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Interplanar binding and lattice relaxation in a graphite dilayer

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High-precision, large-basis-set calculations, in the local-density approximation (LDA) (using the all-electron, full-potential, linear combination of Gaussian orbitals, fitting-function technique), of the cohesive properties and electronic states (bare Kohn-Sham energies) of the isolated *AB* dilayer of graphite are reported. They show that the dilayer interplanar spacing (c axis) differs little from the value for $ABABAB\cdots$ crystalline graphite (0.7% expansion relative to one calculation, 2.5% contraction relative to another, 2% expansion relative to experiment). This result, which differs significantly from a preliminary report of strong c-axis contraction, is related to the weak interplanar binding. The intraplanar lattice spacing (a axis) is virtually identical with the crystalline value for both the graphite dilayer and monolayer. The interplanar binding energy (obtained directly via optimization of the monolayer ground state with the same techniques) is in excellent (perhaps fortuitous) agreement with the experimental value for the crystal, in contrast with crystalline calculations, which are too large (in magnitude) by 40–100% or more. The dilayer cohesive energy agrees well with the crystalline value from an all-electron calculation. Both exceed the experimental value in magnitude by over 1 eV/atom, a problem already known to arise from inadequacies in the LDA treatment of the multiplet structure of the isolated C atom. The dilayer uniaxial compressibility is much larger than calculated for the crystal, apparently another manifestation of weak interplanar binding. Dilayer Kohn-Sham eigenvalues are largely consistent with those calculated self-consistently for the crystal using the same LDA model. Both differ substantially from the non-self-consistent band structure commonly used to parametrize graphite optical properties of interest in astrophysics. Calculated values of the dilayer work function are larger by about 0.6–0.7 eV than the crystalline experimental results. The dilayer density of states at the Fermi level is predicted to be much smaller than for the crystal, while the occupied bandwidth is in reasonable agreement with crystalline experimental results.

I. INTRODUCTION

The weak interplanar binding of $ABAB\cdots$ stacked graphite and concomitant anisotropy of its electronic properties have long been of theoretical (not to mention experimental) interest.[1–10] Graphite monolayers, and to a lesser extent, multilayers of both the same $ABAB\cdots$ stacking[11–15] and others,[16,17] have also attracted attention. This interest arises from the relevance of such systems to understanding of graphite intercalation compounds and because the one-electron energies of a graphite n layer even with $n=1$ provide a reasonable picture of much of the one-electron behavior in the crystal.

Graphite also has been of interest for many years as a likely candidate for an anomalous absorption hump in the interstellar medium found around 225 nm.[18] More recently, graphitic molecules (polycyclic aromatic hydrocarbons) have been suggested as the primary mechanism for strong infrared emissions (at 3.3, 3.4, 6.2, 7.7, 8.6, and 11.3 μm) in the interstellar medium.[19] In the astrophysical context, the graphitic objects are usually assumed to be of monolayer thickness. Typically their optical properties are extracted from fitted one-electron energies[1] or non-self-consistent ones calculated for the bulk crystal.[2–5,11,12] If 2-layers are considered in the astrophysical literature [and they rarely are, although Ref. 19(e) is an exception], it is usually argued that the crystalline interplanar cohesive energy is so small that the temperature at which the graphitic objects are formed would be sufficient to cleave any 2-layer.

On both fundamental and calculational grounds it is known, however, that n layers with $n=1,2,3,\ldots$ can and do behave rather differently from their counterpart crystals.[20–22] The possibility of such behavior is particularly intriguing in the context of the strongly anisotropic binding in graphite, since delamination from the $ABAB\cdots$ crystal to form the *AB* 2-layer *in vacuo* might well be a large perturbation to a weak binding mechanism.

For these reasons we undertook a study of the graphite 2-layer (and treated the 1-layer for comparison). The initial study[23] found strong interplanar contraction, approximately 19% as compared to the experimental value, with greater contraction in comparison with calculated values. Although this preliminary result was consistent with a model calculation by DiVincenzo, Mele, and Holzwarth[7] (and apparently went unquestioned), we found it difficult to adduce a mechanism for such a large contraction.

While beginning an investigation of possible buckling reconstructions of the graphite 2-layer (2L hereafter) it became apparent that, in spite of multiple indications to the contrary, the calculation in Ref. 23 was not stable with respect to some algorithmic limitations (primarily multipole expansion techniques and numerical grid distributions used to calculate primitive integrals) and basis-set characteristics. In fact, the contraction predicted in Ref. 23 was spurious. When these limitations became manifest subsequent to the report in Ref. 23 (which was done in late 1987), they motivated a complete overhaul of the code followed by a complete restudy.

Here we present results of a stable, high-precision calculation. In the remaining sections we summarize methodology, then present results for the total energy, equilibrium lattice parameters, cohesive and interplanar binding energies, uniaxial compressibilities and universal scaling, and for electronic structure at the level of Kohn-Sham eigenvalues and the associated density of states.

II. METHODOLOGY

Within the local-density approximation (LDA) to density-functional theory (DFT), these calculations are entirely first principles: they include all electrons, make no shape approximations for the potential, and are fully self-consistent. The Hedin-Lundqvist (HL) form of LDA was used throughout. We solve the Kohn-Sham (KS) equations with the linear combination of Gaussian-type-orbitals fitting-function (LCGTO-FF) technique[24] as embodied in the FILMS program package.[25] It is important to note that the present version of the code is substantially improved over that used in Ref. 23. Many of the improvements were aimed specifically at difficulties posed by layered systems with highly anisotropic binding and/or complicated unit cells.

The LCGTO-FF procedure uses three Hermite-Gaussian basis sets. The first ("KS" basis) expands the KS orbitals, the second ("Q" basis) the electron number density, and the third ("XC" basis) the LDA exchange-correlation kernels. As experience has grown it has become apparent that an effective technique is to use identical Q and XC bases, denoted as the F basis hereafter.

To ensure a stable calculation it was necessary to use a $9s4p1p_z$ primitive basis contracted to $6s3p1p_z$ for the KS set. This is substantially richer than the uncontracted $6s3p_xp_y3p_z$ KS basis used in the preliminary study[23] and the similar basis previously used by Samuelson and Batra.[3] The present KS basis evolved, by testing and refinement, from the $9s4p$ Hartree-Fock basis by van Duijneveldt.[26] Adaptation to the film environment required tightening of the outer two p functions. Selection of the p_z exponent was guided by experience and test calculations. The contraction coefficients were chosen to be the expansion coefficients for the HL LDA treatment of the C atom. Basis exponents and contraction coefficients are tabulated in Table I.

The F basis was chosen to be $8s2d2p_z$, again much richer than that used in Ref. 23. This basis was constructed by frank empiricism, with particular reliance on previous experience and careful testing to get a good fit over a large range of distances from the nucleus. Unlike the Q basis in Ref. 23, the F basis used here was not generated by Dunlap's rule [see Ref. 25(b) for discussion and additional citations] nor were offsite fitting functions used. Since Ref. 23, we have found that offsite fitting functions tend to preselect certain forms of bonding while use of Dunlap's guideline tends to force the charge density to be too localized around each nuclear site.

TABLE I. Basis-set exponents and KS contraction coefficients.

KS exponent	KS contraction coefficient	F exponent
s type		s type
5182.950	0.0009400	700.00
778.7560	0.0072010	140.00
178.0730	0.0361950	35.000
50.87790	0.1293610	11.000
16.78760	0.3160450	3.6000
6.143620	1.0000000	1.4000
2.403980	1.0000000	0.6000
0.511900	1.0000000	0.2200
0.156590	1.0000000	
p type		d type
9.4645200	0.0419040	0.5000
2.0065800	0.2233730	0.2000
0.6500000	1.0000000	
0.2800000	1.0000000	
p_z type		p_z type
0.1200	1.0000000	0.5000
		0.2000

While searching for equilibrium lattice parameters, we used 19 points in the irreducible wedge of the two-dimensional Brillouin zone (BZ) for BZ integrals. Once found, the stability of the predicted values was tested by recalculation on a 37-point mesh. No meaningful shifts occurred. All calculations were stabilized to an iteration-to-iteration shift in total energy per atom of less than 5 μhartree; most actually achieved better than 1 μhartree (1 hartree = 27.2116 eV).

III. LATTICE PARAMETERS, BINDING ENERGIES, AND UNIAXIAL COMPRESSIBILITY

A. Lattice parameters

Studies of graphite conventionally use hcp unit-cell parameters and notation. Hence the basal lattice parameter is a, the nearest-neighbor distance is $a_{\mathrm{NN}}=a/\sqrt{3}$, the cell height is c, and the 2-layer interplanar separation is $c/2$. Throughout, lengths are given in atomic units a_0.

Because of the anisotropic binding in graphite, we first minimized the total energy with respect to c with a fixed at 4.65 a.u., essentially the monolayer equilibrium found in Ref. 23 and virtually identical with the experimental $T=20\,^{\circ}\mathrm{C}$ crystalline value.[27] The a parameter was then varied with c fixed at its minimum-energy value. The optimized a turned out to be so close to the original one (cf. Table II) that reoptimization of c was unnecessary. The 1L was treated using the same basis sets (except of course

TABLE II. Comparison of calculated values of graphite lattice parameters in different structures, along with experimental values. The entry "2L" refers to the interplanar model of DiVincenzo, Mele, and Holzwarth (Ref. 7). The value of a used in that calculation was not stated explicitly in the publication; the parentheses indicate the value deduced from a footnote.

System and Reference	a (a_0)	c (a_0)	c/a
2L (present)	4.636	12.988	2.802
1L (present)	4.635		
Crystal[a]	4.647	12.903	2.773
Crystal[b]	4.667	13.323	2.854
Crystal[c]	4.674	12.737	2.725
Crystal, Expt. (20 °C)[d]	4.651	12.6782	2.726
2L[e]	4.651	10.232	2.200
"2L"[f]	(4.69)	10.583	2.256
1L[e]	4.622		
1L[g]	4.630		
1L[h]	4.690		

[a] Reference 9.
[b] Reference 8.
[c] Reference 10.
[d] Reference 27.
[e] Reference 23.
[f] Reference 7.
[g] Reference 14.
[h] Reference 13.

for the p_z fitting functions, which can contribute nothing because of symmetry).

The results are shown in Table II, along with those from other calculations on both bulk and 1L graphite and experimental bulk values. (Because there is no crystalline LCGTO-FF code analogous with FILMS, we have used the best available crystalline calculations for comparison.) The most obvious finding is that there is no large reduction of the 2L interplanar separation relative to the measured crystalline value (which is smaller than the LDA calculated values). Relative to the only available all-electron calculation of crystaline graphite lattice parameters,[9] the 2L interplanar separation is predicted to be slightly expanded (0.7%), with the a parameter perhaps very slightly contracted. However, this prediction must be viewed somewhat cautiously, since comparison with a pseudopotential calculation[8] of crystalline graphite yields a predicted 2L c-value contraction of about 2.5%.

Test calculations indicate that the strong contraction found earlier[23] resulted from the combined effects of several deficiencies in the algorithms and control parameters then in use. The most important were multipole moment expansion summations (which appeared to be performing adequately but were not) and inadequacies in the numerical integration grid (used in the XC fitting) then employed. Those algorithmic deficiencies (both since cured) were particularly serious for the case of small, localized Q and XC bases, precisely the situation in Ref. 23. In the setting of the weak interplanar binding of graphite, they drove the calculated 2L to an artificially small interplanar spacing and artificially large interplanar cohesion. (Note that no other system we have studied to date with these computational techniques has exhibited such pathological behavior. After each major code refinement, systems studied previously have been rechecked.)

A simple test of this diagnosis was to redo the calculation at both the former and present minimum energy c values with the refined algorithms but with the basis sets from Ref. 23. The result confirms the diagnosis. With the refined code and the former basis sets, the energy difference (-0.032 eV/atom) between the contracted c value (the Ref. 23 equilibrium) and the present equilibrium c value is virtually identical with the difference found in the present work with the richer basis set (-0.031 eV/atom).

It is interesting that the well-known spurious lattice contraction associated with the LDA (Refs. 28–30) is not obvious in this calculation. This is especially significant because the LDA systematic underestimation is particularly large for weakly bound molecular crystals such as Ne (8.7% contraction),[31] Ar (3.7%),[32] and Kr (0.6–5.8 %).[32,33] As Table II shows, none of the graphite LDA calculations follow this trend; all give c axis dilation. We have not been able to construct a convincing explanation for this behavior.

Prior to our initial report,[23] significant c-axis contraction for graphite in a slab geometry had been predicted by Divincenzo, Mele, and Holzwarth (DMH).[7] They found a 16.5% reduction in a c/a relative to the experimental bulk value using an approximate density-functional model constructed explicitly to study graphitic interplanar binding. (We call this the interplanar model.) DMH approximated the DFT kinetic energy as a Thomas-Fermi term plus gradient correction, invoked the Langreth-Mehl LDA,[34] and approximated the density for crystalline graphite with a superposition of LDA densities for graphite slabs. By considering both full LDA calculations and simpler models with readily interpretable solutions, they attempted to show that these approximations should be realistic for treating interplanar binding in graphite.

Jansen and Freeman[9] had criticized the interplanar model as inadequate for the calculation of crystalline graphite lattice constants. In view of the present findings, it appears that the interplanar model also does not treat the binding in a graphite film or slab adequately. Our calculations suggest that the key deficiency in the interplanar model is probably the assumption of superposed, unrelaxed charge densities.

B. Binding energies

The cohesive energies E_c and interplanar binding energies E_i are tabulated in Table III. (A tabulation of the calculated total energies on grids in a and c is obtainable from authors S.B.T or J.C.B.) These were calculated by use of the atomic local-spin-density total energy using the HL exchange-correlation kernels and the film basis set: $-37.474\,552$ hartree. E_c is not quoted directly by Jansen and Freeman[9] but may be deduced straightforwardly from energies in their paper when combined with its explicit citation of Weinert, Wimmer, and Freeman.[14] Note that Jansen and Freeman report a raw value of $E_i = -0.14$ eV/atom which they then adjust by 40% for "systematic differences" between their film and crystalline full-potential linearized augmented plane wave (FLAPW) programs. The adjusted result, also shown in

TABLE III. Calculated graphite cohesive energies E_c and interplanar binding energies E_i (all in eV/atom) in different structures, along with experimental values. The reference atomic energy for the present calculations is $-1019.742\,519$ eV. See text regarding E_c and E_i for footnote a. As in Table II, "2L" denotes the interplanar model; see text.

System and Reference	$-E_c$ (eV/atom)	$-E_i$ (eV/atom)
2L (present)	8.60	0.03
1L (present)	8.57	
Crystal[a]	8.83	0.14→0.08
Crystal[b]	7.70	
Crystal[c]		0.06
Crystal, Expt.[d,e,f]	7.37;[d]7.39[e]	0.021 (20 °C)[f] 0.027 (0 K)[f]
2L[g]	7.30	0.15
"2L"[h]		0.11
1L[g]	7.15	
1L[i]	8.69	
1L[j]	8.05→8.73	

[a] Reference 9.
[b] Reference 8.
[c] Reference 10.
[d] Reference 35.
[e] Reference 36.
[f] Reference 37.
[g] Reference 23.
[h] Reference 7.
[i] Reference 14.
[j] Reference 13.

Table III, is -0.08 eV/atom.

Before proceeding to the 2L results, consider the checks on both the quality of calculated energies and on the validity of comparison to them which is provided by comparison with the 1L results of Weinert, Wimmer, and Freeman.[14] The present large basis result, $E_c=-8.57$ eV/atom, compares nicely with their large-basis FLAPW value, -8.69 eV/atom. A slightly less favorable match holds for our small-basis result (i.e., the Ref. 23 1L result) and theirs, -7.15 and -7.41 eV/atom, respectively. (In passing, we note that apparently the difference between Zunger's[13] 1L E_c and both ours and those of Weinert, Wimmer, and Freeman[14] is a consequence of the extended Hueckel approximation used by Zunger.)

The overbinding of the 1L with respect to the experimental crystalline value[35,36] which Weinert *et al.* found, and we have confirmed, was traced by them to well-known problems with the LDA's oversimplification of the atomic multiplet structure. This shortcoming is clearly irrelevant to comparisons between calculated solid and film energies. Indeed, the close agreement of the large basis FLAPW calculation of Ref. 14 with our large basis LCGTO-FF calculation is strong support for the validity of comparison of our film results with the FLAPW solid results of Ref. 9.

A central quantity in characterizing graphite cohesion is the interplanar binding energy per atom E_i. In our case the value comes directly from $E_i=E_{c,2L}-E_{c,1L}$. There are no interprogram compatibility adjustments to be made, since the same program, basis, etc., are used in both cases. The present calculated E_i is -0.03 eV/atom as compared with the experimental value for the crystal of -0.021 eV/atom.[37] In itself this is in dramatically better agreement with the experimental value than either the unadjusted result from Jansen and Freeman[9] or the value from the interplanar model.[7] More importantly, Ref. 37 notes that the E_i measurement is at room temperature and suggests a value of $E_i=-0.027$ eV for $T=0$ K, indistinguishable within limits of precision from our calculated value. Some caution with regard to the close agreement with experiment of our static lattice result may be in order, however, in view of the well-known strong temperature dependence of graphite lattice dynamics.[38]

Batra *et al.*[15] obtained $E_i=-0.05$ eV, in seemingly fair agreement with the measured results. However, their calculation is for experimental crystalline lattice parameters, not optimized LDA ones, and they report a large sensitivity of the pseudopotential total energy (0.19 Ry) to the size of the plane-wave basis. It is not completely clear, therefore, to what extent the apparent agreement is meaningful. Both the FLAPW calculation (unadjusted)[9] and the interplanar model[7] give E_i's which are larger in magnitude (factor of 5 to 7) than the measured value. The INDO calculation[10] of E_i is larger in magnitude by almost a factor of 3 and a venerable approximate quantum-mechanical calculation[39] by almost a factor of 4. The wide range of calculated E_i values is indicative of the extreme sensitivity of the predicted interplanar binding energy to computational details and theoretical assumptions.

C. Uniaxial compressibility and universal scaling

The c-axis uniaxial compressibility for four atoms per cell is determined by the equilibrium value of the energy second derivative as

$$k_c=(A_0/2d_{\min})\left[\left.\frac{\partial^2 E_c}{\partial d^2}\right|_{\min}\right]^{-1}$$

with A_0 the basal plane area in the unit cell and $d_{\min}$ the value of $d=c/2$ at the calculated equilibrium configuration. For the hcp space group, the elastic constant c_{33} is just[40]

$$c_{33}=k_c^{-1} .$$

Fitting the nine calculated energies $E(c)$ at fixed a to a functional form based on the so-called universal equation of state (see discussion below; c_0 is the calculated equilibrium value of c)

$$E(c)=C_1[1+C_2(c-c_0)]\exp[-C_2(c-c_0)]+C_3$$

yields $(\partial^2 E_c/\partial d^2)|_{\min}=0.016$ eV$/a_0^2$ for the 2-layer while a nine-point cubic fit gives 0.0182 eV$/a_0^2$. Calculated and measured[41–43] values of k_c are given in Table IV. For the 2L the value given is the average of the results implied by the two fitted second-derivative values. The 2L is roughly 2.5 times more compressible than the experimental crystal, with a larger distinction versus the calculated crystalline data[8,9] and still larger with respect to the interplanar model.[7] There is also a systematic discrepancy between LDA crystalline calculations on the one hand and all available experimental compressibility data on the other. The one available $T=0$ K value of k_c is 35% larger than the average of the LDA calculated values. The average of the room-temperature experimental data is 59% larger.

Jansen and Freeman[9] have provided some analysis of the calculation versus experiment disparity. For our purposes the interrelationship between interplanar binding and k_c may be clarified with calculation of the interplanar scale length L_i (in the harmonic approximation[25(b)]) which appears in the universal equation of state (so named because of its remarkably wide range of applicability),[44,45]

$$L_i=\left[2|E_i| \Big/ \left[\frac{\partial^2 E_c}{\partial d^2}\bigg|_{\min}\right]\right]^{1/2} .$$

The factor of 2 in the numerator is to match the definition of L_S, the surface-surface scale length adopted by Rose, Smith, and Ferrante.[44] For the 2L we find $L_i=1.87a_0$ as contrasted with the values we calculate from the crystalline k_c's, $1.30a_0$ and $1.27a_0$, from Refs. 8 and 9, respectively. The 2L L_i is reasonably in the range of the L_S values of Ref. 44 for bcc metals but on the high side for hcp metals, while the crystalline results extracted from k_c's are in line with the hcp metal results tabulated in Ref. 44. The difference in binding (both magnitude and curvature) between the 2L and the bulk crystal is very evident.

TABLE IV. Uniaxial compressibility, k_c, in units of 10^{-12} cm^2/dyne.

System and Reference	k_c
2L (present)	7.78
"2L"[a]	0.97
Crystal[b]	1.85
Crystal[c]	1.77
Crystal, Expt. (20 °C)[d,e,f,]	2.97,[d] 2.74,[e] 2.70[f]
Crystal, Expt. (0 K)[g]	2.44

[a] Reference 7.
[b] Reference 8.
[c] Reference 9.
[d] Reference 38.
[e] Reference 41.
[f] Reference 42.
[g] Reference 43.

As would be expected, the intraplanar second derivative $(\partial^2 E_c/\partial a^2)|_{\min}$ is much stiffer than the interplanar one. For the 1L intraplanar derivative we obtain (from a quadratic fit) a value of 6.497 eV$/a_0^2$, while for the 2L the value is 6.631 eV$/a_0^2$. The corresponding scale length[24(b)]

$$L_a=\left[|E_c| \Big/ \left[\frac{\partial^2 E_c}{\partial a^2}\bigg|_{\min}\right]\right]^{1/2}$$

is $1.149a_0$ and $1.139a_0$ for the 1L and 2L, respectively. In the crystal, the only readily corresponding combination of elastic constants is $(c_{11}+c_{12})$. From the value of Jansen and Freeman[9] for this sum we estimate a crystalline graphite $L_a=1.25a_0$. Thus, both the 1L and 2L are behaving in uniaxial compression essentially as the crystal does, as would be expected both from the agreement between calculated values of the a parameter and on general grounds of the intraplanar binding mechanisms.

Since both the 1L and 2L are metallic, we may compare L_a with the empirical bulk scale lengths L_b for metals.[44] One finds that these values for 1L and 2L graphite fall in line nicely with those for the bcc alkali metals, but not for any others. A possible explanation for this behavior is provided by looking at chemical bonding in graphite. From that perspective, the 1L strongly resembles a giant polycyclic aromatic system in which all the C atoms are sp^2 hybridized. Of the four valence C electrons per atom, three are involved primarily in localized σ bonds, while the fourth is donated to a delocalized π bond which is the dominant metallic feature. The result is one metallic electron per atom, just as in the alkali metals. Since the 2L can be thought of as two weakly perturbed 1L's from this perspective, the same sort of result would be expected.

IV. KOHN-SHAM ENERGY BANDS AND DENSITIES OF STATES

With the usual caveats about LDA eigenvalues as spectroscopic energies, we show the Kohn-Sham energy bands and densities of states (DOS) for the 1L's and 2L's in Fig. 1 and 2, respectively. The symmetry labeling convention for the two-dimensional Brillouin zone is from Terzibaschian and Enderlein.[46] For comparison, that convention labels as Λ and Σ the points which Tatar and Rabii[5] label conversely (Σ and Λ, respectively). Both conventions differ from those used by Zunger[13] who labels as P,Q what we label as K,M respectively.

The 2L interplanar binding is so weak that, on the scale of Fig. 2, the splitting of the occupied 1L σ bands into pairs cannot be distinguished. This is the reason both for the apparent degeneracy of certain 2L bands in Fig. 2 and, as well, for what appear to be symmetry-forbidden crossings. Although those crossings do not occur, it is not possible to indicate the splittings on the

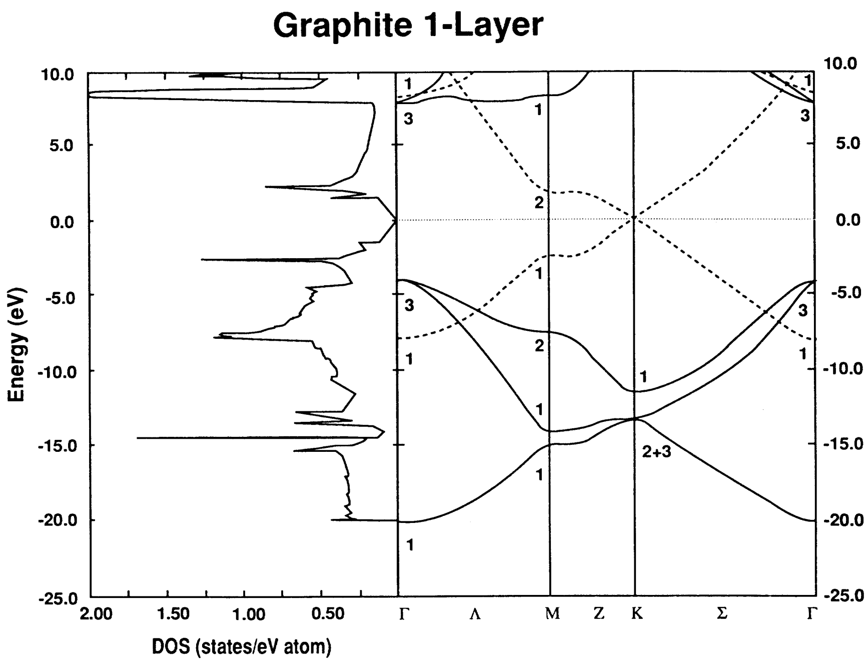

FIG. 1. Bare Kohn-Sham energy bands (eV) and density of states (states/eV atom) for the graphite 1L. Both are referred to E_F as zero of energy. Solid (dashed) curve: even (odd), i.e., $\sigma(\pi)$ symmetry with respect to reflection in the system plane.

scale of the figure. Otherwise, comparison of Figs. 1 and 2, particularly with Ref. 6 (which was also a self-consistent calculation using the HL LDA model) shows no major quantitative nor qualitative differences. There are significant differences with other calculations on both 1L and crystalline graphite. Most of those occur because the other calculations either used another LDA model, were not self-consistent, or both. Note that we can report actual Fermi energies because our calculations have a well-defined vacuum zero of energy, whereas self-consistent calculations on periodically bounded crystals do not.

Table V gives a summary of key one-electron parameters (calculated and measured[47–52]) for both n-layer and

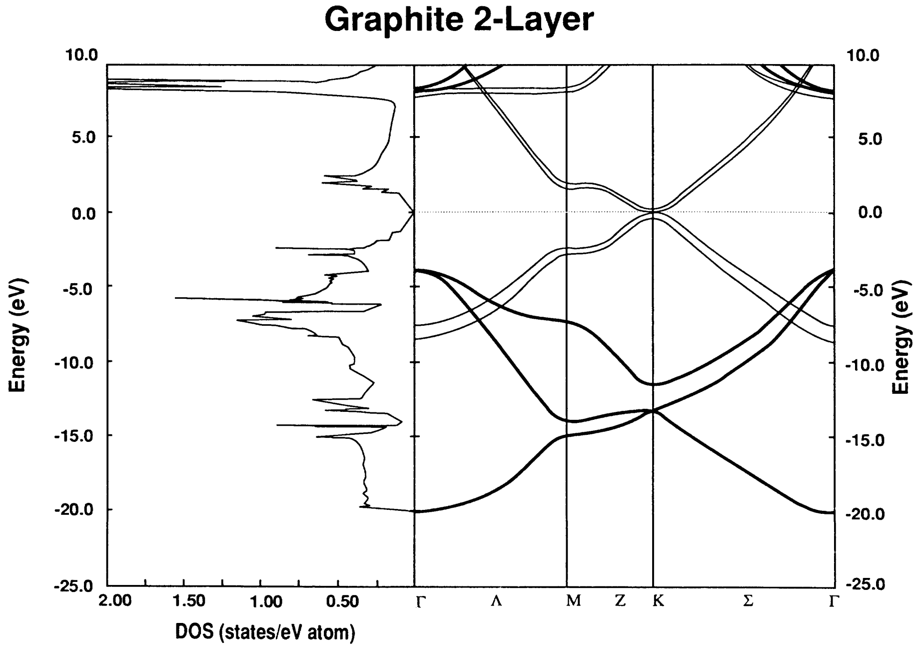

FIG. 2. Bare Kohn-Sham energy bands (eV) and density of states (states/eV atom) for the graphite 2L. Both are referred to E_F as zero of energy. Double-thickness curves represent two bands which cannot be resolved on the scale of the figure.

crystalline graphite. The 2L work function is notably higher than the experimental value for the crystal. Although we would expect as much as perhaps 0.1-eV elevation from the finite basis used here, the actual shift of 0.6–0.7 eV seems too large to be an artifact. It may be that this difference is a static quantum size effect [see Ref. 25(b) for discussion and citations] but with only 1L and 2L data we are reluctant to speculate on the matter.

The density of states at the Fermi level $N(E_F)$ is much smaller for both thin films, a factor of 5 to 6, than what we consider to be the most believable crystalline value, 0.0012 state/eV atom.[5] Since the magnitude of $N(E_F)$ is determined primarily by weak hybridization at the K point of the BZ, this result is qualitatively unsurprising, but the size of the difference is larger than expected. In fact, within numerical precision we cannot rule out the possibility that the graphite 2L is a true semimetal. If so, it might be a candidate for bypassing the obstacles[20] to experimental observation of a quantum size effect in the work function of n layers. Note that both E_F and $N(E_F)$ reported here differ from those reported in the initial calculation.[23] Both changes are a direct result of eliminating the artificial lattice contraption found there.

Some interpretation of results cited in Table V may also be in order. In the cases of Willis, Fitton, and Painter,[2] and Vrăko, Liegener, and Ladik,[52] we deduced some or all of the data for Table V from figures. Regarding $N(E_F)$ for Zunger's calculation,[13] it is clear from a figure that he finds nonzero $N(E_F)$, but we cannot make a reliable numerical estimate. The basic Vrăcko, Liegener, and Ladik[52] calculation is in the Hartree-Fock approximation, which rigorously must have $N(E_F)$ identically zero.[53]

Both the differences between LDA models and the shifts between self-consistency and non-self-consistency are sufficiently large that the effective tight-binding parameters often used in astrophysics to calculate the optical properties of interstellar grains can be and often are significantly modified. Because of the reduced band broadening found here in comparison with Ref. 23 (a consequence of the spurious lattice contraction found there), the calculated values for the tight-binding parameters of the 2L also change. With the same definitions and assumed relationship between γ_1 and γ_2 as described in Ref. 23, we find $\gamma_0 = -2.5 \pm 0.2$ eV, $\gamma_1 \approx -0.1$ eV, and $\gamma_2 \approx 0.01$ eV. The values in common use seem to be from Tatar and Rabii:[5] -2.92, -0.27, and $+0.022$ eV, respectively. Though the present γ_0 is shifted (with respect to Ref. 23) toward the commonly used value, the differences between the two parameter sets are still quite substantial. The source of the difference is primarily the π-band splitting that determines $(\gamma_1 + \gamma_2)$. While that splitting is not large for the crystal, it is much smaller for the 2L.

The same argument applies to the occupied bandwidths, also tabulated in Table V. For the crystal those determined by Jansen and Freeman[9] are slightly narrowed in comparison with those calculated by Holzwarth, Louie, and Rabii[6] but no more so than is consistent with the difference in lattice parameters in the two cases (calculated versus experimental, respectively). Comparison with the Ref. 9 results shows the 2L σ band

TABLE V. Key parameters for LDA energy bands from various calculations and corresponding experimental values. In order, $-E_F$ is the work function, $N(E_F)$ is the DOS at E_F, and the W's are occupied bandwidths. HL is the Hedin-Lundqvist LDA; $X\alpha$ is the X-α parametrized LDA; EH denotes extended Hückel; sc denotes self-consistent; nsc denotes non-self-consistent. Approximate values for footnotes d and g are estimated from figures.

System and Reference	$-E_F$ (eV)	$N(E_F)$ (st/eV atom)	W_σ (eV)	W_π (eV)	W_{tot} (eV)
2L (HL, sc) present	5.23	0.0002	16.2	8.4	20.0
1L (HL, sc) present	4.81	0.0003	16.0	7.9	20.1
Crystal (HL, sc)[a]			17.3	9.1	20.8
Crystal (HL, sc)[b]			15.0	8.7	19.6
Crystal ($X\alpha$, nsc)[c]	8.0	0.0012	14.8	8.0	19.5
Crystal ($X\alpha$, nsc)[d]		≈ 0.02	≈ 16	≈ 8	≈ 20.7
1L (EH, sc)[e]		>0	17.0	5.6	21.2
1L ($X\alpha$, nsc)[f]	8.84	0.0	14.3	7.4	19.3
1L (HF, sc)[g]		0.0	≈ 24	14.2	≈ 34
Crystal, Expt.[h–l]	4.74,[h,i] 4.6[l]		16.0[i]	8.1[j]	20.8[k]

[a] Reference 6.
[b] Reference 9.
[c] Reference 5.
[d] Reference 2.
[e] Reference 13.
[f] Reference 12.
[g] Reference 52.
[h] Reference 47.
[i] Reference 48.
[j] Reference 49.
[k] Reference 50.
[l] Reference 51.

to be broadened and the 2L π band narrowed with respect to the crystal. The 1L calculation by Vračko, Liegener, and Ladik[52] exhibits the excessive occupied bandwidth characteristic of the HF approximation. Their quasiparticle treatment of the one-electron spectrum based on the HF reference state narrows the occupied π-band width from 14.2 eV to 8.8 eV, 0.9 eV larger than the value we predict from bare KS eigenvalues. They did not report the quasiparticle σ bands.

Finally, we find the 1L unoccupied states at Γ several volts above the position reported by Posternak *et al.*[16] The difference may be traceable to the p basis used here. As our focus is on the ground state, the present basis is somewhat limited for the representation of virtual orbitals when compared to a FLAPW basis.

V. SUMMARY

The in-plane lattice parameter of the graphite 2L is essentially identical with the crystalline value (calculated or measured). The interplanar separation is expanded very slightly with respect to the value from an all-electron calculation but modestly contracted with respect to a contemporary pseudopotential result. All are expanded with respect to experimental crystalline values. The dramatic c-axis contraction predicted earlier[7,23] turns out to be spurious. The calculated 2L interplanar binding energy is in remarkably good agreement with measured crystalline values, whereas virtually all prior calculations differ greatly from experiment as well as among one another. The graphite 2L differs from crystalline graphite primarily in its much larger work function and much smaller density of states at E_F; indeed, it may be a semimetal.

Although not as dramatic as the earlier predictions,[7,23] these results still support the view that ultrathin graphite has rather different computed properties from those for crystals. Such differences could be important for the treatment of astrophysically important thin graphitic objects. Finally, calculation of the properties of a system with highly anisotropic binding, such as graphite, is an extremely demanding test of algorithms and associated matters of computational art.

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