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Mono- and dilayer modifications of lithium lattice parameters

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Abstract. Systematic local density treatment (via the all-electron, full-potential, linear combination of gaussian orbitals fitting function (LCGTO-FF) algorithms) of the cohesive properties of mono- and dilayer Li when combined with recent calculations for bulk Li of similar high quality, yields a prediction of modest intraplanar lattice expansion (dilayer: 2.8%, monolayer: 1.6%) and substantial interplanar contraction (dilayer $c/a = 1.46$ versus calculated bulk $c/a = 1.64$). The differences between these predictions and the limited experimental data for Li overlayers on graphite (which exhibit about 6.1% expansion in nearest-neighbour separation) suggest possible substrate or bonding effects in the experiment. The total dilayer cohesive energy is 79.8% of the bulk cohesive energy while for the monolayer the fraction is 63.1%. The interplanar contribution to the dilayer cohesive energy is -0.29 eV. The dilayer uniaxial (c -axis) compressibility is 2.5 times as large as the calculated value for the HCP Li crystal (the latter value is in quite good agreement with available measurements). Mono- and dilayer energy bands (at the level of bare Kohn-Sham eigenvalues) are basically consistent with those calculated self-consistently for the crystal using the same LDA model. However, calculated work function values are larger than measured crystalline values, by more than 0.6 eV, for both the mono- and dilayers.

1. Introduction

In recent years, substantial effort has been devoted toward achieving a theoretical understanding of the electronic properties of ultrathin ($\nu = 1, 2, 3, \dots$ atomic layers) metallic films for their own sake. Much of the effort (see Batra *et al* (1986) for references) has been aimed at determining whether the ν -dependent variations in one-electron properties (e.g. the work function) predicted by jellium models (Schulte 1976, Mola and Vicente 1986, Vicente *et al* 1989) will occur in actual ν -layers. Since such quantum size effects (QSE) are expected to be of the order of the Fermi energy ϵ_F or less, the well-known dependence of one-electron energies on lattice symmetry and parameters means that structure and QSE are critically related. The few studies that have treated the relationship (Feibelman 1983, Ho and Bohnen 1985, Ciraci and Batra 1986, Vicente *et al* 1989) suggest, not entirely conclusively, that ν -dependent structural changes tend to reduce but not eliminate QSE.

Considerably less effort has been devoted to the calculation of structural properties of ultrathin films than to their electronic properties. Most structural studies to date are

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concentrated on 1-layers (1-L hereafter, Mintmire *et al* 1982, Wimmer 1983a, Boettger and Trickey 1984, 1986b, 1989, Batra 1985) or else on modelling of solid surfaces by treatment of rather thick films with inversion symmetry ($\nu = 2s + 1$, $s = 3, \dots, 7$ typically). Relatively little is known about 2-layer (2-L) structural equilibria for example. To our knowledge the only 2-L structural equilibrium calculations reported to date are Feibelman's for Al (1983) and our own for Be (Boettger and Trickey, 1985a) and for graphite (Trickey *et al* 1989, 1990a). Those however have enough unusual and perhaps even counter-intuitive results to make clear that comparative study of 1-LS and 2-LS is important in its own right.

The unusual nature of some of those results is illustrated by the trends in structural parameters, relative to their crystalline values, to be expected from simple coordination number arguments (assuming no symmetry-changing reconstructions). For an unsupported metallic 1-L, the absence of neighbouring layers leads to the expectation of reduced intraplanar separation relative to the bulk value. Addition of a second layer should, on the same grounds, give an intraplanar separation between those for the 1-L and the crystal. Concurrently, the asymmetric 2-L interplanar binding would be expected to reduce the 2-L interplanar separation somewhat from the equilibrium crystalline value. As layers are added, such considerations suggest a smooth increase in the intraplanar separation, rapidly converging to the theoretical bulk value. The interior interplanar separation for a relatively thick film is anticipated to be essentially identical with the bulk crystal value, with smaller values near the faces. We will refer to this picture as the 'coordination model' for the structural parameters of ultra-thin films.

Systematic appraisal of the existing theoretical 1-L and 2-L results reveals that while the coordination model is actually followed in many ways, there are instances of quite different behaviour. (Such comparisons must use calculated quantities exclusively if spurious bond contractions are to be avoided; see section 3 and Boettger and Trickey (1989).) For example, 1-L Al with either the symmetry of the bulk (100) face (Batra 1985) or (110) face (Feibelman 1983, Ciraci and Batra 1986, Boettger and Trickey 1986c) has a lattice contraction predicted to be 5–9% depending on symmetry and calculational details. This decrease is consistent with qualitative expectations from the coordination model. The graphite 1-L is contracted by about 1% compared with the bulk nearest neighbour spacing, while the corresponding 2-L parameter is unaltered from bulk (Trickey *et al* 1989, 1990a) exactly as expected from ordinary carbon bonding and coordination arguments. The coordination model also holds for the interplanar separation in the graphite 2-L (a 19% decrease with respect to the calculated crystalline value). The model fails for the Be 2-L interplanar spacing, which is *expanded* by about 2.7%, while simultaneously it succeeds for the intraplanar spacing of the same system which is contracted by 3.6% (Boettger and Trickey 1985a; bulk values from Chou *et al* 1983).

The most dramatic deviation from the coordination model found thus far, however, is for the alkali metals, which even for the 1-L (Boettger and Trickey 1989) do not conform to those expectations. (Note that Wimmer, 1983a, predicted bond contraction in the Cs 1-L by comparison with *experimental* lattice parameters for the crystal, a problematical procedure as discussed below.) For these, the intraplanar separation is either the same as that of the bulk crystal or *expanded*. The Li 1-L is the extreme example: in comparison with the latest calculation (Trickey *et al* 1990b) for HCP Li ($a_{nn} = 5.66$ au; see section 3), the Li 1-L nearest neighbour spacing ($a_{nn} = 5.78$ au) is expanded by 2.1%.

The question immediately arises as to how the Li 2-L will behave. It is particularly interesting in view of what is known experimentally about Li 1-LS on graphite. Ignatiev

and Fan (1986) have reported a lattice expansion of 6.1% relative to the bulk Li crystalline nearest neighbour spacing (we use the value tabulated by Dacorogna and Cohen, 1986). Their data were accompanied by speculation that perhaps Li_2C_2 was formed instead of the intended Li 1-L. (They did not speculate on possible incommensurate phase formation.) On the face of it, however, their finding is in qualitative accord with our prediction, hence perhaps in disagreement with the bond contraction predicted for 1-L Cs by Wimmer (1983a). The latter remark is conditional, not only because of the aforementioned problem of using experimental data for the crystal but also because Wimmer found the bond contraction to depend sensitively on 5p states which, of course, are completely absent in the Li 1-L. The problem of Li 1- and 2-L lattice parameters is also of intrinsic importance in the closely related matter of understanding Li-graphite intercalation systems, (Samuelson and Batra 1980, Posternak *et al* 1983 and references in both) because of the distinctive ν -layer behaviour summarized at the outset.

To address these issues systematically, we have calculated the cohesive and one-electron properties of Li 1- and 2-Ls in a way which enables direct comparison with recent high-precision calculations for crystalline Li. In order, the remaining sections summarize methodology, present the total energies, equilibrium lattice parameters, cohesive energies, uniaxial compressibilities and universal scaling lengths, and conclude with electronic structure (at the level of Kohn–Sham eigenvalues). As noted, we have treated the cohesive properties of the Li 1-L previously (Boettger and Trickey 1986b, 1989). Though calculated with earlier versions of the codes used, all those results are consistent with the present findings.

2. Methodology

The customary local density approximation (LDA) to density functional theory (DFT) is implemented entirely as a first principles methodology by (a) inclusion of all electrons, (b) retention of the full potential (no ‘shape’ approximations), and (c) full self-consistency at every set of lattice parameters. These characteristics are achieved by solution of the Kohn–Sham (KS) equations with linear combination of Gaussian-type functions, fitting-function (LCGTO–FF) techniques (Mintmire *et al* 1982) as embodied in the FILMS program package (Boettger and Trickey 1986b, 1989). The Hedin–Lundqvist (HL) form of LDA was used throughout.

In LCGTO–FF the KS orbitals are expanded in the first of three Gaussian basis sets (the ‘KS’ basis). The two additional basis sets are to expand the electron number density (‘Q’ basis) and similarly, the LDA exchange–correlation kernels (‘XC’ basis). (Cartesian Gaussians of proper atomic-like symmetry are formed by contraction of the Hermite Gaussians used for analytical calculation of matrix elements.)

To assure stable, reliable results for both the 1- and 2-Ls, we tested several bases. The s-submanifold of the KS basis which resulted was obtained from the van Duineveldt (1971) 9s Li basis by contracting the five tightest members of the latter using as coefficients the atomic Li 1s orbital expansion coefficients determined by van Duineveldt. The KS p-submanifold is comprised of a 2-Gaussian contraction obtained from the two most compact functions and their coefficients as given by Dunning and Hay (1977) combined with a diffuse Gaussian (exponent = 0.14) suitable for crystalline-like environment. An additional diffuse p_z function was added (exponent = 0.06) to ensure a good description of the vacuum region. The resulting (9s3p+1 p_z /5s2p+1 p_z) basis is shown in table 1.

Table 1. Basis set exponents and KS basis contraction coefficients.

ks functions—exponents	ks functions—contraction coefficient
<i>s-type</i>	
1359.446 60	0.000 844
204.026 470	0.006 485
46.549 541 0	0.032 466
13.232 594 0	0.117 376
4.286 148 00	0.294 333
1.495 542 00	1.000 000
0.542 238 00	1.000 000
0.073 968 00	1.000 000
0.028 095 00	1.000 000
<i>p-type</i>	
1.488 000 00	0.038 770
0.266 700 00	0.236 257
0.140 000 00	1.000 000
0.060 000 00	1.000 000 (p_z only)
<hr/>	
o and xc Basis function exponents	
<hr/>	
<i>s-type</i>	<i>d-type</i>
2718.893 20	2.000 000 00
408.052 940	0.660 000 00
93.099 082 0	0.300 000 00
26.465 188 0	0.120 000 00
8.572 296 00	0.060 000 00
2.991 084 00	
1.200 000 00	<i>p_z-type</i>
0.550 000 00	0.800 000 00
0.240 000 00	0.320 000 00
0.120 000 00	0.140 000 00
0.060 000 00	0.060 000 00

The Q and xc bases were chosen to be identical: 11s5d for the 1-L and enriched for the 2-L by adding four p_z functions to describe the asymmetric environment of each atom. The fit basis used for both Q and xc is also shown in table 1.

Among several refinements made in FILMS recently the introduction of linear triangle Brillouin zone (BZ) integration is the most noteworthy. The specific implementation is summarized in the Appendix. It is to be noted that, to ensure stability and precision over a quite substantial range of lattice parameters, we used a much denser mesh of points (37 versus 19 points in the irreducible wedge) for sums over the two-dimensional BZ than in our previous Li 1-L work.

All calculations were stabilized to an iteration-to-iteration shift in total energy of less than 1 μ H (1H = 27.2117 eV).

3. Lattice parameters, cohesive energies, uniaxial compressibility and universal scaling

Although the $T = 0$ K, $P = 0$ kbar phase of Li is widely accepted to be close-packed, the specific phase is still subject to uncertainty (Gooding and Krumhansl 1988). Because

Table 2. Comparison of calculated and measured Li lattice parameters.

System	<i>a</i> (au)	<i>c</i> (au)	<i>c/a</i>
2-L (present)	5.81	8.50	1.46
1-L (present)	5.74	—	—
1-L ^a	5.78	—	—
HCP crystal ^b	5.65	9.28	1.644
HCP crystal ^c	5.77	9.41	1.63
1-L, expt ^d	6.24	—	—
HCP crystal, expt. ^e	5.88	9.62	1.637
Li ₂ molecule, expt. ^f	5.049	—	—
Li ₂ molecule, calc. ^g	5.182	—	—
Li ₆ ring ^g	5.599	—	—
Li ₃ deformed FCC segment ^h	5.820	—	—
Li ₆ deformed FCC segment ^h	5.927	—	—

^a Boettger and Trickey (1989).^e Barrett (1956).^b Trickey *et al* (1990b).^f Herzberg (1950).^c Dacorogna and Cohen (1986).^g Förner and Seel (1987).^d Ignatiev and Fan (1986).^h Boustani *et al* (1987).

of calculational difficulties intrinsic to very small inter-phase energy differences, modern LDA calculations have been restricted to phase-stability comparisons among HCP, FCC and BCC. A recent first principles, full-potential, all-electron LDA calculation on crystalline Li (Trickey *et al* 1990b) finds HCP as preferred among those three as the ground-state phase, in confirmation of earlier pseudopotential (Dacorogna and Cohen 1986) and LMTO (Boettger and Albers 1989) determinations. We therefore assume HCP ordering for the reference crystal.

The coordination model (as well as calculational experience) then motivates the choice of the Li 1- and 2-LS as hexagonally ordered. The unit cell parameters are *a* and *c*, with $c/2 = d$ the interplanar separation. Since our previous calculations show that the 1-L cohesive energy is roughly two-thirds the bulk cohesive energy, the appropriate energy minimization strategy is to optimize the 1-L total LDA energy E_{tot} with respect to *a*, then the 2-L E_{tot} with respect to *c* at that optimum 1-L *a*, then reoptimize both *a* and *c* in the 2-L. The last step turns out to be almost unnecessary.

Calculated lattice parameters are in table 2, along with calculated and measured results for crystalline Li, the Li₂ molecule, and some small Li_{*n*} clusters. To reiterate, except where noted, all comparisons with crystalline lattice parameters are with respect to *calculated* values. This is essential if actual lattice contraction is to be distinguished from the systematic contraction with respect to experimental values for a given phase that is a well-known deficiency of current LDA models (see Jansen *et al* 1984, Boettger and Trickey 1985b, Blaha and Schwarz 1987).

A striking result of this calculation is the substantially smaller (11.0%) *c/a* for the 2-L than the crystal, 1.46 and 1.64 respectively. (This comparison is with respect to the Trickey *et al* (1990b) results and not those of Dacorogna and Cohen (1986) in order to base the comparison on an all-electron calculation using the same choice of LDA model.) A second striking result is that intraplanar lattice *expansion* with respect to bulk is predicted for both the 1-L (5.74 versus 5.65 au or 1.6%) and the 2-L (5.81 versus 5.65 au or 2.8%). This behaviour is precisely the reverse of that found in 2-L Be (Boettger and Trickey 1985a) and discussed in section 1.

The only available experimental data (Ignatiev and Fan 1986) on Li nearest neighbour distances in ultra-thin films are for what were intended to be Li on graphite

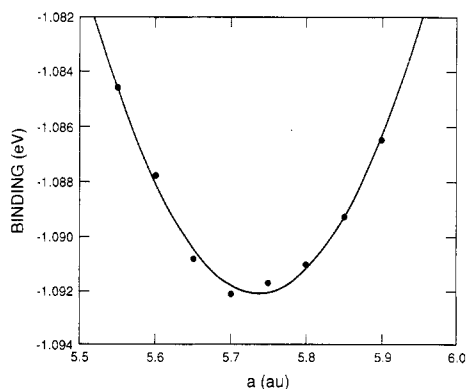


Figure 1. Cohesive energy for the Li 1-L as a function of a .

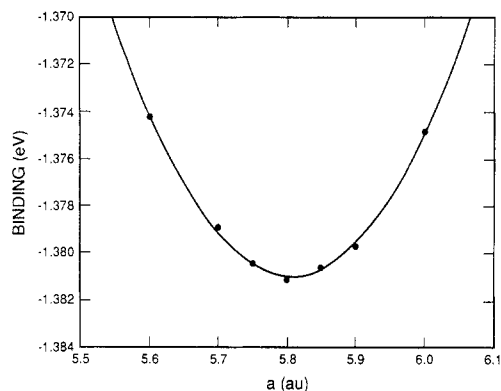


Figure 2. Cohesive energy for the Li 2-L as a function of a .

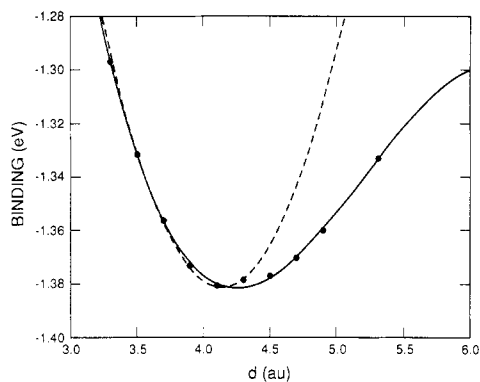


Figure 3. Cohesive energy for the Li 2-L as a function of interplanar separation d .

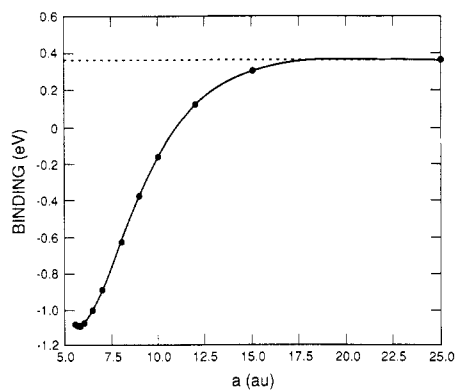


Figure 4. Dissociation of the Li 1-L to the separated atom limit.

substrates. If the authors' expressed reservations are ignored, the reported experimental value for Li 1-L lattice expansion is 6.1%. Thus, although the HL LDA gives a somewhat contracted set of lattice parameters in all phases (note calculated versus measured values for the crystal in table 2 for example), the measured and calculated trends agree qualitatively. Both predict moderate expansion in a_{nn} . Quantitatively, the calculated values are much smaller, 1.6% and 2.8% ($\nu = 1, 2$ respectively).

The 1- and 2-L a -values also may be compared with bond lengths in the Li_2 molecule and in Li_n clusters. For example, the experimental Li_2 bond length is 5.049 au (Herzberg 1950). The CCSD calculation by Förner and Seel (1987) finds 5.182 au for Li_2 and 5.599 au for the interatomic spacing in the Li_6 ring. Thus the absence of a central atom in the planar Li_6 ring causes substantial bond contraction relative to both the Li 1-L and the crystal. Hartree-Fock plus CI calculations carried out by Boustani *et al* (1987) on a wide variety of Li_n clusters show planar geometries preferred for $n \leq 6$. In the present context those planar geometries can be understood as weakly deformed segments of the 1-L. However, both the Li_5 and Li_6 planar clusters have bond lengths greater than that of the Li 1-L: 5.82 au for Li_5 , 5.93 au (average) for Li_6 , 5.74 au for the 1-L. Since CI calculations do not have the LDA bond contraction problem mentioned just above, direct comparison

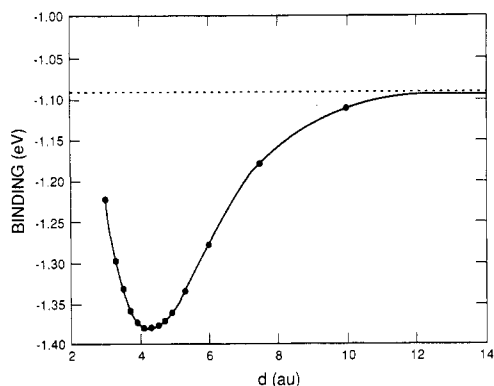


Figure 5. Dissociation of the Li 2-L to the isolated 1-L limit.

of these cluster bond lengths with the *experimental* value of the crystalline bond length is justified. That comparison supports the hypothesis of lattice expansion in the 1-L compared to the crystal.

The cohesive energies E_c and interplanar binding energies E_i are tabulated in table 3. These are referenced to the proper atomic energies, to wit, the LSDA values from the HL exchange–correlation kernels. The 2-L $E_c = -1.38$ eV/atom is 79.8% of the bulk E_c while the 1-L $E_c = -1.09$ eV/atom is only 63.1%. The interplanar contribution to the 2-L cohesive energy is -0.29 eV. Although this interplanar binding is the same order of magnitude as found in the Be 2-L case (Boettger and Trickey 1985a), it is a much larger fraction of the cohesive energy than in that case (21% versus 11%). Consistent with their smallness, the Li_n clusters are bound by less than 60% of even the 1-L cohesive energy.

Figure 1 shows the 1-L $E_c(a)$ together with a quadratic fit to those data. The quality of the fit is very good (RMS deviation = 0.000 24 eV) and illustrates the harmonic nature of the binding curve near equilibrium. Similarly, figure 2 shows the same quantities for the 2-L, with the harmonic character of the a -axis binding again clearly evident (RMS deviation = 0.00014 eV). In contrast the 2-L E_c as a function of interplanar separation (see figure 3) is highly anharmonic. Here we located the minimum of $E_c(d)$ with a cubic fit to the ten calculated points nearest the minimum (RMS deviation = 0.0014 eV). That fit is shown in figure 3, along with a quadratic (the best fit to the points below c_{\min} alone), to illustrate the severe asymmetry of the interplanar binding energy with separation.

The anharmonicity in $E_c(d)$ will have an important consequence for the physical behaviour of the Li 2-L, namely a strong temperature dependence for the interplanar separation. For example, an energy 300 K above the $E_c(d)$ minimum gives the midpoint of the classical turning points at $d = 4.35$ au. Thus a room temperature c/a in excess of 1.50, as compared to the $T = 0$ K value of 1.464, is not improbable. Of course these are rough static lattice arguments but they illustrate the way in which the lattice dynamics of the Li 2-L will be highly anharmonic and anisotropic and the significant temperature dependence which must accompany those characteristics.

Figures 4 and 5 give the dissociation curves for the 1-L into atoms and the 2-L into two 1-Ls. For the 1-L, the paramagnetic atomic limit (the ν -layers are not spin-polarized) is achieved by a separation of about 20 au. More importantly, the 2-L has essentially achieved its separated 1-L limit by an interplanar separation of about 12 au. This latter result suggests that for a Li 4- or 5-L system, the two surface layers should be effectively decoupled. Thus, we might expect the surface properties of a thin film of Li to have converged to their limiting values for $\nu = 5$.

Table 3. Calculated and experimental Li cohesive energies E_c and interplanar binding energies E_i (all in eV/atom).

System	E_c	E_i
2-L (present)	-1.38	-0.29
1-L (present)	-1.09	—
1-L ^a	-1.11	—
1-L ^b	-1.01	—
Crystal ^c	-1.73	—
Crystal, expt. ^d	-1.66	—
Li ₂ ^{e,f,g}	-0.53, -0.35, -0.24	—
Li ₆ ring ^f	-0.46	—
Li ₅ deformed FCC segment ^g	-0.56	—
Li ₆ deformed FCC segment ^g	-0.63	—

^a Boettger and Trickey (1989).

^b Wimmer (1983b); note that this is at the experimental crystalline value of a_{nn} .

^c Trickey *et al* (1990b).

^d Anderson and Swenson (1985).

^e Wilkinson (1963).

^f Förner and Seel (1987).

^g Boustani *et al* (1987).

Table 4. Uniaxial compressibility, k_c , in units of 10^{-12} cm² dyn⁻¹.

System	k_c
2-L (present)	4.57
HCP crystal ^a	1.81
HCP crystal, expt. ^b	1.76

^a Dacorogna and Cohen (1986).

^b Anderson and Swenson (1985).

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

$$k_c = (A_0/d_{\min})(\partial^2 E_c/\partial d^2|_{\min})^{-1}$$

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 crystal, the elastic constant c_{33} is (Seitz 1940)

$$c_{33} = 1/k_c.$$

The cubic fit around the minimum of $E_c(c)$ cited above gives $\partial^2 E_c/\partial d^2|_{\min} = 0.14$ eV au⁻² for the 2-L. Calculated and measured values of k_c for compression along c are displayed in table 4. The Li 2-L is some 2.5 times more compressible along that axis than the bulk crystal.

This behaviour is a dramatic yet unsurprising contrast with, for example, 2-L graphite (Trickey *et al* 1990a). In the Li 2-L, the HCP symmetry means that every atom is at an open site with respect to the other plane. Graphite on the other hand has two atoms out of the four in its parallelogram unit cell which are overhead to one other. (These are the atoms at the vertices of the parallelogram.) The coordination model therefore suggests that at sufficiently small values of d the compressibility in graphite 2-LS should be reduced relative to the bulk crystal value while that for the Li 2-L will be increased.

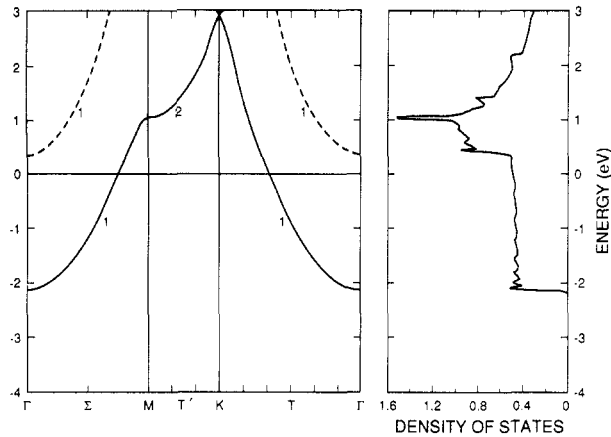


Figure 6. Li 1-L energy bands and density of states (states $\text{eV}^{-1}/\text{atom}$).

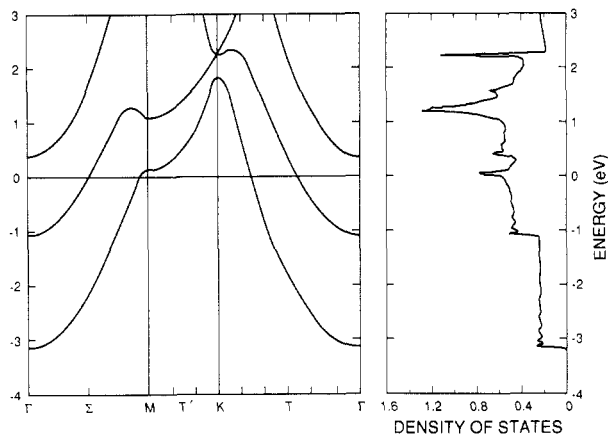


Figure 7. Li 2-L energy bands and density of states (states $\text{eV}^{-1}/\text{atom}$).

The effect is accentuated by the fact that the Li 2-L is deficient with respect to its metallic bulk counterpart in terms of the volume of electron liquid available for compression along the d direction. Graphite bonding is, in contrast, of molecular crystal character in both the 2-L and bulk. This, coupled with shrinkage of the d -parameter in both 2-Ls, argues for increased compressibility, i.e. a softer system, for the Li 2-L relative to the crystal and the converse for a 2-L like graphite, exactly as is found.

Two of us (Boettger and Trickey 1989) have treated the relationship between E_i and k_c elsewhere. The central quantity is the scale length L_i for the interplanar energy, which appears in the empirically discerned universal equation of state (Rose *et al* 1983, Vinet *et al* 1989, Boettger and Trickey 1989). Here L_i is given by

$$L_i = [2E_i/(\partial^2 E_c/\partial d^2)_{\min}]^{1/2}$$

with the factor of 2 in the numerator to accord with the definition of L_s , the surface-surface scaling length, used by Rose *et al*. For the 2-L, $L_i = 2.04$ au as compared with $L_s = 1.95$ au and the bulk scaling length $L_B = 1.04$ au obtained empirically by Rose *et*

Table 5. Work function $\Phi(= -\epsilon_F)$, density of states at ϵ_F , and total occupied bandwidth W (from Kohn-Sham energy bands) as calculated, with corresponding experimental values where available.

System	Φ (eV)	$N(\epsilon_F)$ (states eV/atom)	W (eV)
2-L (present)	3.58	0.56	3.2
1-L (present)	3.53	0.50	2.2
1-L ^a	3.53	0.56	2.17
BCC crystal ^b	—	0.48	3.6
BCC crystal ^c	—	0.49	3.8
HCP crystal, expt. ^d	2.90	—	—

^a Wimmer (1983b); note that this is at the experimental crystalline value of a_{nn} .

^b Moruzzi *et al* (1977).

^c Papaconstantopoulos (1986).

^d Michaelson (1977).

al. A purely theoretical value of L_B is 1.14 au (Trickey *et al* 1990b). If the empirical L_S is scaled by the ratio of these two L_B s (theoretical to empirical) the predicted result is $L_S = 2.19$ au. Together these results suggest that the upper layers of a cleaved Li surface will behave in compression rather like the Li 2-L.

As expected, the intraplanar second derivatives are much stiffer. In the 1-L, the intraplanar derivative is the only compressibility. From the quadratic fits mentioned previously, the values of $\partial^2 E_c / \partial a^2|_{\min}$ for the 1-L and 2-L respectively are 0.43 eV au⁻² and 0.32 eV au⁻². As can be seen from figures 1–5, the energetics of compression along the a -axis are almost completely independent of c -axis compression. An excellent approximation for calculation of the a -axis scale length

$$L_a = [2E_{\text{bind}} / (\partial^2 E_{\text{tot}} / \partial a^2|_{\min})]^{1/2}$$

therefore is to choose

$$E_{\text{bind}, 1-L} = E_c \quad E_{\text{bind}, 2-L} = E_c + E_i/2$$

that is, in the 2-L one-half of the interplanar binding energy is removed for each plane. The values of L_a are then 1.59 au and 1.96 au for the 1-L and 2-L respectively, whence it is apparent that the 2-L binding is quite isotropic and rather different from that of bulk Li (recall the calculated $L_B = 1.14$ au).

4. Kohn–Sham energy bands and densities of states

With the usual caveats about LDA eigenvalues as non-rigorous estimators of spectroscopic energies, we show the Kohn–Sham energy bands and densities of states (DOS) for the 1- and 2-Ls in figures 6 and 7 respectively. The symmetry labels for the two-dimensional Brillouin zone follow the conventions given by Terzibaschian and Enderlein (1986). Comparison with the bulk BCC (Moruzzi *et al* 1978), FCC (Boettger and Trickey 1985b), and HCP (Trickey *et al* 1990b) energy bands shows no surprising differences in light of the differing symmetries and LDA models involved. Wimmer's 1-L energy bands (which were calculated at experimentally determined lattice parameters for the crystal) likewise differ little from the present results.

We summarize the key features of the Kohn–Sham bands in table 5. The most remarkable result is the consistent disparity, over 20%, between all calculated values of

the work function, Φ and the measured value (Michaelson 1977). Various jellium estimates ($r_s = 3.28$ au) give $\Phi = 3.25$ eV (Lang and Kohn 1971), 3.4–3.7 eV (Alldredge and Kleinman 1974) 2.21 eV (Sahni and Ma 1980), and 3.22 eV (Perdew and Wang 1988). The Sahni and Ma treatment is HF, while the rest are LDA. The LDA jellium predictions agree well with the present values of 3.53 eV (1-L) and 3.58 eV (2-L). All disagree with the measured value by at least 10%.

The experimental data reviewed by Michaelson were already about a decade old at that time. In an appendix, Michaelson remarks on the wide variation of those original data. By now it is reasonably clear that remeasurement of the Li work function is needed. We note that the variation of Φ between 1- and 2-LS may signal a weak quantum size effect (Feibelman and Hamann 1984); until we have completed a systematic study of the 3-L and 4-L (a computationally challenging task) this speculation must remain untested.

Turning to the density of states, we note that the 1-L valence DOS has a single low-energy step function while the 2-L DOS has two such steps. These are the expected signatures of the one and two occupied parabolic valence bands respectively. Comparison with the parabolic valence DOS of the solid (e.g. Moruzzi *et al* 1978) shows that at least in this respect the 2-L is a long way from resembling the crystal. Details of the evolution of the ν -layer DOS to that for the bulk solid remain to be elucidated.

5. Conclusions

Li 1- and 2-LS are predicted to have non-trivial intraplanar lattice expansion. This prediction is at least qualitatively in accord with the quite limited experimental data, but in contradiction with the result predicted for Cs. If taken literally, the experimentally determined 1-L intraplanar expansion atop graphite is sufficiently larger than the theoretical prediction for the isolated 1-L to suggest significant substrate effects.

The Li 2-L is predicted to exhibit substantial interplanar lattice contraction as well. The interplanar binding energy curve is strongly anharmonic, with the result that the actual spacing of a Li 2-L system will be strongly temperature dependent.

Finally, the consistent disparity of all calculations of the Li work function with respect to the rather old experimental value makes clear the need for remeasurement.

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Appendix

The current version of the FILMS program package is one which has undergone substantial refinement in the past year to attain both speed and precision improvements in multilayer

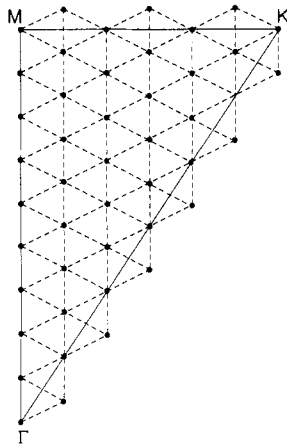


Figure 8. BZ scan for irreducible wedge.

calculations. Details of those algorithmic developments will be presented elsewhere. In the context of the present results, one significant improvement to the method for performing Brillouin zone integrals, must be summarized here. For the BZ integrals there are two changes with respect to previous versions of FILMS.

The simpler change is to use a 37-point mesh rather than the 19-point one used before. More significantly, all BZ integrals now are evaluated with the linear triangle method (Wang and Freeman 1979). As in our previous work on hexagonal films, the new BZ integration mesh is of explicit hexagonal symmetry. A diagram of the triangular division of the irreducible wedge of the first BZ is shown in figure 8. Note that in order to achieve certain desirable properties (see below) the triangles must in some cases extend beyond the boundaries of the irreducible wedge.

Two major advantages arise from utilizing the BZ mesh and triangular partitioning of figure 8. First, the resulting linear triangle integration will not exhibit the potential problems with linear integration schemes first noted by Kleinman (1983) in the context of the analogous three-dimensional technique, linear tetrahedral integration. He showed that the misweighting of k -points in standard applications of the linear tetrahedral schemes results in very slow convergence of the values of integrals as the number of points in the BZ scan is increased. Jepsen and Anderson (1984) followed up by pointing out that the key problem is that for a uniformly distributed mesh of points in the BZ, it is possible (in fact, common) for the linear scheme to result in a non-uniform weighting of those points. They used a two-dimensional example for which they showed that a simple rearrangement of the division into triangles eliminates that particular difficulty.

In general, the linear triangular scheme will work best if the BZ points exhibit the symmetry of the reciprocal space lattice, the weight of a given point for a filled band is equal to its star weight, and the triangles themselves exhibit the symmetry of the lattice. The scheme implemented in FILMS meets these requirements; see figure 8. Specifically, integration of a filled band will reduce to a simple histogram integration using standard star weights for the mesh points. The new scan also incorporates the inversion symmetry of the MK axis automatically. This inclusion yields a density of states curve which clearly exhibits the structure appropriate to the band flattening at the zone boundaries (recall figures 6 and 7), whereas the earlier scheme was not guaranteed to do so.

References

- Allredge G and Kleinman L 1974 *Phys. Rev. B* **10** 559
 Anderson M S and Swenson C A 1985 *Phys. Rev. B* **31** 668

- Barrett C S 1956 *Acta Crystallogr.* **9** 671
- Batra I P 1985 *J. Vac. Sci. Technol. A* **3** 1603
- Batra I P, Criaci S, Srivastava G P, Nelson J S and Feng C Y 1986 *Phys. Rev. B* **34** 8246
- Blaha P and Schwarz K 1987 *J. Phys. F: Met. Phys.* **17** 899
- Boettger J C and Albers R C 1989 *Phys. Rev. B* **39** 3010
- Boettger J C and Trickey S B 1984 *J. Phys. F: Met. Phys.* **14** L151
- 1985a *Phys. Rev. B* **32** 1356
- 1985b *Phys. Rev. B* **32** 3391
- 1986a *Phys. Rev. B* **34** 3604
- 1986b *J. Phys. F: Met. Phys.* **16** 693
- 1986c 26th Sanibel Symposium poster paper, unpublished
- 1989 *J. Phys.: Condens. Matter* **1** 4323
- Boustani I, Pewestorf W, Fantucci P, Bonačić-Koutecký V and Koutecký J 1987 *Phys. Rev. B* **35** 9437
- Chou M Y, Lam P K and Cohen M L 1983 *Phys. Rev. B* **28** 4179
- Ciraci S and Batra I P 1986 *Phys. Rev. B* **33** 4294
- Dacorogna M M and Cohen M L 1986 *Phys. Rev. B* **34** 4996
- Dunning T H and Hay P J 1977 *Methods of Electronic Structure Theory* ed H F Schaeffer (New York: Plenum) p 1
- Feibelman P 1983 *Phys. Rev. B* **27** 1991
- Feibelman P and Hamann D R 1984 *Phys. Rev. B* **29** 6463
- Förner W and Seel M 1987 *J. Chem. Phys.* **87** 443
- Gooding R J and Krumhansl J A 1988 *Phys. Rev. B* **38** 1695
- Herzberg G 1950 *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* 2nd edn (Toronto: Van Nostrand Reinhold)
- Ho K M and Bohnen K P 1985 *Phys. Rev. B* **29** 3446
- Ignatiev A and Fan W C 1986 *J. Vac. Sci. Technol. A* **4** 1415
- Jansen H J F, Hathaway K B and Freeman A J 1984 *Phys. Rev. B* **30** 6177
- Jepsen O and Anderson O K 1984 *Phys. Rev. B* **29** 5965
- Kleinman L 1983 *Phys. Rev. B* **28** 1139
- Lang N D and Kohn W 1971 *Phys. Rev. B* **3** 1215
- Michaelson H B 1977 *J. Appl. Phys.* **48** 4729
- Mintmire J W, Sabin J R and Trickey S B 1982 *Phys. Rev. B* **26** 1743
- Mola E E and Vicente J L 1986 *J. Chem. Phys.* **84** 2876
- Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
- Papaconstantopoulos D A 1986 *Handbook of Band Structures of Elemental Solids* (New York: Plenum)
- Perdew J P and Wang Y 1988 *Phys. Rev. B* **38** 12228
- Posternak M, Baldereschi A, Freeman A J, Wimmer E and Weinert M 1983 *Phys. Rev. Lett.* **50** 761
- Rose J H, Smith J R and Ferrante J 1983 *Phys. Rev. B* **28** 1835
- Sahni V and Ma C Q 1980 *Phys. Rev. B* **22** 5987
- Samuelson L and Batra I P 1980 *J. Phys. C: Solid State Phys.* **13** 5105
- Schulte F K 1976 *Surf. Sci.* **55** 427
- Seitz F 1940 *Modern Theory of Solids* (New York: McGraw-Hill) pp 94–5, 373–4
- Terzibaschian T and Enderlein R 1986 *Phys. Status Solidi b* **133** 443
- Trickey S B, Diercksen G H F and Müller-Plathe F 1989 *Astrophys. J.* **336** 137
- Trickey S B, Müller-Plathe F, Diercksen G H F and Boettger J C 1990a *Phys. Rev. B* at press
- Trickey S B, Nobel J A, Blaha P and Schwarz K 1990b unpublished
- van Duijneveldt F B 1971 *IBM Research Report* RJ945
- Vicente J L, Paola A, Razzitte A, Mola E E and Trickey S B 1989 *Phys. Status Solidi b* **155** K93
- Vinet P, Rose J H, Ferrante J and Smith J R 1989 *J. Phys.: Condens. Matter* **1** 1941
- Wang C S and Freeman A J 1979 *Phys. Rev. B* **19** 793
- Wilkinson P G 1963 *Astrophys. J.* **138** 778
- Wimmer E 1983a *Surf. Sci.* **134** L487
- 1983b *J. Phys. F: Met. Phys.* **13** 2313