

'ELASTIC' MODES IN INTERACTION OF THE IMPURITY ATOMS GOVERNING THE TENDENCY TO DECOMPOSITION OF THEIR INTERSTITIAL SOLUTION WITHIN THE F.C.C. FULLERITE

Dmytrenko O. P., Kulish M. P., Leonov D. S.⁽¹⁾, Tatarenko V. A.^{(2)*}

Sub-Faculty of Physics of Functional Materials, Taras Shevchenko Kyiv National University,
2/1 Academician Glushkov Prospekt, UA-03022 Kyiv-22, Ukraine

⁽¹⁾ Department of Physics of Nanostructured Materials, Technical Centre, N.A.S.U.,
13 Pokrovs'ka Str., UA-03070 Kyiv-70, Ukraine

⁽²⁾ Department of Solid State Theory, G. V. Kurdyumov Institute for Metal Physics, N.A.S.U.,
36 Academician Vernadsky Blvd., UA-03680 Kyiv-142, Ukraine

* Fax: +(380) 44 4242561; E-mail: tatar@imp.kiev.ua

Introduction

The calculations in a majority of previous works for the fulleride (A_qC_{60}) crystals were performed within the framework of the rigid-lattice model, neglecting the distortion relaxation of the host fullerite (C_{60}) crystal caused by the interstitial impurity atoms (A —metal cations, hydrogen, oxygen, rare-gas atoms, *etc.*). However, an each impurity atom is a source of a static distortion field, and the resulting field is a superposition of all such fields generated by individual impurity atoms. This is a reason why the host-crystal distortions depend on the A -atoms' configurations, *i.e.* on a type of a spatial bulk distribution of interstitial atoms.

A given work seeks to find a functional relationship between the amplitudes of the doping-induced structure-distortion waves and of the static concentration waves. A semiphenomenological model is constructed here within the scope of the statistical-thermodynamic treatment and using the lattice-statics simulation method [1, 2]. In this model, the effects caused by the presence of q solute A atoms over available interstices (per 'primitive' unit cell) on the static inherent reorientations and/or displacements of the solvent C_{60} -fullerene molecules from the 'average'-lattice 'sites' as well as on the lattice parameter a of the elastically-anisotropic 'face-centred cubic' C_{60} crystal (Fig. 1) are taken into account.

The (indirect) 'strain-induced' interaction [1, 2] between the interstitial A atoms 'by means of the host crystal', as any dipole-dipole-like interaction, is highly directionally anisotropic and long-range. That is why the (*macroscopic*) total volume-dependent energy of the single-crystallite A_qC_{60} fulleride becomes a functional of boundary conditions, *i.e.* the shape and spatial-orientation variants of a product crystallite phase, and that modifies the Gibbs statistical thermodynamics of the martensitic-like or constant-composition phase transformation of the C_{60} lattice upon a further doping by the A atoms from the pristine f.c.c. structure to the b.c.t. one within the experimentally-determined phases manifesting themselves in different proper-

ties for doing a conductivity, increasing a microhardness, *etc.* By means of the proposed interstitialcy model, it may be possible to overcome such an obstacle in the analytic thermodynamical treatment of data from the integrated X-ray and electron diffraction, TEM, HREM, SEM, and AFM studies (see Refs. in [3]) of abnormalities caused by the A -atoms' redistributions in the f.c.c.-fullerite-derived A_qC_{60} phase. Although such a phase is expected to be insulating at low doping levels ($q \ll 3$), it is clear that an understanding the origin of this crystalline structure and its interplay with A -doped fullerides based on the b.c.t. fullerite (or on the low-temperature s.c. one) will have important consequences for an ongoing process of an unveiling the bulk high- T_c -superconductivity origin as well as the current-carrier pairing mechanism, the causes of twin formation and the factors of microhardness increase, *etc.*, which are dependent on the spatial arrangement of A atoms.

Results and discussion

As a result of numerical analysis of the nonanalytic wave-vector-dependent Fourier components, $E, \sim^{AA}(\mathbf{k})$, of spatial-dispersion energies, $E^{AA}(\mathbf{r})$, of the *bulk-controlled* 'strain-induced' interaction

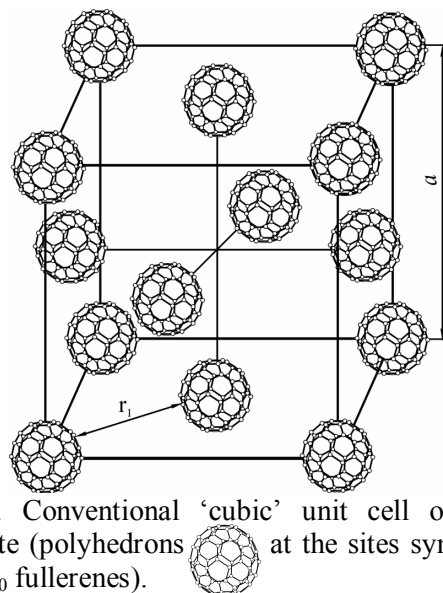


Fig. 1. Conventional 'cubic' unit cell of f.c.c. fullerite (polyhedrons at the sites symbolize the C_{60} fullerenes).

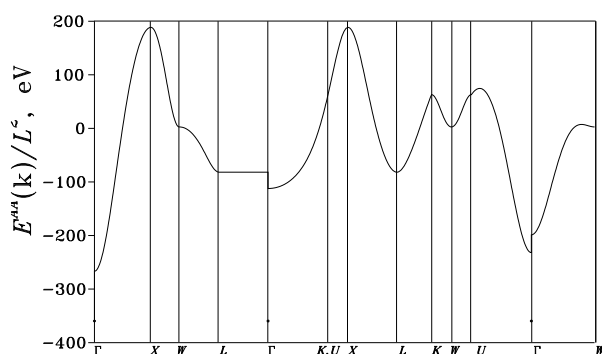


Fig. 2. Dispersion curves, $E, \tilde{AA}(\mathbf{k})/L^2$ ($\mathbf{k} \neq \mathbf{0}$), for strain-induced $A-A$ interaction between small atoms of an A impurity in their nonstoichiometric solution on octahedral interstices of the f.c.c. crystal consisting of large spherical particles of radius, the much greater than typical atomic ones, with a lattice parameter and the elastic properties similar to a C_{60} fullerite [3, 4], and the concentration coefficient of dilatation equal L at introduction of A atoms. $\times$ —the value of $E, \tilde{AA}(\mathbf{0})/L^2$.

between the octahedral A atoms within the scope of the quasi-harmonic approximation of the C_{60} crystallite natural vibrations, the absolute minimum value of these quantities falls into the singular central point Γ ($\mathbf{k} = \mathbf{0}$) of the f.c.c.-lattice first Brillouin zone and is equal to the (negative) total energy, $E, \tilde{AA}(\mathbf{0})$, of the 'strain-induced' interaction ('attraction') between one chosen octahedral A atom and the rest of them within the nonstoichiometric intercalation crystalline A_qC_{60} compound, if the intrinsic elastic moduli (in the Voigt designations) of the 'pure' C_{60} crystal are as follows: $C_{11} \approx 22.7$, $C_{12} \approx 9.8$, $C_{44} \approx 12.3$ (in GPa) [4], and its lattice parameter is $a_0 \equiv a(q=0) \approx 1.404$ nm [3, 4]. Figure 2 shows the predicted arrangement of dispersion curves for $E, \tilde{AA}(\mathbf{k})$ (in units of the square of concentration coefficient of the linear f.c.c.- C_{60} -lattice dilatation due to dissolving A atoms, L^2) in symmetry directions in the first Brillouin zone.

Besides, for instance, the values of the $A-A$ 'pairwise' 'strain-induced' interaction energy, $E^{AA}(r_I), E^{AA}(r_{II}), \dots, E^{AA}(r_{VI})$, for the 1st, 2nd, ..., 6th octahedral-interstitial co-ordination spheres with radii $r_I = a/\sqrt{2}$, $r_{II} = a$, ..., $r_{VI} = a\sqrt{3}$ in a real space, respectively, are in the following ratio: $-28.3 : 8.0 : -8.6 : -1.3 : 5.6 : 2.3$, *i.e.* such a 'strain-induced' interaction energy has a substantially nonmonotonous ('quasi-oscillating') dependence on the interatomic distance r_n ($n=0, I, II, \dots$; see Fig. 3). (If $a = 1.417, 1.414, 1.404, 1.400$ nm, then $r_I = 1.002, 1.000, 0.993, 0.990$ nm and $r_{II} = 1.417, 1.414, 1.404, 1.400$ nm, respectively.)

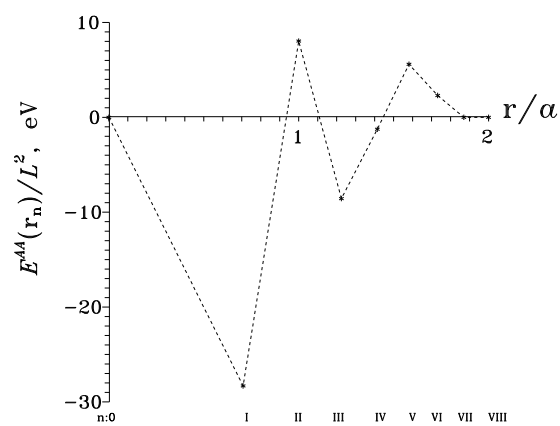


Fig. 3.

Conclusions

When *no* the fully-screened electrostatic (or weak Lennard-Jones-type) $A-A$ interatomic interaction exists, the absolute thermodynamical instability of a homogeneous solid solution of A atoms in C_{60} crystal with respect to arbitrary (not infinitesimal) concentration fluctuations ('heterogeneities') may be considered as a precursor effect associated with the possible isostructural (not spinodal) decomposition reaction [5] in the A -atoms' subsystem in view of the above-mentioned behaviour of the character-

istic function, $E, \tilde{AA}(\mathbf{k})$, in the vicinity of reciprocal-lattice point Γ (*i.e.* within the instability range in $\mathbf{k}$ -space) [2]. (According to Ref. [5], at the early stage of spinodal decomposition, amplitudes of all concentration waves, whose wave vectors belong to the instability range about $\mathbf{k} = \mathbf{0}$, would be increased exponentially with time.)

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