RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 2 15 JULY 1985

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Structure and properties of a beryllium dilayer

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(Received 7 January 1985; revised manuscript received 18 March 1985)

All-electron, density-functional calculations on an hcp Be dilayer find c/a at equilibirum to be 1.69 ± 0.03, $a = 4.20 \pm 0.02$ a.u. (Kohn, Sham, Gaspar) or $c/a = 1.69 \pm 0.02$, $a = 4.10 \pm 0.03$ a.u. (Hedin and Lundqvist). In either case there is very weak interplanar bonding. While these structural properties are noticeably different from those of the bulk crystal, the dilayer work function (Hedin and Lundqvist) is essentially identical to the experimental bulk value.

Beryllium has bulk properties which are quite odd when compared, for example, with Li. The electronic configuration of Be is, in contrast, quite simple. That contrast makes Be an especially important material for fundamental materials physics. Here, we present a structural stability study of dilayer hcp Be which shows that the system is both every bit as odd as its bulk counterpart and also strikingly different. A parallel systematic study of the structural stability of monolayer first-row systems (Li, Be, B, Ne) will be presented separately.[1]

For context, there are two recent methodologically different studies of the structure and electronic properties of crystalline Be. One used contemporary local density-functional (LDF) and *ab initio* pseudopotential techniques with a plane-wave basis,[2] while the other employed restricted Hartree-Fock theory and a linear combination of Gaussian-type orbitals (LCGTO) basis.[3] The calculated lattice parameters agreed well with each other and with experiment (hcp with c/a reduced 3% from ideal). No other structural property comparisons were possible between the two calculations. The LDF study also found decent agreement with experiment for the cohesive energy, bulk modulus, and Poisson ratio. Concurrently there has been extensive work at the Hartree-Fock level (and beyond) on Be clusters whose symmetry is that of crystalline surface fragments [most of the relevant references are cited in the recent cluster calculations of Be_n ($n = 7, 10, 13$) by Pacchioni, Pewestorf, and Koutecky[4]].

In the midst of all this activity there is a striking scarcity of thorough inquiry into Be films. Five groups have published Be monolayer results in the context of broader studies,[5-9] but only one of those[5] calculated structural properties. The dilayer has, prior to this work, been treated only once to our knowledge.[6] That was a Hartree-Fock calculation of the electronic states for a Be dilayer fixed at the experimental bulk geometry. The principal prediction of that study was that the Be dilayer is a semimetal.

Methodological aspects of this study may be disposed of by noting the use of an improved version of the LCGTO charge and exchange-correlation fitting function techniques for LDF calculations presented by Mintmire, Sabin, and Trickey.[5] Refinements included adaptation of the linear triangular interpolation scheme[10] for determination of the Fermi surface, use of a more symmetric Brillouin zone scan, and acceleration of the fitting of the exchange-correlation functional by use of the fitted charge as reference. It should be noted that these are all-electron calculations with off-site (bond-centered) fitting functions and that the codes retain full Hermitian (complex) secular matrices throughout in order to allow nearly arbitrary symmetry. Therefore, even with a relatively compact basis ($6s2p$ for the one-electron states) the calculations are quite demanding of computational resources. That basis has been much tested[5,11] and shown to be satisfactory for structural energy differences of the sort at issue here.

Two LDF models were used: (1) $X\alpha$ with $\alpha = \frac{2}{3}$ (i.e., Kohn-Sham-Gaspar),[12] and (2) Hedin-Lundqvist (HL).[13] Very recent work on bcc Fe (Ref. 14) as well as our own on fcc vs bcc Li (Ref. 15) indicates that for some systems the HL model gives bulk lattice parameters which are contracted (with respect to experimental values), while the bulk lattice parameters predicted by $X\alpha$ for those systems are closer to experiment. The HL work function on the other hand appears (e.g., Refs. 8 and 9) to be the more realistic of the two. For these reasons, we have performed roughly equally extensive calculations for HL (18 combinations of c/a and a, not counting initial explorations on a coarser grid) and for $X\alpha$ (21 combinations). The qualitative behavior of the calculated bulk properties is unequivocally consistent in the two models.

The calculated $X\alpha$ total energies (with respect to the lowest total energy, all in Hartree a.u.) are plotted in Fig. 1 as a function of a for four values of c/a. These results were obtained by variation of the hcp lattice parameter a over $4.15 \leq a \leq 4.35$ a.u. in steps of 0.05. At each a, c/a in the range from 1.53 to 1.80 in steps of 0.05 or 0.06 was explored over a sufficient segment of that range to find the energy minimum. On the basis of these calculated data, we evaluate the minimum energy configuration to be at $a = 4.20 \pm 0.02$ a.u., $c/a = 1.69 \pm 0.03$ a.u. The corresponding series of HL calculations ranged over $4.05 \leq a \leq 4.15$ a.u. in steps of 0.05 a.u. with $1.60 \leq c/a \leq 1.82$ in steps of 0.02 or 0.03. We find the HL minimum energy configuration to be $a = 4.10 \pm 0.03$ a.u., $c/a = 1.69 \pm 0.02$. (The qualitative behavior of the HL energy curves differs little from Fig. 1.) The first result is, therefore, that in contrast with the bulk (in which c/a is contracted about 3% from ideal) the dilayer c/a is *expanded* about 3.5% from ideal. This dilation of c/a occurs *both* because a contracts and c expands with respect to bulk (averages of the two sets of experimental values[2] yield $a_{\text{expt}} = 4.32$ a.u., $c_{\text{expt}} = 6.77$ a.u.).

At the HL energy minimum, the calculated dilayer cohesive energy is -3.22 eV/atom, while the corresponding $X\alpha$ equilibium cohesive energy is -2.70 eV/atom. By comparison, the same orbital basis yields[9] a monolayer Be cohesive energy of -2.87 eV/atom (HL) and -2.41 eV/atom ($X\alpha$). (The bulk value is -3.32 eV/atom experimentally and -3.60 eV/atom from an HL calculation.[2]) The second feature revealed by these calculations is, therefore, that the interplanar binding of a Be dilayer (relative to the monolayer) is rather weak, only -0.35 eV/atom in HL and -0.29 eV/atom in $X\alpha$. For comparison, this interplanar binding is less than 10% of the bulk Be cohesive energy (and in fact is only about 50% larger in magnitude than the cohesive energy of bulk Xe). This finding suggests the possibility of observing a very soft dilayer interplanar vibrational mode.

Since these are paramagnetic calculations, the most appropriate cluster calculations with which to compare the dilayer cohesive energy are those with singlet ground states. Pacchioni *et al.*[4] have considered fragments of hcp mono-, di-, and trilayers, all with nearest-neighbor distance fixed at 4.2 a.u. The lowest singlets they find in their configuration interaction calculations have cohesive energies of -0.671 eV/atom (13 atom monolayer fragment), -0.51 eV/atom (10 atom dilayer fragment), and -0.72 eV/atom (13 atom trilayer fragment). Though there are methodological differences (LDF vs CI), it would be implausible to attribute the large difference between these cluster cohesive energies and our dilayer result (-3.22 or -2.70 eV/atom) to those differences. It seems clear that those differences arise instead because the dilayer, like the monolayer,[5] is metallic (see below) with the metallic electron delocalization manifesting istelf strongly in the shift from cluster-fragment binding (i.e., localized) to film binding. Cluster calculations of the kind mentioned are clearly rather far from reproducing the energetics of the film, although they evidently have other uses.

The calculated values of the work function and occupied bandwidth are given in Table I. For comparison, we have displayed the calculated results for a Be monolayer and the calculated and measured results for bulk Be. (Note that our

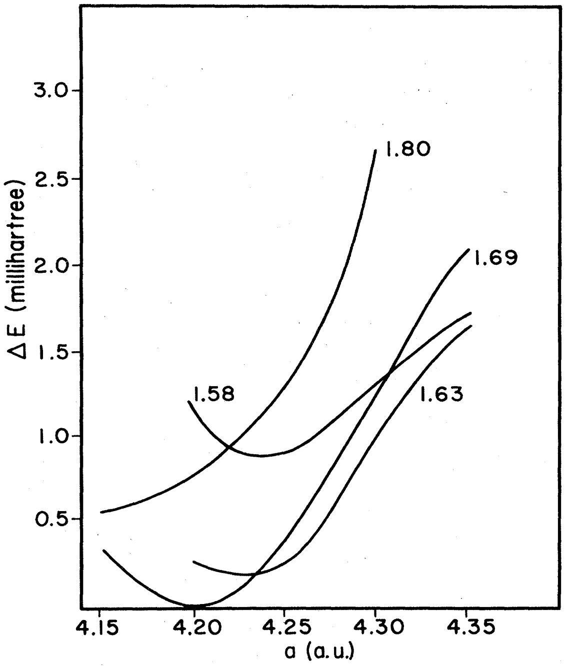

FIG. 1. Shift in ground-state total energy $(X\alpha)E$ with respect to its minimal value in millihartree as a function of lattice parameter a for the c/a ratios indicated adjacent to each curve. Note that $c/a = 1.569$, 1.586 are the experimental and calculated bulk values, respectively (Table I, Ref. 2).

TABLE I. Work functions and occupied bandwidths (all in eV).

	$2L$-$X\alpha$	$1L$-$X\alpha$	$2L$-HL	$1L$-HL	Bulk	
					Calculated (HL)	Experiment
Work function	3.93	3.50[a]	5.11	4.80[a] 5.19[c]		5.10 ± 0.002[b]
Occupied Bandwidth	9.19	6.13[a]	9.52	6.44[a] 5.93[c]	11.156[d]	11.1 ± 0.1[e]

[a] Reference 1.
[b] Reference 16.
[c] Reference 8.
[d] Reference 2.
[e] Reference 17.

monolayer results[1] differ modestly from those of Ref. 9 primarily because the orbital and fitting bases used in Ref. 1 are substantially richer than those tractable for the dilayer. To a lesser degree those differences are in part attributable also to the program improvements cited above.) The $X\alpha$ work function may be dismissed by noting its usual extreme underestimate with respect to experiment. The HL dilayer work function is indistinguishable from the experimental bulk value while the corresponding monolayer value is 6.3% below. The occupied bandwidth comparison is not as good. However, the dilayer HL calculation does pick up 85.3% of the measured occupied bandwidth[17] while the $X\alpha$ result is only slightly smaller.

In conclusion, these calculations show that the hexagonal Be dilayer should be a metal with lattice parameters and c/a ratio which are distinctly different from those of the crystal. The interplanar bonding is very weak, so that the film is quite soft along the c axis. Apparently the Fermi level (the only spectroscopic property which is rigorously determinable directly from local density eigenvalues) is almost the only aspect of the dilayer which can be expected to behave like a bulk surface. We find no indication that the dilayer properties will have any quantitative resemblance to those of crystalline fragments of like symmetry.

One of us (S.B.T) thanks A. B. Kunz, T. O. Woodruff, and W. J. Powers for the opportunity to be a guest in the Institute for Condensed Matter Studies of Michigan Technological University. We thank Gar Hoflund, at the University of Florida, for providing us with the data of Ref. 17 prior to publication. This work was supported in part under National Science Foundation Grant No. DMR-82-18498 and performed in part under the auspices of the U.S. Department of Energy.

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