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

Valentine A. Tatarenko, Constantin L. Tsyman, Yelena T. Oltarzhevskaya

Department of Solid State Theory (06) at the Institute for Metal Physics; 36 Academician Vernadsky Blvd, Kiev-142, 252180 Ukraine

Tel.: (+7) 044 4440530
Fax.: (+7) 044 4442561

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-anysotropically “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 (macrosopic) 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 interstitialcy 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 Ag 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 fullerides based on the BCT
fullerene ( or on the SC one) will have important consequences for an
ongoing process of an unveiling the bulk high-Tc-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 \( \hat{E}_{AA}(k) \) 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 \( \Gamma(k=0) \) 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 AqC60, 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 \( \hat{E}_{AA}(k) \) (in units of the square of concentration
coefficient of the linear FCC-C60-lattice dilatation due to dissolving A
atoms, \( L_2 \)) in high-symmetry directions in the Brillouin zone.

Besides, for example, the values of the A-A "pairwise" "strain-
induced" interaction energies \( E_1, E_2, \ldots, E_6 \) for the 1st, 2nd, \ldots 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 \( \hat{E}_{AA}(k) \) in the
vicinity of reciprocal-lattice points \( \Gamma \) (i.e. the instability range in \( k \)-
space), when no the fully-screened electrostatic A-A intercationic
interaction exists. (According to Ref> (**), at the early stage of
spinodal decomposition, amplitudes of all concentration waves whose
wave vectors belong to the instability range about \( k=0 \) will increase
exponentially.)