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## Electronic structure of the bulk and layers of the alkaline earths (Be–Ba)

G Pari<sup>†</sup>, Vijay Kumar<sup>‡</sup>, A Mookerjee<sup>†</sup> and A K Bhattacharyya<sup>§</sup>

<sup>†</sup> S N Bose National Centre for Basic Sciences, Salt Lake, Calcutta-91, India

<sup>‡</sup> Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam-603 102, India

<sup>§</sup> Department of Engineering, University of Warwick, Coventry C47 7AL, UK

E-mail: pari@boson.bose.res.in, kumar@igcar.ernet.in,  
abhijiti@boson.bose.res.in and ashok.bhattacharyya@warwick.ac.uk

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**Abstract.** We report the results of electronic structure calculations for the bulk and layers of the alkaline earths (Be–Ba) made using the linearized muffin-tin orbital method within the local density approximation. In agreement with experiments, bulk calcium and strontium are found to undergo a metal–semi-metal transition under compression, whereas for each of these elements a single (100) layer is found to have vanishing density of states at the Fermi energy at normal pressure. A layer of Ba, on the other hand, exhibits a similar behaviour under expansion. As compared to the bond length for the bulk, there is an expansion for a single layer in all of the cases. This expansion is large for Mg, which is consistent with the large bond length of the Mg dimer. The binding energy for a single layer is close to its value for dimers but it increases by a large amount for three layers. These results are discussed in terms of the changes in the s–p/d hybridization with the reduction in the coordination, and its importance for understanding the properties of clusters of transition metals.

### 1. Introduction

The alkaline-earth elements, Be–Ba, are currently attracting much interest due to their unusual properties in low dimensions. Their atoms have the closed-shell  $ns^2$  electronic configuration which makes the dimers of these elements very weakly bonded, with an expansion in the bond length as compared to the bulk. This behaviour is opposite to the contraction usually found in the bond length of metal dimers. Since in the bulk these elements are metallic, a non-metal–metal transition occurs in the clusters with increase in size. Furthermore, surfaces of Be and Mg have been studied experimentally [1, 2] as well as theoretically [3–5], and have been found to show an expansion, contrasting with the contraction generally found for metal surfaces. These elements are also of interest if one wishes to learn the effects of core electrons on the electronic structure: going down the column, the electronic configuration changes in an interesting way. While Be has no p electrons in the core, Mg has 2p electrons in the core, whereas, for Ca, the 3d electrons start playing an important role. For Sr, the 3d electrons in the core affect the 4d wavefunction, while, for Ba, 4f electrons also start to become occupied. Of particular interest are Ca, Sr, and Ba, since atoms of these elements have no d electrons, but in the bulk, d electrons do get partially occupied. Therefore, in low dimensions, different s–p/d hybridizations and orbital occupancies could lead to interesting variations in properties.

The bulk properties of these elements have been successfully studied [6, 7] in detail using the density functional theory (DFT) within the local density approximation (LDA) [8, 9]. DFT calculations by Feibelman [4] for surfaces of Be and Mg have shown p-to-s electron transfer to be responsible for the expansion of these systems in low dimensions. It has been suggested that similar expansions are possible for the rest of the column, perhaps due to the d/f-to-s electron transfer.

The purpose of the present work is to achieve an understanding of the behaviour of the alkaline earths (Be–Ba) in low dimensions, with an emphasis on the role of the d electrons. In particular, we study the electronic structure of a single layer and slabs of three and five layers, taking the view that knowledge of the electronic properties of layers could provide a bridge between the atom and the bulk, and help in understanding the properties of the clusters, overlayers, and intercalation compounds. In view of the interesting possibilities for non-metal–metal transitions in low dimensions, these systems have attracted attention from experimentalists [10] as well as theoreticians in the past. Wimmer [11] has studied the electronic properties of hexagonal monolayers (coordination 6) of alkaline earths, but he did not optimize the interatomic distances. The main finding of his work is a low density of states for Be and Mg at the Fermi energy ( $E_F$ ), whereas for the heavier elements (Ca–Ba), the d electrons start playing an important role with increasing density of states at  $E_F$ . The beryllium hexagonal monolayer has also been studied by Mintmire *et al* [12] using an LDA  $X_\alpha$  calculation within a linear combination of atomic orbitals (LCAO) approach. They obtained a binding energy of 2.64 eV/atom and a 5% contraction in the interatomic distance in equilibrium for the monolayer as compared to the bulk.

We have considered a (100) layer of an fcc lattice which has coordination 4. This coordination may even be less than in certain clusters with about ten atoms. Therefore, it is expected to give important information about the role of d electrons in such systems. We have optimized the lattice constant of the monolayers and calculated the equilibrium properties of these systems. As a reference, we have made systematic LDA-based first-principles calculations for these elements in the bulk so that we can compare our results with the published data.

The calculated pressure parameters, for the bulk, of all of the systems agree well with the results from earlier theoretical and experimental studies [6, 13, 14]. For Ca and Sr, there is a metal–semi-metal transition as a function of pressure, in agreement with the findings of previous work [7]. However, we report here a similar transition as a function of dimension, i.e. in going from the bulk to a single layer. Also, for each of these elements, a monolayer shows an expansion in bond length, agreeing well with Feibelman's suggestion. This expansion is, however, unusually large for Mg single layers, which is very similar to the case for a Mg dimer.

Section 2 describes the methodology used. In section 3 we present our results, while concluding remarks are given in section 4.

## 2. The method of calculation and crystal structure

We have made use of the semi-relativistic tight-binding version of the linear muffin-tin orbitals (TB-LMTO) method within the atomic sphere approximation (ASA) [15, 16] and the LDA to calculate the electronic structure of these systems. In this method, localized MTOs are used as the basis. The exchange–correlation potential has been calculated using the von Barth and Hedin exchange–correlation scheme [17]. The eigenvalues were calculated for 250  $\vec{k}$ -points for the bulk and 84 or more  $\vec{k}$ -points for the single layers/slabs, uniformly distributed over the irreducible wedge of the Brillouin zone (BZ). Self-consistency in energy and moments was achieved, to an accuracy of  $10^{-5}$  Ryd and  $10^{-4}$  respectively. We have considered: Be 2s and

2p; Mg 3s, 3p, and 3d; Ca 4s, 4p, and 3d; Sr 5s, 5p, and 4d; and Ba 6s, 6p, 5d, and 4f orbitals as the valence states. In the case of the hcp structure, the  $c/a$  value was taken to be the same as that obtained from experiments.

For the single-layer calculations, we have constructed a tetragonal unit cell with  $c = 4a$  from the fcc lattice [18] such that the atomic layer is separated from the layer in the neighbouring unit cell by seven layers of empty spheres. From this tetragonal unit cell, a tetragonal primitive cell was constructed with a volume equal to half of the unit cell ( $a_0 = a/\sqrt{2}$  and  $c = 4a$ ). For three and five layers, we have constructed the tetragonal primitive cell with  $a_0 = a/\sqrt{2}$  and  $c = 5a$  and  $6a$  respectively, maintaining the same number of layers of empty spheres as before. For simplicity, we have made the calculations for Be and Mg, which crystallize in the hcp lattice, and Ba, which has the bcc structure, by using the aforementioned fcc layer, as our primary objective is to understand the effects of s–p/d hybridization in low dimensions. For pressure studies, we have varied the reduced volume  $V/V_0$  of the unit cell from 1.2 to 0.7, in steps of 0.05. The equilibrium lattice parameters and bulk modulus ( $B_0$ ) were calculated using the Birch [19] equation of state.

### 3. Results and discussion

#### 3.1. Bulk

We performed calculations for bcc, fcc, and hcp structures for all of the elements, with the experimental value of the atomic volume, using Andersen’s force theorem, and found the experimental structure to be of lowest energy. For pressure studies, lowest-energy structures of different elements were considered. The calculated equilibrium lattice parameters,  $B_0$ , and the cohesive energies,  $E_{coh}$ , are given in tables 1 and 2. These are in good agreement with the earlier theoretical studies and agree reasonably well with the experimental results within the limitations of the LDA.

**Table 1.** Calculated equilibrium bulk lattice parameters (au) and  $B_0$  (Mbar) for the alkaline earths.

	Equilibrium lattice parameters			$B_0$		
	Present	Earlier	Experiment <sup>a</sup>	Present	Earlier	Experiment
Be	4.22 ( <i>a</i> ) 6.61 ( <i>c</i> )	4.21 <sup>b</sup> 6.63 <sup>b</sup>	4.33 6.78	1.356	1.4 <sup>b</sup>	1.1 <sup>c</sup>
Mg	5.91 ( <i>a</i> ) 9.60 ( <i>c</i> )	5.97 <sup>d</sup> 9.69 <sup>d</sup>	6.07 9.85	0.421	0.421 <sup>d</sup>	0.4 <sup>d</sup>
Ca	10.00	10.02 <sup>d</sup>	10.55	0.212	0.193 <sup>d</sup>	
Sr	10.86	10.87 <sup>d</sup>	11.49	0.164	0.16 <sup>d</sup>	
Ba	8.81		9.49	0.07		

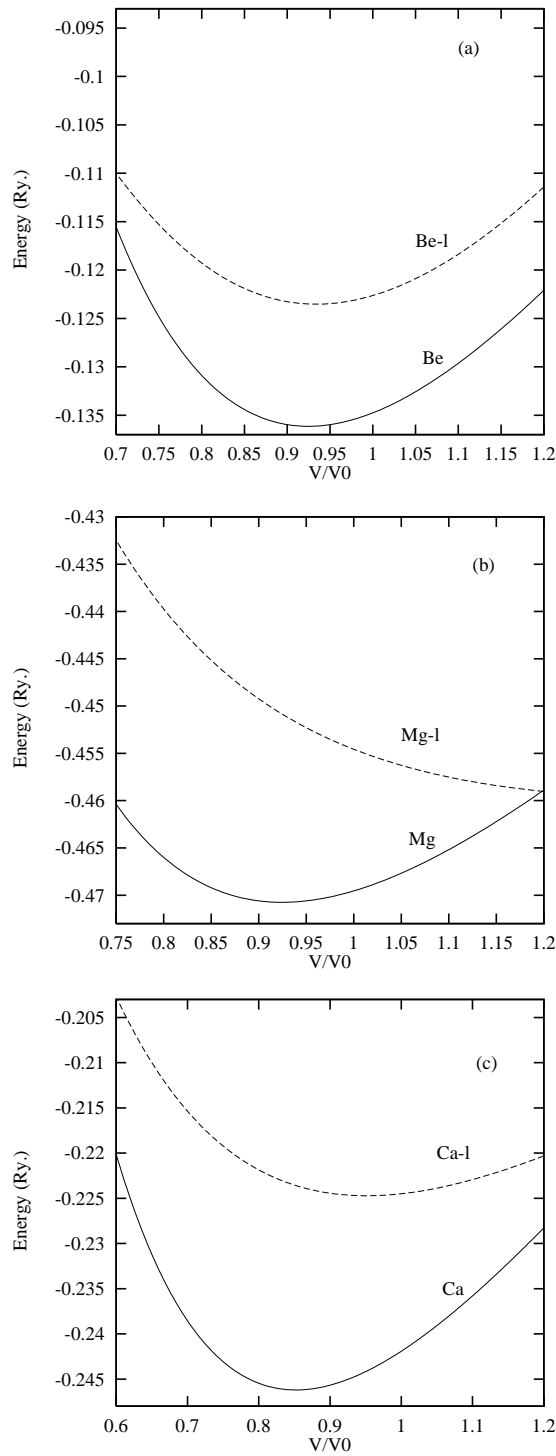
<sup>a</sup> Reference [18].

<sup>b</sup> Reference [3].

<sup>c</sup> Reference [14].

<sup>d</sup> Reference [6].

The total energy as a function of the reduced volume is shown in figure 1 for different elements with their respective ground-state structures. The figure clearly shows that all of the systems stabilize at volumes which are slightly below the experimental value,  $V_0$ . The



**Figure 1.** (a)–(e) Variation of the total energy as a function of the reduced volume for Be–Ba. The y-axis represents the energy with respect to reference values which are  $-29.22$  and  $-29$  Ryd for Be,  $-399$  and  $-398.88$  Ryd for Mg,  $-1358$  and  $-1357.88$  Ryd for Ca,  $-6353$  and  $-6352.87$  Ryd for Sr, and  $-16260$  and  $-16259.88$  Ryd for Ba bulk and single layers respectively.

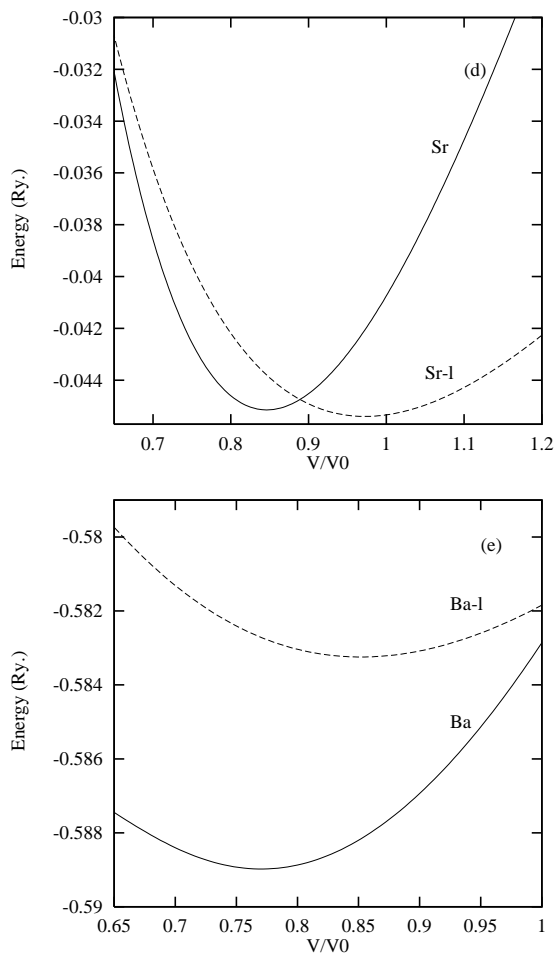


Figure 1. (Continued)

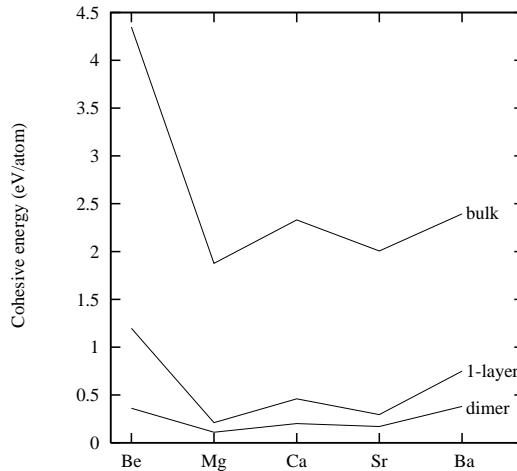
Table 2. Calculated cohesive energies ( $E_{coh}$ ) for the bulk, single layers, and dimers, in eV/atom.

	Bulk			Single layer	Dimer <sup>b</sup>
	Present	Earlier <sup>a</sup>	Experiment <sup>a</sup>		
Be	4.35	4.08 <sup>c</sup>	3.33 <sup>d</sup>	1.20	0.36
Mg	1.88	1.69	1.53	0.21	0.11
Ca	2.33	2.24	1.83	0.46	0.20
Sr	2.01	1.89	1.70	0.29	0.17
Ba	2.39		1.99	0.75	0.38

<sup>a</sup> Reference [6].<sup>b</sup> Reference [13].<sup>c</sup> Reference [3].<sup>d</sup> Reference [20].

underestimation of the equilibrium lattice parameters increases as we go down the column (group II-A). For Be and Mg, the value is about 2.5%, in which case the p orbitals play an important role in the bonding. For Ca and Sr, the decreases are 5.19% and 5.44% respectively,

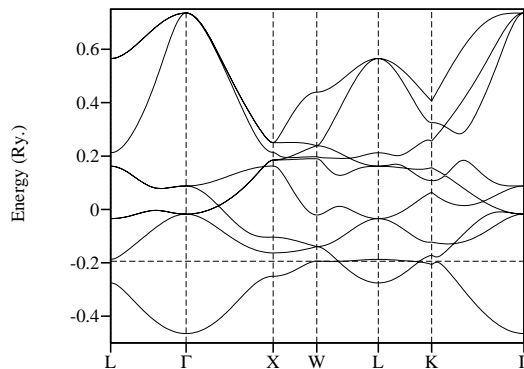
whereas for Ba it is 7.16%. This clearly indicates that the order of underestimation due to the LDA increases with increasing angular momentum of the orbital. It is also clear from tables 1, 2 and figure 2 that  $E_{coh}$  (and also the bulk modulus) varies systematically, depending on the electronic configuration; i.e., from Be to Mg it decreases drastically from 4.34 to 1.87 eV/atom due to the orthogonality of the Mg 3p orbitals to the 2p core. The absence of p electrons in the core of Be means that the effective scattering potential is greater than it is for Mg, which provides a larger contribution to  $E_{coh}$ . For the same reason,  $E_{coh}$  oscillates through the series Mg–Ba.



**Figure 2.** Plots of  $E_{coh}$  for the bulk, single layers, and dimers [10] of the alkaline earths.

In order to understand the role of empty levels above the filled s levels, we have performed calculations with and without those orbitals. These calculations show that Be and Mg are metallic even without p orbitals, indicating that s–p hybridization is not so important for describing the metallicity of these elements. However, for Ca and Sr, calculations without 3d and 4d electrons respectively show an insulating ground state, rather than the actual metallic ground state, indicating that s–d hybridization plays a crucial role in these elements. Moreover, configurations without 3d and 4d electrons for these elements lie significantly higher in energy.

In figure 3 we present the band structure of Sr in the bulk in order to discuss the s–p/d



**Figure 3.** The band structure of bulk Sr at  $V/V_0 = 1$ . The horizontal dashed line shows  $E_F$ .

hybridization. This agrees well with earlier calculations. The single band at the bottom is mainly due to the 5s orbital, the bands just above  $E_F$  are predominantly due to 4d electrons, and the topmost triplet is due to the 5p electrons. The position of  $E_F$  clearly shows a low density of states and a flat 4d band very close to  $E_F$ . The band structure of the remaining elements is also similar to those reported earlier [7]. The topology of the bands calculated near  $E_F$  along the high-symmetry directions, W to L and L (note the band crossing) to K, is such that the s band carries more d character due to a strong s–p/d hybridization, which makes the system semi-metallic with a small pressure. The calculated occupation numbers of the d electrons ( $n_d$ ) for different elemental systems are given in table 3. This table shows that this number increases in going from Ca to Ba, as one would expect due to the increasing extent of the d orbitals leading to a greater s–d hybridization. For Ba, the calculated ground-state occupancy of the 4f level is 0.028.

**Table 3.** Calculated d occupation numbers,  $n_d$ , for the bulk and single layers of Ca, Sr, and Ba.

	Bulk		Single layer
	Present	Earlier <sup>a</sup>	
Ca	0.53	0.55	0.38
Sr	0.59	0.64	0.35
Ba	0.88	0.88	0.60

<sup>a</sup> Reference [7].

### 3.2. Layers

In order to understand the behaviour of a single layer of an alkaline earth, we relaxed the bonds in the  $x$ – $y$  plane, unlike in the earlier surface relaxation studies [3–5] of Be and Mg, where a film of seven or more layers was considered and the relaxation of the outer layer was studied. The calculated values of  $E_{coh}$ ,  $n_d$ , and the (equilibrated) bond length for the single layer, as well as the corresponding values for the bulk, at the experimental  $a_0$ , are given in tables 2 and 4 respectively. We have compared the calculated values with available results on dimers. Figure 2 shows the behaviour of  $E_{coh}$  for the single layer and dimer along with the bulk, and the general trends exhibited by the three cases are similar. These results are also in agreement with the trends obtained by Wimmer [11] for a hexagonal monolayer of these elements, except that his values of the cohesive energy are higher than those obtained by us. This is mainly due to the higher coordination number in hexagonal layers. Also, some differences can arise due to different methods of calculation.

**Table 4.** Calculated equilibrium bond lengths (au) for the bulk, single layers, and dimers of the alkaline earths. (Note: for Be and Mg, the equilibrium bond lengths for the bulk are given in terms of a fcc lattice.)

	Equilibrium bond length		
	Bulk	Single layer	Dimer <sup>a</sup>
Be	4.16	4.17	4.66
Mg	5.90	6.74	7.35
Ca	7.07	7.30	8.08
Sr	7.68	8.05	
Ba	7.63	8.01	

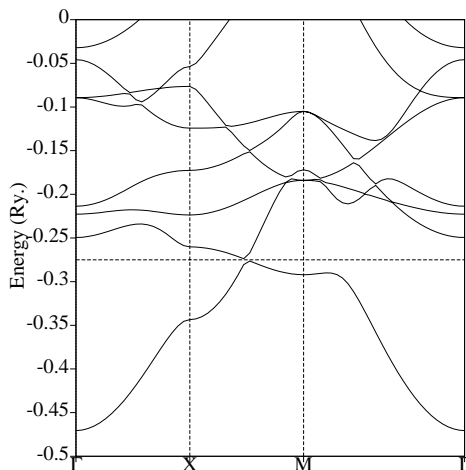
<sup>a</sup> Reference [13].



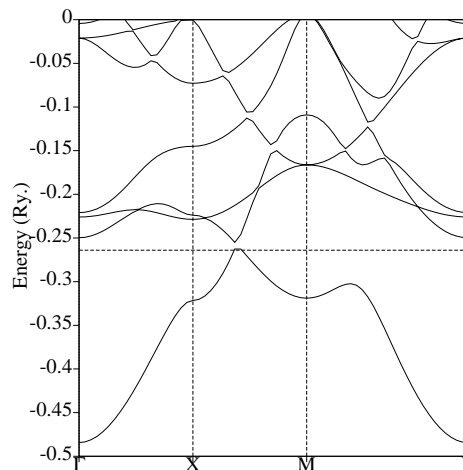
One can see from figures 1(a)–1(e) that the monolayers stabilize at a higher bond length than the bulk, i.e., there is an expansion in the bond length which is in good agreement with the results [3, 4] obtained for Be and Mg (0001) surfaces. Importantly, for the single layers, the curve is flatter than that for the bulk, indicating that the layers are loosely bound as compared to the bulk due to the lower coordination. Tables 2 and 4 clearly show this. It is to be noted that this expansion is quite small for Be monolayers but very large for Mg, as is also the case for the dimers. It is known that the metallization in Be occurs much faster than that in Mg [21]. This is due to the absence of p electrons in the core of Be. However, our value for the expansion in Be monolayers is much smaller than the outward relaxation of the top layer, obtained for its (0001) surface. There could be two reasons for this.

- (a) One is the different methods of calculation used. It is to be noted that for the surface, Feibelman and Stumpf [5] obtained 2.7% expansion in the interlayer distance, whereas Holzwarth and Zeng [3] obtained only 2.1% within the LDA. Both of these values are smaller than the 5.8% expansion obtained from experiment [1]. Also, as mentioned earlier, Mintmire *et al* [12] obtained a contraction in the Be hexagonal monolayer within the LDA using a LCAO basis set. Therefore, a small increase for the (100) layer of Be seems to be quite consistent. The use of the generalized gradient approximation (GGA) for exchange and correlation instead of the LDA has been shown to improve agreement with experiment, and we think that for the monolayer the expansion could also be slightly more within the GGA.
- (b) The other reason could be that, at the surface, there is no lateral expansion, and the only way that the effect of the p-to-s demotion could show up is through an expansion in the interlayer separation. There is a correlation between the value of  $E_{coh}/atom$  for the single layer and the expansion. For larger  $E_{coh}$ , say that for Be, the expansion in  $a$  is very very small, while for smaller  $E_{coh}$ , say that for Mg, it is quite large. The variations of  $E_{coh}$  for the bulk, single layers, and dimers are consistent (see table 2 and figure 2). The cohesive energy of the layers is closer to the value for dimers, and the difference from the bulk cohesive energy is large. However, the cohesive energy increases significantly in going from one layer to three layers. This is in agreement with the fast metallization observed [10] for Ba bilayers on Ni(100). There is a reduction in the number of d electrons in going from the bulk to a layer, but it is not very drastic despite the small expansion. It is therefore likely that in clusters of these elements, the d electrons play quite a significant role, as a contraction in the bond length could enhance the participation of d electrons in the bonding.

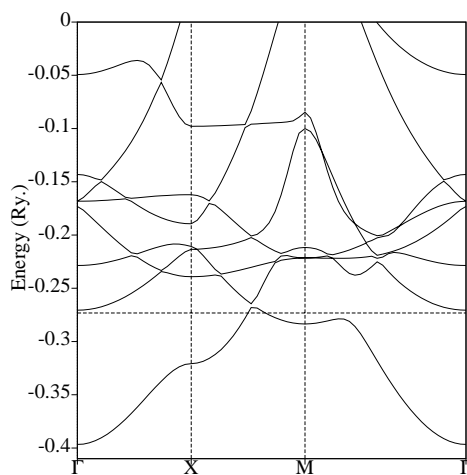
Figure 4 shows the band structure of the Sr monolayer. A comparison of figures 3 and 4 thus shows the metal–semi-metal transition. This mainly arises due to the lower coordination number of the single layer which depopulates the d bands and makes the DOS zero at  $E_F$ , causing Ca and Sr to be semi-metallic. This is due to a change in s–d hybridization. It can be seen from figure 5 that with compression ( $V/V_0 = 0.70$ ), there is an increase in the s–d hybridization due to the reduced bond length, and it opens up a small gap, indicating the nature of the gap to be of hybridization type. However, it is to be noted that a Ba single layer is metallic at the equilibrium lattice constant, and develops a low DOS only in an expanded lattice at around  $V/V_0 = 1.55$  (see figure 6) due to a decrease in the s–d hybridization. The calculated densities of states (DOS) for the single layer as well as three and five layers are given in figure 7 along with the bulk results for Be to Ba. It is important to note that the DOS for the bulk and that for the layers are in different structures, and we have made the comparison to give an overall picture. The states present on the higher-energy side are due to the empty spheres. Monolayer calculations clearly show that Be, Mg, and Ba are metallic, as



**Figure 4.** The band structure of a Sr single layer at  $V/V_0 = 1$ .



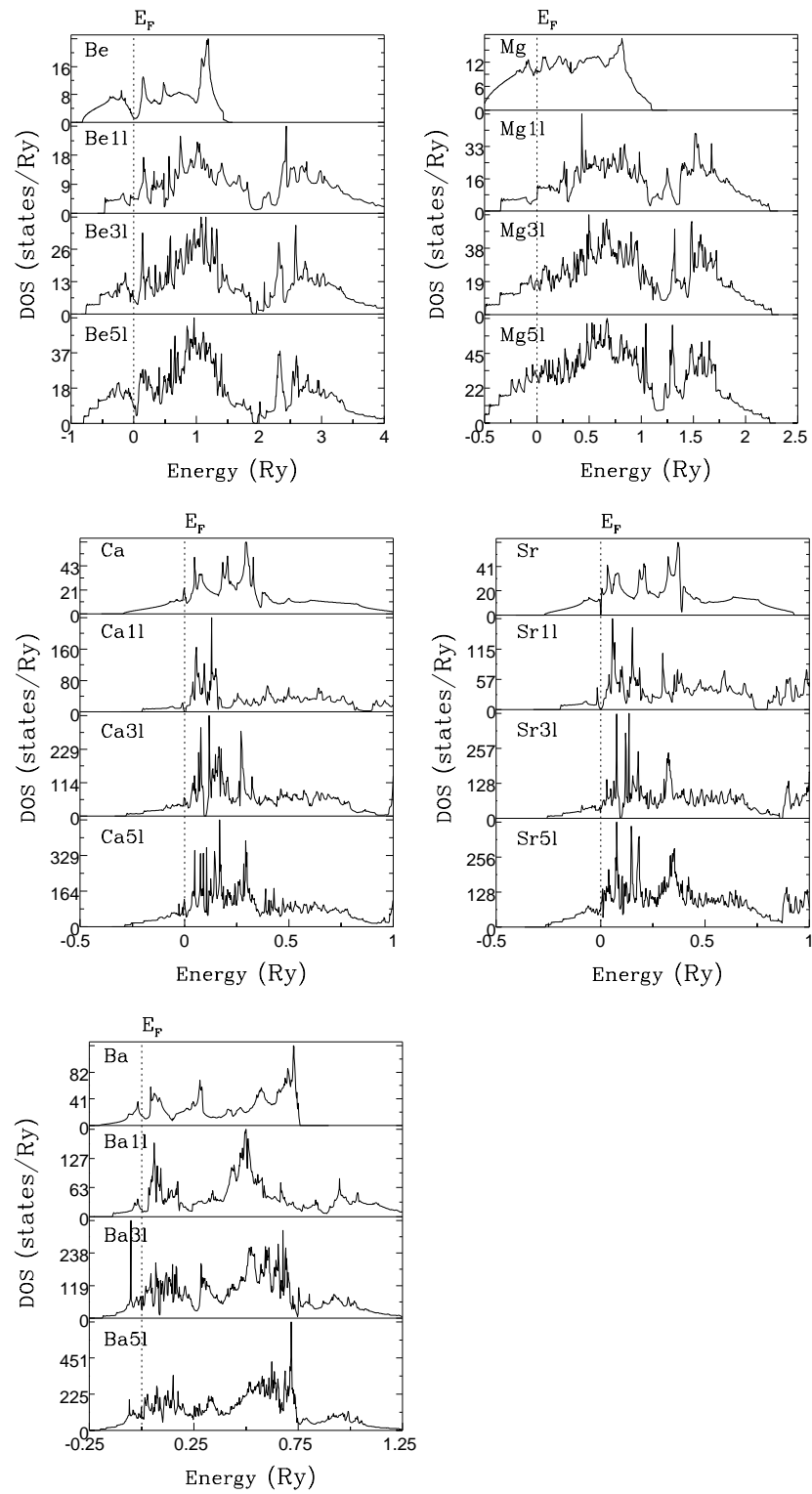
**Figure 5.** The band structure of a Sr single layer at  $V/V_0 = 0.70$ .



**Figure 6.** The band structure of a Ba single layer at  $V/V_0 = 1.55$ .

in the bulk. A similar behaviour was obtained by Wimmer [11] for the hexagonal monolayers of these elements. However, (100) layers of Ca and Sr, which have 3d and 4d valence states respectively, show a transition from the metal (bulk) to the semi-metal with vanishing density of states at  $E_F$ . The gap at  $E_F$  increases with pressure, and then collapses at higher pressures, also as in the bulk, indicating the importance of the effects of s–d hybridization. These figures clearly show that the width of the s band (just below  $E_F$ ) is smaller than the value for the bulk, due to the lower coordination number of the atoms, which provides a smaller nearest-neighbour interaction in the single layer. Also, it is to be noted that the width increases as the number of layers increases. For five layers, it is almost the same as in the bulk. The width of the occupied band decreases in going from Be to Ba. This is in agreement with the results obtained by Wimmer for hexagonal monolayers.

The calculated DOS at the central layer of the five-layer slab looks similar to that of the bulk (note that the structures are different for the layers and the bulk), suggesting that seven



**Figure 7.** The total density of states of the bulk (ground-state structure) and layers of the alkaline earths. Here 1l, 3l, and 5l stand for single layer, three layers, and five layers respectively.

layers are sufficient for the central layer to behave as if it is in the bulk. The large expansion in the bond length of the Mg single layer is consistent with that of the Mg dimer. With a reduction in the coordination number, there is a demotion of the electrons from p to s or d to s–p levels, which leads to an expansion in the bond length of the layers of alkaline earths.

#### 4. Conclusions

The calculated ground-state properties of the alkaline earths Be–Ba are in good agreement with the findings of experimental and earlier theoretical studies. We find that the order of underestimation of the lattice constant due to the LDA increases as one goes down the column. Calculations without 3d and 4d electrons for Ca and Sr give much lower binding energies, indicating the importance of the s–p/d hybridization. The pressure studies further confirm the crucial role of d bands. Our single-layer calculations also show the importance of s–p/d hybridizations. Monolayers of Be, Mg, and Ba are metallic at the equilibrium lattice constant, whereas monolayers of Ca and Sr are semi-metallic.

Furthermore, monolayer calculations show an expansion in the bond length. This is in contrast to the contraction generally found for surfaces of metals, but is very much consistent with Feibelman's prediction. This expansion is anomalous for Mg, as is also the case for the dimer. The p-to-s or d-to-s–p demotion of electrons is the reason for this expansion, as can be seen from table 4. Importantly, single layers of Ca and Sr show a metal–semi-metal transition. A lower coordination number weakens the s–p/d hybridization and leads to a vanishing DOS at  $E_F$ . As a function of pressure, the strength of the s–d hybridization increases, and the s and d bands repel each other, which in turn opens up a very small gap at  $E_F$ . The Ba single layer develops an almost zero DOS at  $E_F$  only for a large expanded lattice. The trends exhibited by the calculated cohesive energies for the single layers are consistent with those shown by the bulk and the dimer.

Calculations with three and five layers show all of them to be metallic, like the bulk, and the calculated values of the occupation number of electrons for the different states indicate that the central atom in seven or more layers may behave like that in the bulk. The cohesive energy increases very significantly in going from a single layer to three layers. We hope that these results will help in the understanding of the properties of clusters and other low-dimensional structures of such elements, and will interest experimentalists in looking for metal–semi-metal transitions in layers.

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