

Macroscopic and Bulk - Controlled Elastic Modes in an Interaction of Interstitial Alcali Metal Cations within a Face-Centered Cubic Crystalline Fullerine

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The calculations in a majority of previous works for the fulleride (AqC_{60}) crystals were performed within the framework of the rigid-lattice model, neglecting the distortion relaxation of the host fullerene (C_{60}) crystal caused by the interstitial alkali-metal (A) cations. However, each cation is a source of a static distortion field, and the resulting field is a superposition of such fields generated by all cations. This is a reason why the host-crystal distortions depend on the A -cations configurations, i.e. on a type of a spatial bulk distribution of interstitial cations.

The given paper seeks to find a functional relation between the amplitudes of the doping-induced structure-distortion waves and of statistic concentration ones. A semiphenomenological model is constructed here within the scope of statistical-thermodynamic treatment and using the lattice-statistics simulation method(*). In this model the effects due to the presence of q solute A cations over available interstices (per unit cell) on the statistic inherent reorientation and/ or displacements of the solvent molecules from the "average-lattice" sites" as well as on the lattice parameter a of the elastically-anisotropic "cubic" C_{60} crystal are taken into account .

The (indirect) "strain-induced" interaction between the interstitial A cations "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-crystalline fulleride AqC_{60} becomes a functional of boundary conditions, i.e. a shape and a spatial-orientations variants of a product phase, and that modifies the Gibbs statistical thermodynamics of the martensitic-like constant-composition transformation of the C_{60} lattice upon a further doping by A atoms

from the pristine FCC structure to the BCT one within experimentally determined phases manifesting themselves in different properties for doing a conductivity. With an aid of a proposed interstitial model it may be possible to overcome such an obstacle in the analytic thermodynamical treatment of data from the electron-diffraction and TEM studies of abnormalities associated with A-cationic redistribution's in the FCC-fullerene-derived A C₆₀ phase. Although such a phase is expected to be insulating at low doping levels ($q < 3$), it is clear that an understanding the origin of this crystalline structure and its interplay with A-doped fullerenes based on the BCT fullerene (or on the SC one) will have important consequences for an ongoing process of an unveiling the bulk high-T_c-superconductivity origin as well as the pair-formation mechanism, which are dependent on a spatial arrangement of A cations.

As a result of numerical analysis of the nonanalytic wave-vector dependence of the Fourier components $\hat{E}_{AA}(\mathbf{k})$ of spatial-dispersion energies of the *bulk-controlled* "strain-induced" interaction between the A cation within the scope of the quasi-harmonic approximation of the C₆₀-crystal natural vibrations, the absolute minimum value of these quantities exists at the singular central point $\Gamma(\mathbf{k}=0)$ of the FCC-C₆₀-crystal first Brillouin zone and is equal to the (negative) total energy $\hat{E}_{AA}(0)$ of the "strain-induced" interaction ("attraction") between one chosen octahedral a cation and the rest of them within the intercalation crystalline compound AqC_60 , if the intrinsic elastic moduli (in the Voigt designations) of the "pure" C₆₀ crystal are $C_{11}=22.7$, $C_{12}=9.8$, $C_{44}=12.3$ (in GPa) (**), and its lattice parameter is $a_0=a(q=0)=14.04$ Å. Figure 1 shows the predicted arrangement of dispersion curves for $\hat{E}_{AA}(\mathbf{k})$ (in units of the square of concentration coefficient of the linear FCC-C₆₀-lattice dilatation due to dissolving A atoms, L₂) in high-symmetry directions in the Brillouin zone.

Besides, for example, the values of the A-A "pairwise" "strain-induced" interaction energies E₁, E₂, ..., E₆ for the 1st, 2nd, ... 6th octahedral-interstitial coordination spheres in the real space respectively are in the -28.3:8.0:-8.6:-1.3:5.6:2.3 ratio, i.e. such a "strain-induced" interaction energy has a substantially nonmonotonic("quasi-oscillating) dependence on an intercationic distance (see Fig. 2).

The absolute thermodynamical instability of a homogeneous solid solution of A cations in C₆₀ crystal with respect to arbitrary infinitesimal concentration fluctuations (heterogeneity's) as a precursor effect associated with the possible spinodal-decomposition reaction in the A cations subsystem may be considered in view of the above-mentioned behavior of the characteristic function $\hat{E}_{AA}(\mathbf{k})$ in the vicinity of reciprocal-lattice points Γ (i.e. the instability range in \mathbf{k} -space), when no the fully-screened electrostatic A-A intercationic interaction exists. (According to Ref> (***)¹, at the early stage of spinodal decomposition, amplitudes of all concentration waves whose wave vectors belong to the instability range about $\mathbf{k}=0$ will increase exponentially.)



