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Electrostatic effects in the cohesion of an intercalant lattice

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Electrostatic contributions to cohesion of an intercalated ion lattice are examined. Employing a sandwich model consisting of point charges and fixed bounding compensating charge sheets, we obtain a minimum in the electrostatic energy at a finite intercalant density, unlike the situation for any isotropic solid. Scaling arguments are applied to yield analytic results for the constant energy surfaces and potential energy as a function of intercalant density. The results suggest the additional importance of nonelectrostatic contributions to cohesion of intercalant lattices in the graphite intercalation compounds.

A variety of recent experimental investigations of the graphite intercalation compounds have revealed that, in addition to staging, a rich variety of phenomena related to the *in-plane* order of the intercalated species, especially the alkali metals (K, Rb, and Cs), occur in these systems.[1] The theoretical understanding of cohesion and the origin of these phenomena in the intercalated compounds is not well developed. In addressing this problem we have observed that the electrostatic contributions to the total energy in the intercalation compounds possess several unique properties which distinguish these materials both from ordinary metallic and from ionic crystals. In donor intercalation compounds, excess negative charge is distributed almost uniformly over the carbon planes and the metal ions carry the compensating positive charge. While the Madelung constants of such structures have been calculated recently,[2] no detailed study of the Coulomb contribution to the cohesive energy has been attempted. We have discovered that so long as the graphite-intercalant-graphite sandwich thickness is constrained by some other effect (e.g., hard-core repulsion between the metal and carbon atoms), then the electrostatic energy has a *stable minimum* for a particular value of the in-plane intercalant density. Furthermore, as the sandwich thickness d varies (as the alkali-metal donor is changed, for example), the most stable intercalant density scales in a particularly simple way, varying as $1/d^2$. This implies that on electrostatic grounds at least, the in-plane distance between intercalants is determined solely by the c-axis lattice constant. So far as we know, these effects have no analog in the theory of cohesion for isotropic solids.

In order to demonstrate these observations, we present results for the electrostatic energy of the simplest possible system having the essential features of charge separation in the graphite intercalation compounds. As Fig. 1 shows, we model the intercalant ions by point charges $+q$ placed in a triangular two-dimensional lattice with lattice separation a. The bounding carbon planes are represented by isotropic sheets of negative charge with surface charge density $-q/\sqrt{3}a^2=-q/2A_0$, where A_0 is the two-dimensional unit cell area. This density is chosen such that whatever the value of the in-plane lattice constant a each unit cell is electrically neutral. The planes are symmetrically placed on each side of the point-charge lattice and the separation between them is d. Naturally the model ignores the atomicity of the carbon planes. It also ignores the fact that excess negative charge will not be distributed uniformly on the carbon planes but will screen the positive ions by accumulating around them.[3] Nevertheless, the model should provide useful information for the graphite intercalation compounds, especially those in which the intercalant species is pointlike and in which the graphite planes are significantly spread apart by

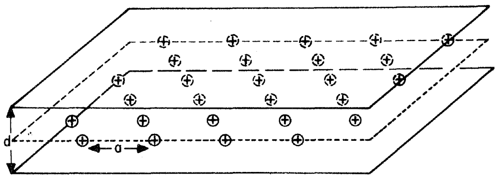

FIG. 1. Sandwich model of a triangular intercalated ion lattice between two compensating charge sheets.

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the intercalant. The alkali compounds KC_8, RbC_8, and CsC_8 satisfy these requirements.

The calculation of electrostatic energies for this model was performed using an extension of the Ewald decomposition technique used for simple metals.[4] The formula for the Coulomb energy $U(d,a)$ is

$$U(d,a)=\frac{q^2}{2}[\,U_{ii}(a)+U_{is}(d,a)+U_{ss}(d,a)]\ , \tag{1a}$$

where U_{ii} is the electrostatic energy of the lattice of point ions

$$U_{ii}=\frac{2\pi}{A_0}\sum_{G_{\|}}{}'\frac{1}{G_{\|}}\operatorname{erfc}\left[\frac{G_{\|}}{2\sqrt{\eta}}\right]-3\frac{\sqrt{\pi}}{A_0\sqrt{\eta}}+\sum_{R_{\|}}{}'\frac{1}{R_{\|}}\operatorname{erfc}(\sqrt{\eta}R_{\|})-\frac{2\sqrt{\eta}}{\sqrt{\pi}}\ , \tag{1b}$$

where $\vec{R}_{\|}(\vec{G}_{\|})$ are the real (reciprocal) lattice vectors parallel to the basal plane, the primed sums delete the $R_{\|}(G_{\|})=0$ term, and $\sqrt{\eta}$ is the usual Gaussian convergence parameter employed in the Ewald decomposition. The last two terms in Eq. (1a) giving the ion-sheet and sheet-sheet energies may be combined to yield

$$U_{is}+U_{ss}=\frac{\pi d}{A_0}+\frac{\sqrt{\pi}}{\sqrt{\eta}A_0}\ . \tag{1c}$$

A similar formula for layers of point charges has been used in the literature.[5] Eq. (1) permits very rapid computation of $U(d,a)$ for a range of sandwich thicknesses d and lattice constants a.

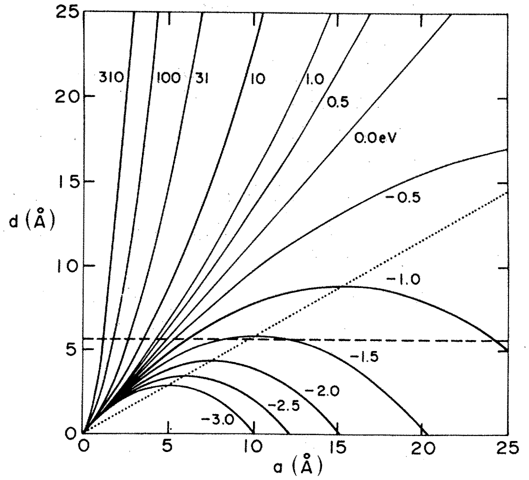

FIG. 2. Constant potential surfaces in the a,d plane where a is the near-neighbor intraplane spacing and d is the intersheet spacing. Dotted line is the locus of potential minima and the dashed horizontal line corresponds to $d=5.41$ Å, an intersheet separation appropriate for KC_8.

Our results for the Coulomb energy are given as a contour plot in Fig. 2. Observe that for fixed d (e.g., along the horizontal dashed line in Fig. 2) $U(d,a)$ does indeed have a minimum, thus, there is a stable lattice spacing $a_{\min}$ as asserted above. In the upper left-hand corner of the figure, that is, for $d/a\gg 1$, $U(d,a)$ rises very steeply since the repulsive interactions between the ions are becoming unscreened. In the limit $a\to 0$, $d>0$ the energy diverges: $U(d,a)\to+\infty$. The $d=0$ axis corresponds to the collapsing of the sandwich to a single plane. In this situation U is finite and negative. Notice that for $d=0$, $U(d,a\to 0)\to-\infty$, so that as the point $a=0$, $d=0$ is approached, U diverges to either $+\infty$ or $-\infty$, depending on the direction of approach. Another universal property which clarifies many of the features of Fig. 2 is the scaling rule

$$U(\lambda d,\lambda a)=\frac{1}{\lambda}U(d,a),\quad \lambda>0\ . \tag{2}$$

Equation (2) immediately implies the following:

(1) all negative-energy contours of $U(d,a)$ are similar, i.e., have the same shape;

(2) all positive-energy contours are similar, but are different from the negative energy contours;

(3) the zero-energy contour is a straight line (we find $a=0.87d$ on the zero-energy contour);

(4) the lattice constant $a_{\min}$ for which $U(d,a)$ is minimized is directly proportional to the fixed-sandwich thickness d.

In fact, the scaling rule [Eq. (2)] and the simple linear dependence of U on d [Eq. (1c)] lead to a particularly simple form for the constant energy contours given in Fig. 2. Equation (1c) requires that

$$U(d,a)=U(0,a)+C\frac{d}{a^2}\ , \tag{3}$$

where C is a constant, specific to the intercalant lattice for the two-dimensional close-packed lattice in our model, $C=2(\pi/\sqrt{3})$. If U is determined at a single point [$U_0=U(d_0,a_0)$ is given] then $U(d,a)$ may be completely reconstructed:

$$U(d,a)=\frac{a_0}{a}U_0+\frac{C}{a}\left[\frac{d}{a}-\frac{d_0}{a_0}\right]\ . \tag{4}$$

Then a constant energy contour for energy E is obtained as the locus of points (a,d) which satisfy

$$E=\frac{a_0}{a}U_0+\frac{C}{a}\left[\frac{d}{a}-\frac{d_0}{a_0}\right]\ , \tag{5}$$

which are parabolic trajectories:

$$a^2E + a\left[C\frac{d_0}{a_0} - a_0U_0\right] - Cd = 0 . \tag{6}$$

Thus, the $E=0$ trajectory is a line as asserted in (3) above, with slope $(d_0/a_0)-(a_0U_0/C)$. Similarly the locus of potential minima $(a_{\rm min}, d_{\rm min})$ is given by

$$d_{\rm min} = \frac{1}{2}\left[\frac{d_0}{a_0} - \frac{a_0U_0}{C}\right]a_{\rm min} , \tag{7}$$

which describes a line with half the slope of the zero potential trajectory. This result implies that the equilibrium point ion density is proportional to $1/d^2$ as noted above.

It is worth reemphasizing what we mean by a "stable electrostatic minimum." According to Earnshaw's theorem,[6] no collection of charges can even be stable under Coulomb forces alone. The difference between our sandwich model and, for example, an ordinary hcp metal is the mode of instability. As Fig. 3 shows, a three-dimensional hcp structure collapses to zero volume by a contraction of all three dimensions simultaneously. This electrostatic behavior would be reinforced by the exchange energy ($-0.916/r_s$ Ry in jellium)[7] which is attractive and, in fact, stronger than the Coulomb attraction. In our model system, zero volume is reached by first the collapse of the planes ($d \rightarrow 0$) then a uniform two-dimensional collapse ($a \rightarrow 0$). If $d \rightarrow 0$ is prevented by some other effect like core repulsion, then the system remains stable for a finite in-plane lattice constant. (Naturally, a similar isotropic mechanism is invoked to explain why an hcp metal does not collapse.)

In Fig. 3 we have shown the Coulomb energy as a function of a for $d=5.41$ Å, which corresponds to the sandwich thickness in stage one potassium graphite. The analytic form of this curve is given by Eq. (5). For large a it is attractive and scales as $1/a$, and for small a it is repulsive, going as $1/a^2$. Interestingly, this small a behavior mimics the density dependence of the kinetic energy in the quantum model of a simple metal.[7] The minimum in this curve of $U=-1.6$ eV for $a=8.9$ Å at a stoichiometry $C_{26}K$. This considerably underestimates the packing density in the real first-stage material C_8K. The Coulomb energy at the actual stoichiometry is $U=-0.4$ eV. Thus the system sacrifices ≈ 1.2 eV/K atom of Coulomb energy to achieve its desired configuration. Where does it gain back these 1.2 eV? A leading candidate is the "commensuration energy," that is, the energy which the intercalant gains by conforming to the graphite lattice. Another source of binding energy is the increased exchange of the excess electrons in the graphite plane at higher density. No reliable estimates currently exist for either of these contributions to the total energy in alkali-metal intercalation compounds. Finally, Fig. 3 demonstrates conclusively why K atoms do not pack at their ionic radii, 1.33 Å, in the intercalant plane. The Coulomb energy at this packing is $U \approx 12$ eV; thus, the system at this density would lose an enormous energy, ≈ 13 eV/K atom, which is unlikely to be compensated for by other attractive contributions to the total energy.

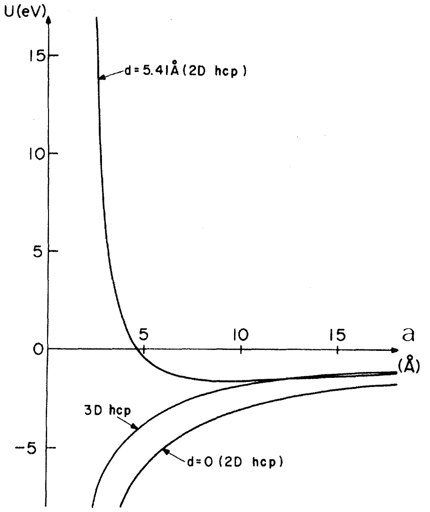

FIG. 3. $U(a,d)$ for $d=5.4$ Å. Sandwich potential is compared with results for two- and three-dimensional hexagonal close-packed lattices with a uniform compensating background.

In summary, we have found that the electrostatic energy of a hexagonal array of ions situated in-between two fixed compensating charge sheets exhibits a minimum at a finite ionic density. This situation is peculiar to the reduced dimensionality of the system and is not possible in isotropic solids. Finally, the electrostatic model considerably underestimates the in-plane density indicating the importance of other electronic contributions to cohesion in these compounds.

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