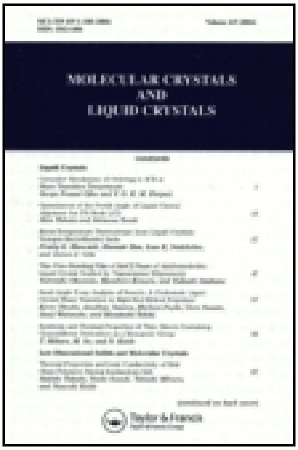

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Cohesive Energy Studies of Intercalated Graphite Compounds: The Madelung Energies of C_6Li and C_8K

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To cite this article: Robert Melville Metzger (1982): Cohesive Energy Studies of Intercalated Graphite Compounds: The Madelung Energies of C_6Li and C_8K, Molecular Crystals and Liquid Crystals, 85:1, 97-107

To link to this article: http://dx.doi.org/10.1080/00268948208073635

Mol. Cryst. Liq. Cryst., 1982, Vol. 85, pp. 97–107
0026-8941/82/8501-0097$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

COHESIVE ENERGY STUDIES OF INTERCALATED GRAPHITE COMPOUNDS: THE MADELUNG ENERGIES OF C_6Li and C_8K[a]

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Received for publication October 1, 1981

The Madelung energies E_M of the lamellar intercalated compounds C_6Li and C_8K are -4.571 eV/atom of Li and -2.478 eV/atom of K respectively, assuming full charge transfer. E_M becomes more negative when the counterion coordination becomes greater, and depends critically on Coulomb contributions in directions normal to the graphite planes. Born-Haber cycle estimates of the enthalpy of formation of C_8K (-0.93 eV to -1.79 eV, depending on which band theory estimate of the Fermi energy shift is used) bracket the experimental value of -1.208 eV.

INTRODUCTION

A recent review[1] has stressed anew that cohesive energy calculations[2] would be useful in understanding the stability, ionicity and transport properties of graphite lamellar compounds, or, as they are also called, graphite intercalation compounds.

In these crystals[3,4] the two-dimensional hexagonal sp^2 ordering of graphite is preserved, but electron donors M(M = metal atoms) or electron acceptors X(X = halogens,

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[a] Research performed in part at Centre Paul Pascal, CNRS, Domaine Universitaire, Université de Bordeaux I, F33405 Talence, France, and supported in part by NSF-DMR-80-15658.

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metal halides, nitric acid, sulfuric acid) can intercalate between the graphite planes, thereby altering the band structure of graphite slightly, but shifting the location of the Fermi energy considerably. This gives rise to a 4 to 10-fold increase in conductivity[1] and even to superconductivity[5].

Many of these lamellar compounds exhibit disorder in the arrangement of the intercalates (e.g. "islands"[6]) but some are well-ordered "ideal" crystals. For the same intercalant R (R = M or X) many stoichiometric compounds with graphite can be prepared: these intercalates are labelled by "stages" n[7]: their formula is $C_{na}R$, where a = number of moles of C per mole of R at n = 1. Thus first-stage lithium-graphite is C_6Li, second-stage is $C_{12}Li$, etc.

Pure graphite has the Bernal structure[8]: the adjacent planes of carbon atoms, with interplanar distance 3.354 A, overlap in a "staggered" configuration (ABABAB...) such that three out of six hexagon corner atoms of plane B are over hexagon centers of plane A.

In the "ideal" first-stage intercalation compounds[3,4] the graphite planes are "eclipsed" (AAA stacking) but the intercalate is inserted either with "perfect registry" (AαAαAα...) or selects, depending on stoichiometry or space group considerations, two or three or four different sites over hexagon centers, denoted α, β, γ, δ: thus AαAβAαAβ, or AαAβAγAα..., or AαAβAγAδAα... stacking may result; if we do not know, or wish to specify, the details of intercalate registry we denote the first-stage compounds stacking by AωAωAω...

Second-stage compounds have two graphite planes between successive planes of intercalates: the ideal stacking is[3,4] ABωBCωCAωABω..., where the registry of graphite planes C over planes A and B is such that three of the hexagon corner atoms of plane C are over hexagon centers of plane B and over hexagon corners of plane A, and such that the registry of B over A is equivalent to that of C over B, and to that of A over C.

Third-stage compounds have three successive graphite layers between intercalate layers, with ideal stacking ABAωACAωABAω....

Fourth-stage compounds have four graphite layers between them, with ideal stacking ABABωBCBCωCACAωABABω.... If successive graphite layers are present without intercalates, their interplanar distance in all these compounds, ordered or not, is close to 3.354 Å.

Electron donors tend to increase the covalent in-plane C-C bond distance slightly[9,10]; electron acceptors have a much weaker effect[11]. Also, as the stage *n* is increased there is a systematic increase in the in-plane C-C bond distance[9,10].

CHARGE TRANSFER

The amount of charge transfer, ρ, from the intercalant to carbon, is open to question[1,2,12-20]. Early work[2,16-20] assumed that the bonding between carbon and intercalate was primarily ionic. A later, more conservative, definition bypassed the question of partial covalency of that bonding, and defined f as the fraction of a free electron or hole introduced per atom of intercalate[12].

The present discussion shall be restricted to what is known about the amount of charge transfer, ρ, in C_6Li and C_8K. Physical measurements on C_6Li (electron spin resonance and heat capacity[21], Knight shift[22] and conductivity anisotropy[15]) have been interpreted to indicate that Li is a dilute metal in C_6Li with charge transfer $\rho \approx 0.1$[1,21]. The (weak) Knight shift is probably mediated by the partially filled[23] graphite π^* band[22]. The low conductivity anisotropy and closeness of the graphite planes are attributed to covalent bonding effects[15]. The nearest-neighbor Li-Li distances are 30% larger in C_6Li than in bulk Li metal.

Similar physical measurements have been made on C_8K (electron spin resonance[25,26], heat capacity[26] and conductivity anisotropy[20]). Early estimates for C_8K were $\rho = 0.3$ to 0.4[1,2,17]. The nearest-neighbor K-K distances in C_8K are 7.3% larger than those in bulk K metal.

Two band structure calculations exist for C_6Li[27-31] and three for C_8K[31-35], along with studies of the expected changes in the graphite band structure upon intercalation[23,36-40]. The first C_6Li band structure calculation[27-30] shows that C_6Li is a π^* band metal with 1/6 electron per C atom in the graphite π^* orbital; the Fermi energy shift is $\Delta E_F = E_F(C_6Li) - E_F(\text{graphite}) \approx 2.31$ eV; an exact estimate of ρ is not attempted, since in a band structure calculation it depends on arbitrary anisotropic limits of integration of the total valence charge density function; the Li atom has a residual cusp-like Li 2s contact density and shows some covalent bonding effects between Li and the graphite planes. One might guess however from the C_6Li calculation that f, (and even ρ) may be as high as 0.9. The other C_6Li calculation[31] gives $\Delta E_F = 1.82$ eV but obtains a rather neutral LiC_6 lattice because the Li 2s band overlaps with the partially occupied C π^* band (instead of lying, empty, 1.7 eV above it[27-30].

For C_8K a preliminary band calculation suggests ΔE_F = 1.60 eV[35] whereas the other calculation obtains ΔE_F = 1.27 eV[31] and a low ionicity lattice[31].

COHESIVE ENERGY

It has recently been stated[28] that, given the extensive charge delocalization in C_6Li, neither image-force field calculations[41] nor Madelung energy calculations based on a point-charge lattice would be helpful in understanding C_6Li. But since fractional point charges at atomic sites are *equivalent, by Gauss' theorem, to a set of* non-overlapping spheres of uniform charge, and since the band theory calculations have not yet obtained a self-consistent description of the fractional charge transfer in C_6Li or C_8K, therefore a simple-minded Madelung energy calculation[42] may still shed some light on the problems of cohesion in these intercalated graphite lattices.

For graphite-electron donor lamellar compounds the enthalpy of formation can be defined as:

$$\Delta H_s \equiv \Delta H_f^\circ(C_nX,\ c, 298.15K) - \Delta H_f^\circ(X,\ g, 298.15K) \\ -\Delta H_f^\circ(C,\ \text{graphite},\ 298.15K) \qquad (1)$$

where the ΔH_f° are standard enthalpies of formation. Using a Born-Haber cycle, ΔH_s can be written, for an idealized $\rho = 1$ lattice[2], as:

$$\Delta H_s = (I_D - A_{graphite}) + E_M + (E_d - E_r) + \Delta E_F \\ + E_{del} \qquad (2)$$

where I_D is the first gas-phase ionization potential of the electron donor, $A_{graphite}$ is the electron affinity of graphite (= work function) = 4.39 eV[1], E_M is the Madelung energy, $E_d - E_r$ is a "net van der Waals energy" that includes all short-range multipole, dispersion, and hard-core repulsion energies, ΔE_F is the displacement of the Fermi level of graphite upon intercalation, and E_{del} is an electron delocalization energy. Of these terms, $E_d - E_r$ and E_{del} could be assumed to be small or negligible in a first, crude calculation.

For a fractionally ionized lattice described by a uniformly distributed set of partial charges, the Madelung energy (calculated for $\rho = 1$):

$$E_M = \sum_i \sum_j q_i q_j r_{ij}^{-1} \tag{3}$$

scales as $\rho^2 E_M$ and the cost of ionization as $\rho(I_D - A_{graphite})$[43] but no energy minimum of $\rho^2 E_M + \rho(I_D - A_{graphite})$ can be found at intermediate charge transfer[42] unless one abandons the linear interpolation $\rho(I_D - A_{graphite})$[44]. The cohesive energy of the $\rho = 1$ lattice is[42]

$$U = \Delta H_s - (I_D - A_{graphite}) = E_M + (E_d - E_r) + \Delta E_F + E_{del} \tag{4}$$

Without prejudice as to what the experimental charge transfer is in either C_6Li or C_8K, a Madelung energy calculation is reported here for the $\rho = 1$ lattices of these compounds, to help understand the energetics of formation of the crystals.

MADELUNG ENERGY CALCULATIONS

The computer programs CELMAP and EWALD have been described previously[45] and have been used on the DEC VAX 11/780 at the Centre Paul Pascal. In order to evaluate two-dimensional lattice sums, a one- and two-dimensional extension[46] of Ewald's fast-convergence algorithm[47] has been added and tested[48].

The crystal structures used are given in Tables 1 and 2. For C_6Li Guerard and Herold[49] decided that the AαAαAα structure fit their X-ray data best, but the choice between several possible space groups was not easy[49].

Table 1 Assumed Crystal Structures for C_6Li [Refs. 49,50]

	Structure 1 (Ref. 49)	Structure 2 (Ref. 50)
Stacking:	Aα	AαAβAγ
Cell Constants:	a=4.305Å,c=3.706Å, γ=120°	a=4.305°,c=11.118Å, γ=120°
Space Group:	P6/mmm	P6/mmm(for C atoms)
Atom Positions:	C at 1/3,0,0;etc. Li at 0,0,1/2;etc.	C1 at 1/3,0,0;etc. C2 at 1/3,0,1/3; etc. Liα at 0,0,1/6 only Liβ at 2/3,1/3,1/2 only Liγ at 1/3,2/3,5/6 only

Table 2 Assumed Crystal Structures for C_8K [Refs. 3,26,51, 52]

	Structure 3 (Refs. 3,26,51)	Structure 4
Stacking:	AαAβAγAδ	AαAβAγAδ
Cell Constants:	a=4.961,b=8.592,c=23.76Å	a=4.965,b=8.599, c=21.584Å
Space Group:	Fdd2	Fdd2
Atom Positions:	K at 0,0,1/8;etc. C1 at 0,1/6,0;etc. C2 at 0,1/3,0;etc. C3 at 1/4,1/12,0;etc. C4 at 3/4,1/12,0;etc.	

Recently, low-temperature surface measurements on C_6Li[50] seemed to be in better accord with an AαAβAγ stacking. For C_8K the structure of Rüdorff and Schulze[26], as quoted in Ref. (3), is given as Structure 3; the inferred graphite-to-graphite interplanar distance of 5.94Å is close to 3.35 + 2(1.33)Å, where 1.33Å is the ionic radius of K^+. The structure of C_8K has been reexamined[52]: new lattice constants, implying some *c*-axis "compression", were obtained, and the space group was considered as a "trilled" set of 3 Fddd unit cells 120° from each other[52]. In view of the small Madelung energy differences between the two C_6Li structures (see below) and of the complications of a Madelung energy calculation for a trilled (three-fold twinned) structure, the old space group[3] and the new cell dimensions[52] were combined as structure 4 of Table 2. The new *c* axis[52] does agree reasonably with an independent measurement[53] for C_8K.

The resulting Madelung energies are listed in Table 3. For C_6Li the difference in energy between the Aα and the AαAβAγ structure is small: the latter is more stable by a mere 0.059 eV. However, the Madelung energy is *very* three-dimensional. The two-dimensional slice consists of the graphite plane at $z = 0$, (with each atom carrying a charge of $-1/6$) plus "half" Li atoms at $z = 1/2$ and at $z = -1/2$, each carrying a charge of $+0.5$ (a two-dimensional calculation is very sensitive to symmetry about the plane of the slice). The gain of 3.527 eV in binding energy as one includes the third dimension for the C_6Li structure is a self-evident consequence of the fact that the Coulomb interactions in the (0001) slice are mostly repulsive;

Table 3 Madelung Energies E_M for Fully Ionic Structures (eV/Atom of Alkali Metal)

Compound	Structure	Graphite Interplanar Distance (Å)	Dimensionality	E_M (eV)
C_6Li	1	3.706	3	-4.512572
C_6Li	2	3.706	3	-4.571088
C_6Li	1	(0001) slice	2	-1.044171
C_8K	3	5.94	3	-1.898892
C_8K	4	5.396	3	-2.478283

the only surprise is the magnitude of that gain.

For C_8K, the shorter stacking distance in structure 4 provides a considerable gain over E_M for structure 3 (a 10% lattice contraction gives a 30.5% increase in binding energy). Also, C_6Li is more strongly bound than C_8K because it is a structure of higher charge density along the c axis: a 45.6% shorter graphite interplanar distance translates into a lattice energy increase of 84.5% for C_6Li over C_8K.

An approximate comparison has been made between the stabilities of the AαAβAγ structure and the AαAβAγAδ structure by the following calculation: structure 2 of C_6Li was stretched in the c direction until the graphite layers were 5.396Å apart (their distance in structure 4 of C_8K): the Madelung energy shifted from -4.571088 eV to -2.217760 eV. This result, when compared with the last entry in Table 3, shows that, at constant graphite interplanar separation the lattice stability sequence is:

$$A\alpha A\beta A\gamma A\delta > A\alpha A\beta A\gamma > A\alpha \qquad (4)$$

This conclusion is self-evident from simple arguments that better counterion coordination will increase the magnitude of the Madelung energy[42]. It also has received experimental confirmation in the possible bulk phase transition from AαAβAγ (low temperature) to Aα (high T) in C_6Li[50], and AαAβAγAδ (low T) to AαAβ (high T) in C_8Rb[54]. The improvement in the Madelung energy with better counterion coordination has also been observed in studies of the cohesion of the lamellar Li-doped titanium sulfides, Li_xTiS_2[55].

DISCUSSION

One may wish to compare the results given in Table 3 with other calculations and with experiments. The ionization potentials I_D for Li and K are 5.39 eV and 4.34 eV respectively[1]. The correction to $A_{graphite}$ = 4.39 eV[1] due to Fermi level shifts, ΔE_F, is estimated at 0.86 eV[2,41], 1.82 eV[31], or 2.31 eV[28] for C_6Li, and 0.74 eV[2,41], 1.27 eV[31], or 1.60 eV[35] for C_8K. If one neglects E_{del} and $E_d - E_r$ in eq. (2) and assumes $\rho = 1.0$, the enthalpy of formation of C_6Li and C_8K (relation to pure solid graphite and alkali metal atom gas) is:

$$C_6Li{:}\quad \Delta H_s = 5.39 - 4.39 - 4.57 + (0.86 \text{ to } 2.31) = -2.26 \text{ to } -3.71 \text{ eV} \tag{5}$$

$$C_8K{:}\quad \Delta H_s = 4.34 - 4.39 - 2.48 + (0.74 \text{ to } 1.60) = -0.93 \text{ to } -1.79 \text{ eV} \tag{6}$$

Thus, the formation of both C_6Li and C_8K is thermodynamically favored. The enthalpy of formation of C_8K has been measured electrochemically: ΔH_f = -1.208 eV[56] for the reaction:

$$K\ (g) + 8C\ (\text{graphite}) \rightarrow C_8K\ (c) \tag{7}$$

and our eq. (6) brackets that value.

Finally, a previous calculation of the bonding energy in cesium-graphite compounds by image force theory yields[41] an energy $k\Delta W_Q + \Delta W_\Sigma$ = -2.10 eV for C_8Cs, a value roughly comparable to our Madelung energy for C_8K, except that the graphite interplanar distance in C_8Cs (5.94Å) is larger than that of C_8K (5.396Å). Thus this image force theory value of -2.10 eV is fairly close to E_M = -1.90 eV for the (false) structure 3 of C_8K in Table 3.

In conclusion, despite valid theoretical concerns[28] Madelung energy calculations have been shown to be interesting numerical aids to guide chemical intuition about the bonding in alkali metal graphites.

It is a pleasure to thank Drs. P. Delhaes, S. Flandrois, A. Pacault, and A. Marchand for their generous hospitality in Bordeaux, and Drs. N. A. W. Holzwarth, J. E. Fischer, A. H. Thompson and G. Volpilhac for informal discussions.

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