostatic interactions and excluded molecular volume dominate in the packing of these highly ionic compounds. It could be a useful comparison with a simple system of two LJ particles, one for the K atom and one that simulates, at zero order, the C_{60} molecule (of $\epsilon=21$ kJ/mol and $\sigma=9.15$ Å, Ref. 42). There are very clear and classical works on the structures of simple ionic crystals,⁴³ studying the crystalline stability of fcc, bcc, and hcp structures as a function of the ionic radius. These structures could be a very useful reference and they should give us the stable, high temperature plastic phases of K_nC_{60} crystals. To our knowledge, there is no such study for crystals similar to the series K_nC_{60} , $4 \leq n \leq 6$.

ACKNOWLEDGMENTS

Z.G. thanks an invitation of the Department of Physics of the University of Porto Alegre and the kind hospitality of its people. Z.G. also thanks A. Cheng and M. L. Klein interesting comments and further information on their calculations in Ref. 18. We acknowledge the Supercomputer Center of the University of Porto Alegre, where part of these calculations were performed.

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