ENERGY COMPONENTS IN $K(THF)_xC_{24}$ LATTICES

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Introduction

The ion-ion, ion-dipole and dipole-dipole interaction energies of a three-comp- onent crystal lattice are explicited and calculated by the Ewald-Kornfeld method, and the relationships thus derived are applied to the $K(THF)_xC_{24}$ (x=1 or 2, THF = tetrahydrofuran) intercalation compounds of graphite to obtain information on the orientation of the dipolar THF molecules in the lattice.

The ternary graphite intercalation compounds (TGIC) $K(THF)_xC_{24}$ (in which THF=tetrahydrofuran and x≈1.2 or 2.2) differ from the simpler binary compounds such as KC_8 and KC_{24} in that they contain a dipolar molecule within the crystal lattice. It is generally admitted that in a binary GIC of the heavy alkali metals (K to Cs), the metal atom is ionized to a large extent and is not covalently bonded to the C atoms, and that its valence electron is delocalized among the C atoms of the two-dimensional (2D) graphitic planes. The TGIC therefore contains two coexisting lattices, namely an ionic lattice due to the charge transfer between the metal

atom and the carbon (or "graphene") layers, and a lattice of dipoles residing on the organic molecules.

One can therefore expect the existence of three components contributing to the energy balance: ion-ion, ion-dipole and dipole-dipole interactions.

The $K(THF)_xC_{24}$ compounds

The title compounds were first identified by Nominé and Bonnetain [1]. Pure products were prepared by the action of THF vapor on pure, solid KC_{24}[2] as in the reaction

$$KC_{24} + THF(excess) \longrightarrow K(THF)_xC_{24}$$

$$(1)$$
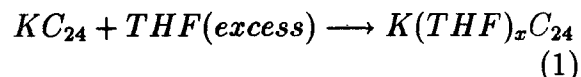
where $x \approx 2.2$. The so-called "rich" phase which is formed can lose part of the intercalated THF when submitted to specific conditions of cryo-pumping to yield a new "lean" phase[2,3] with $x \approx 1.2$.

Both the rich and the lean phase are first-stage compounds. The main difference in their structural parameters resides in the distance d_1 separating the graphene layers on either side of the intercalate.

460

A major problem arises in the theoretical calculation of a number of characteristics - such as the Madelung energy - of these and similar compounds which contain components whose stoichiometry is non-integral. Thus, in the present case, lodging 2.4 molecules of THF on the 2D monoclinic C_{48} lattice of the lean phase is impossible, and attempting to eliminate the problem by changing the formula of the compound $[K_2(THF)_{2.4}C_{48}]_2$ to $[K_{20}(THF)_{24}C_{480}]_2$ is senseless since the indexation requires that the 2D lattice contain 48 C atoms, not 480. For the time being, we shall therefore seek a first approximation to the solution by restricting the problem to the compositions $[K_2(THF)_2C_{48}]_2$ for the lean phase and $[K(THF)_2C_{24}]_2$ or $K(THF)_2C_{24}$ for the rich phase.

Tetrahydrofuran is a cyclic ether C_4H_8O, with two pairs of lone p electrons on the oxygen atom. Its geometrical characteristics have been determined by electron diffraction[4] and microwave spectroscopy[5], and since the sum of the internal angles is 540°, the mean conformation of the molecule must be plane. Its dipole moment p, equal to 1.63 Debye units, is equivalent to $0.54 \, 10^{-29}$ Cm. The position of the THF molecules within the crystal lattice is, of course, subject to the steric requirements due to their bulk.

Energy components

When adding the ion-ion or Madelung energy, the ion$\longleftrightarrow$dipole and the dipole-dipole energies evaluated by an extension of the Kornfeld method[6-11] the total interaction energies are found to be[12]:

Lean phase, $[K_2(THF)_2C_{48}]_2$, monoclinic, $E_{interaction}$= -2.409 eV

Rich phase, $K(THF)_2C_{24}$, orthorhombic, $E_{interaction}$= -1.517 eV
Rich phase, $[K(THF)_2C_{24}]_2$, monoclinic, $E_{interaction}$= -1.570 eV
and the most likely configuration for the dipoles are θ_1= 0, θ_2= 0, θ_3= γ, θ_4= $\gamma+\pi$ for the monoclinic lean phase and φ_1=0, φ_2=0, φ_3=0, φ_4=π for the monoclinic rich phase and φ_1=0, φ_2=0 for the orthorhombic rich phase.

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