

Calculated electronic structure of metallic multilayers formed by noble and transition metals

A.M. Mazzone^a

C.N.R., Istituto LAMEL, Via Gobetti 101, 40129 Bologna, Italy

Received 3 October 2001

Abstract. Full-potential Linearized Augmented Plane Wave calculations are performed to investigate the properties of the electronic charge of metallic multilayers formed by non-magnetic and magnetic elements (*i.e.* Ag, Cu and Fe). The multilayer structure is of the type A_n , A_nB_n or $(AB)_n$ where A , B indicate Ag, Cu and Fe and n is the number of layers of the element A or B . The problem addressed by this study is the transition from the 2D behavior of the isolated monolayer to the 3D bulklike character. Therefore the calculations, carried out at paramagnetic level, illustrate the dependence of the density of states on the multilayer thickness and composition. For the three elements the main feature of the inter-layer coupling is the absence of charge intermixing and hybridization. For structures with a number of layers $n \leq 5$ the density of states bandwidth has a decrease, with respect to the bulk value, approximately proportional to the reduced coordination. At the critical thickness $n = 5$ and above, a noticeable difference exists between the charge in the outer layers, with reduced coordination and bandwidth, and the central layers with a bulklike density of states. Averaging between these contributions leads to the re-installment of bulklike properties. These results are in essential agreement with analytical band theories and quantum mechanical calculations for similar systems and with experiments.

PACS. 07.05.Tp Computer modeling and simulation – 73.20.At Surface states, band structure, electron density of states

1 Introduction

Thin metallic films constitute one of the key ingredients in the development of new storage devices characterized by high density and miniaturization and their practical interest has fueled intensive researches, both theoretical and experimental. Generally, the thickness of these structures is of a few atomic layers and the systems more commonly adopted consist on sandwiched structures with the magnetic elements intercalated between the non-magnetic ones, the latter ones being used for quantum confinement or as an epitaxial constraint during film growth.

Known properties of multilayers are quantum-well states, oscillatory magnetic coupling and conductivity [1]. These properties are attributed to a 2D electronic structure, as in the isolated monolayer. It is known, in fact, that this system is closer to the atomic limit rather than to the bulk behavior. In the self-standing monolayer there is no periodicity of the electron wavefunction in the normal direction and the dispersion of the electronic charge is confined within the plane of the film. In experiments, however, the pure 2D behavior may be perturbed by interactions with the supporting substrate and/or by inter-layer coupling. Recent experiments on angle-resolved photo-emission spectroscopy for the system one monolayer

Ni/Cu(100) lead to the conclusion that the properties of the Fermi surface agree well with the theoretical predictions for bulk Ni [1]. This finding has been contradicted in [2,3]. In [2,3] the development of the electronic structure with the thickness h is also traced with angle-resolved photo-emission spectroscopy. Various 3d transition metals have been used and the results indicate that the monolayer and the bulk have a very different electronic structure. The discrepancy with [1] is attributed to the critical dependence on h of the electronic charge, which may cause the transition to the bulk behavior by the addition of one or two planes.

It is therefore important to assess which are the modifications of the electronic charge induced by the thickness. The current state of the literature does not allow a comprehensive answer to this question. In fact, a number of studies have been dedicated to thin metallic films and overlayers (essential references are [4,11]. More recent studies are [12,15]). However these studies are directed at the understanding of the general properties of surface magnetism and very few analyze the changes of the electronic structure as a function of h [12,15].

This state of the art has motivated this contribution, which complements and extends a previous study on metallic structures of finite size carried out at semi-empirical level [16]. In the present study the electronic

^a e-mail: mazzone@lamel.bo.cnr.it

charge of metallic multilayers, of both homogeneous and compound structure, has been calculated using the Full potential Linearized Augmented Plane Wave (FLAPW) method. The multilayer components are Ag, Cu and Fe, which are all treated at paramagnetic level. The results focus on the functional dependence of the density of states (DOS) on the multilayer thickness and composition.

2 Computational details

The structural properties of metallic multilayers, grown by epitaxial deposition, have been the object of a detailed experimental characterization. Though intermixing and strained interfacial layers are reported, a reasonable first order approach is that the deposited film has the same structure of the substrate. On this basis, in [7] a simple tetragonal $L1_0$ lattice has been adopted as a plausible structure for unsupported multilayers and this assumption has been also used in this study.

Accordingly, the multilayers are treated in a slab geometry with infinite lateral x, y dimensions. Periodicity along z is obtained by repeating the multilayer structure with an intervening vacuum region of thickness ~ 30 Å. The layers have a *fcc* (100) lattice with the a_o bulk lattice parameter. In the case of FeAg the (001) plane of Fe is rotated 45° with respect to Ag so that there is an exact matching of their 2D square nets. The multilayer composition is either a pure A_m structure, formed by m layers of the element A , or a modulated structure $A_m B_m$, or $(AB)_m$, where $(AB)_m$ indicates the m th replica of the AB bilayer. In the following the multilayer thickness h indicates the number of planes n forming its structure.

The evaluation of the electronic charge has been carried out using FLAPW. In this method electron wave functions, charges and potentials are expanded in spherical harmonics inside the muffin-tin (MT) spheres about the atoms, while for the interstitial region between the spheres a plane wave expansion is adopted. The properties of the system concerned are obtained by iterating to self-convergence the charge distribution obtained by superimposing atomic charges.

Extensive theoretical studies of metallic systems have been performed using FLAPW. In fact the method has been applied to the characterization of different bulk phases of noble and transition metals and in studies of magnetic properties of metallic monolayers (see the references quoted in the Introduction). In this last case, the comparison with other methods shows that the self-consistent nature of the approach, coupled with an extremely advanced software, leads to a realistic description of the spatial localization of d electrons as well as of the s, p expansion into vacuum.

For FLAPW calculations the program WIEN97 [17] has been used. The parameters of these calculations are taken from [15]. The MT sphere radii are chosen to be $R_{mt} = 1.16$ Å for all atoms considered in the present work. For the wave-functions spherical harmonics with angular momentum up to $l_{\max} = 10$ and plane waves up to an energy cutoff $K_{\max}^2 = 17$ Ry are employed. For electron

densities and potentials these parameters are $l_{\max} = 6$ and $|G_{\max}|^2 = 144$ Ry. The core electrons are accounted for by a fully relativistic treatment while valence states are described scalar relativistically. The DOS and the Fermi energy E_f are evaluated using the analytical tetrahedron method with 1000 k values (approximately 130 values in the irreducible part of the Brillouin zone). Electron exchange and correlation are accounted for using the LDA functional as well as GGA implemented in the Perdew-Burke-Ernzerhof functional. The reliability of LDA and GGA was confirmed by separate calculations on ground state properties of bulk *fcc* Ag and Cu and *bcc* Fe (see below). In these calculations systematic trends have been observed. GGA leads to a decrease of the total energy E_t with respect to LDA. The relativistic Hamiltonian generates a decrease of the interstitial charge and an increase of E_t . In both cases, however, the changes are limited and the differences fall below 0.1, 0.2%.

Owing to the reduced symmetry of layered structures, FLAPW calculations are extremely costly, in terms of computer times, and this especially applies to the evaluation of spin effects. The effective need of this evaluation has therefore to be accurately checked. Spin-polarized calculations of Cu(100) five-layers and Fe(100) three-layers show a non-magnetic behavior of the central layers [15]. This last finding is, however, in contradiction with [12], the difference between the two calculations arising from the optimized lattice used in [15]. Total energy calculations of Fe/Ag monolayers [4] indicate that the magnetic states are noticeably lower in energy than the paramagnetic one. However the dependence on the structural parameters is equal for all states and appears correctly described, a part from an energy scaling, by the paramagnetic state. These results suggest that, unless the details of the electronic charge are needed, a realistic and consistent representation of the electronic configuration can be performed without including spin effects. On this basis, non-spin polarized calculations have been applied to all systems considered in this work.

The DOS bandwidth used in the following section is obtained from the intercepts of the DOS-*vs.*- E distribution with the value 1atom and is normalized to the bulk value. The error arising from this evaluation is in the range 10% and is sufficiently low to clearly show the attainment of the bulk limit.

3 Results

FLAPW calculations for crystalline Ag, Cu and Fe are presented in Figure 1. For Ag and Cu the bulk DOS shows the general shape known for *fcc* noble metals [15, 20]. The DOS is essentially concentrated in a single-peak structure, entirely below the Fermi level (at -10 eV in these calculations). Though the peak has a structured shape, it does not split into separate lobes and is therefore fully characterized by the second-order moment of DOS, which is in the range 2 eV (plus 2 eV tailing) for both Ag and Cu. On the contrary, for *bcc* Fe a deep gap separates bonding from antibonding states. The bandwidth of Fe is in the

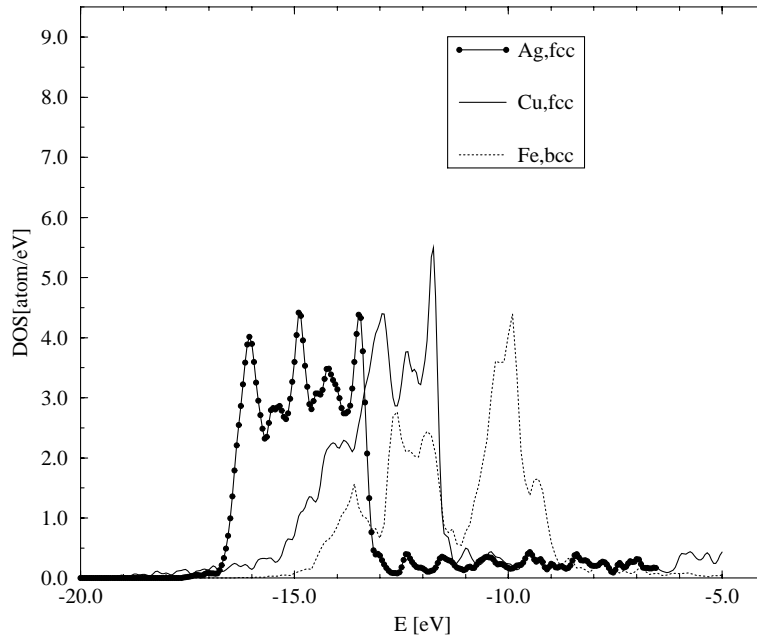


Fig. 1. DOS of the crystalline solids.

range 5 eV with a not negligible tailing above the Fermi energy. These are also literature results and are reported, for instance, in [14].

As an introduction to multilayer calculations, it is recalled that an analytical formulation of DOS for a 2D structure is possible, provided that the lattice has a simple square shape and there is only one s band [19]. In this case the DOS values at the band center and at its edge are given, respectively, by

$$D \sim (a_o/\beta) \ln(\tan(kx/2)) \quad (1)$$

$$D = 1/(4\beta) \quad (2)$$

where a_o is the nearest neighbor distance. β is an Hamiltonian matrix element and represents the inter-site coupling energy.

According to the equations above, the DOS bandwidth is 4β . Furthermore a sharp peak occurs at the band center, *i.e.* at $kx/2 = \pi/2$, where D reaches infinity. In a three-dimensional system a term $\cos(k_z a_o)$ is added to the Fermi surface. This extends the bandwidth from 4β to 6β and the divergence at the band center is replaced by the known square root dependence on E . In the tight-binding formulation the reduction $4/6$ is interpreted as the effect of the lower coordination in the 2D lattice in comparison with the 3D case [19].

Though this simple behavior can be noticeably altered by an accurate account of the lattice structure and of the interatomic forces, the main effect to be expected in passing from 3D to 2D is a remarkable sharpening of the DOS bandwidth and an increase of its peak value. The occurrence of these effects is illustrated in Figure 2, where the DOS of bulk Ag is compared with the one of Ag multilayers of variable h . Furthermore the projection of the DOS

of Ag_n in s , p and d components shows that in the multilayer, as in the crystalline solid, the central main peak arises from the d contribution whereas the charges outside its shoulders are s and p charges. Therefore the reduction of the DOS bandwidth has to be attributed to the limited radial extent of d electrons and to the reduced coordination in the multilayers. For $h \geq 2$ the effect is also a consequence of the absence of empty electronic states in the neighboring layers with which the charge in a given layer may couple.

However from Figure 2 it is seen that the increase of the monolayer thickness reverts the DOS shape to its bulk-like features. A quantitative description of this effect is presented in Figure 3 which shows the h dependence of the DOS bandwidth for pure A_n multilayers. In these calculations the DOS is constructed from the projection of the charge on the average multilayer atom. At $h = 1$ (Fig. 3) the bandwidth reduction, with respect to bulk value, is in the range 0.5. This result appears in excellent agreement with the factor $4/6$ predicted by equation (2), if one accounts for the crude nature of the analytical model. The increase of h produces a continuous increase of the bandwidth which attains the bulklike value at $n \sim 5$. This critical thickness is equal for the three elements and the systematic nature of the effect is attributable to the primary dependence of DOS on the presence of neighboring atoms, rather than on the details of the electronic structure. The study of the coordination shows, in fact, that at $h = 5$ this parameter attains the bulk value 12 in the central layer, while the atoms in the outer layers are undercoordinated. Therefore the DOS shape changes from a bulklike shape at the multilayer center to the peaked form of the isolated monolayer at its extremities. In the averaged projection used in Figure 3 this distribution appears as the re-installment of the bulklike bandwidth.

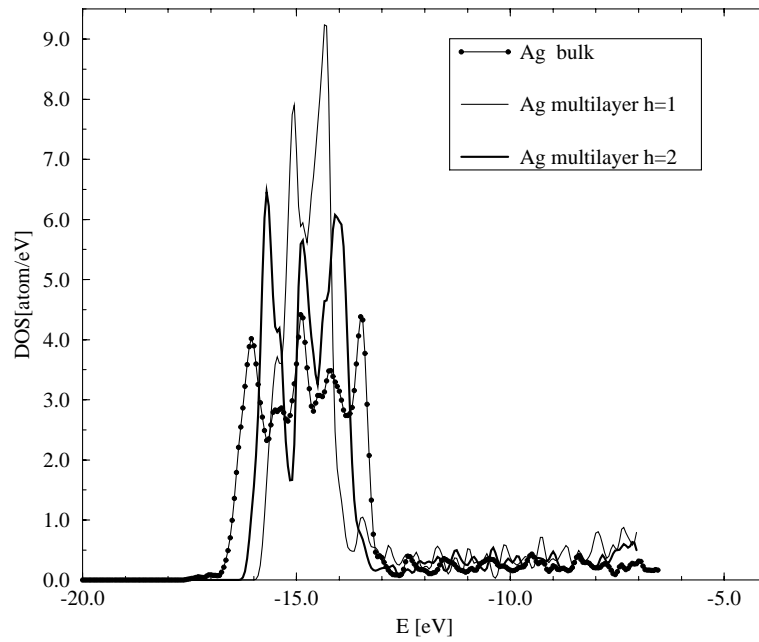


Fig. 2. Comparison of DOS-*vs.-E* distribution for *fcc* Ag and Ag_n with $n = 1, 2$. Projection on the average atom.

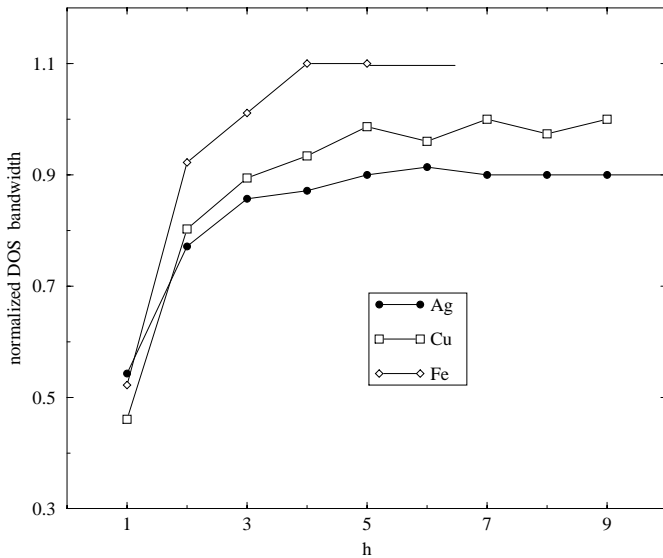


Fig. 3. Dependence of the DOS bandwidth on the multilayer thickness h . The bandwidth is expressed as a ratio with the bulk value. Homogeneous multilayers with A_n composition. Projection on the average atom.

The absence of charge intermixing and hybridization is clearly evident for compound multilayers. The DOS of these systems is illustrated by Figures 4 and 5. These figures refer to compositionally-modulated structures of the type $(AB)_n$ (Fig. 4) and A_nB_n (Fig. 5). In spite of the apparent diversity, the charge in these systems is dictated by a similar, central property, that is the absence of important effects of intermixing and hybridization. In fact, the electronic charge of $(AB)_n$ (Fig. 4) consists of two well separate contributions arising from the DOS of the A and B component. Furthermore this property is not al-

tered by the increase of n . Similarly, the data in Figure 5 demonstrate that the development of the charge towards the bulk limit is almost equal for A_n and A_nB_n . As shown by Figure 5A, in fact, the Ag component of Ag_2Cu_2 has the same peaks and bandwidth of Ag_2 in Figure 2. Despite this, the plots in Figure 5B would suggest a different progression towards the bulk limit for A_n and A_nB_n . In this figure the DOS of Ag_3Cu_3 is compared with the ones of bulk Ag and Cu. Though the peak locations of the multilayers are fairly coinciding with the bulk ones, a more structured shape, suggesting overlapping of the Ag and Cu charges, is observed for Ag_3Cu_3 . This property arises from the average projection used in these calculations. The charge thus constructed results, in fact, from the sum of the Ag_3 and Cu_3 contributions and gives a representation of the charge mediated between the ones in the Ag and Cu layers. In a layer-by-layer projection the charge retains the A_n features, as shown by the example of Ag_2Cu_2 in Figure 5A.

As a final remark, it is added that results similar to the ones illustrated in Figures 4 and 5 have been found for Fe/Ag and Fe/Cu systems. For the sake of brevity, these results have been omitted.

4 Conclusions

Two main conclusions can be drawn from this study. In the first place a bulklike bandwidth of DOS is observed at $h \sim 5$. This charge arises from averaging on an uneven distribution which consists of inner bulklike layers and outer layers, where the DOS retains the narrow bandwidth of the isolated monolayer. Angle-resolved photo-emission spectroscopy on Ag/Cu multilayers, reported in [18], indicates a critical thickness in agreement with $h = 5$.

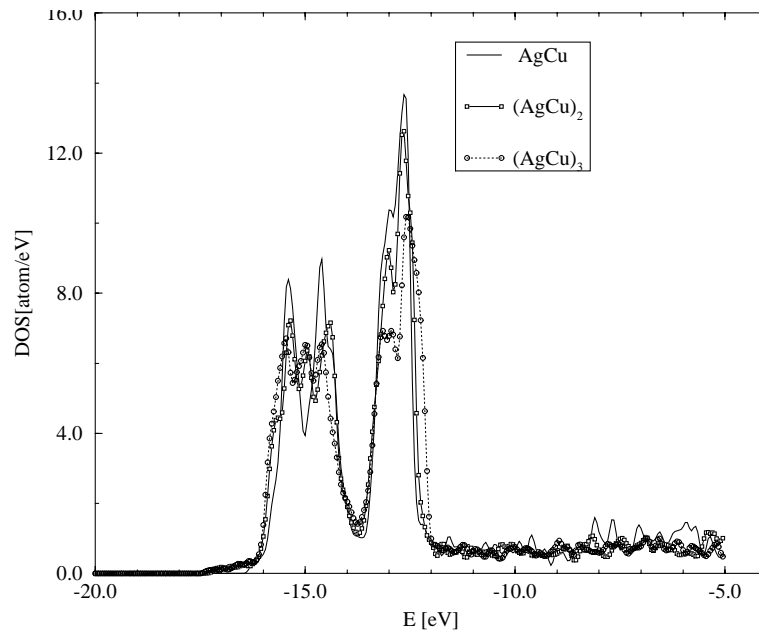


Fig. 4. DOS-*vs.*-*E* distribution as a function of *h* for $(AB)_n$ multilayers. Projection on the average atom.

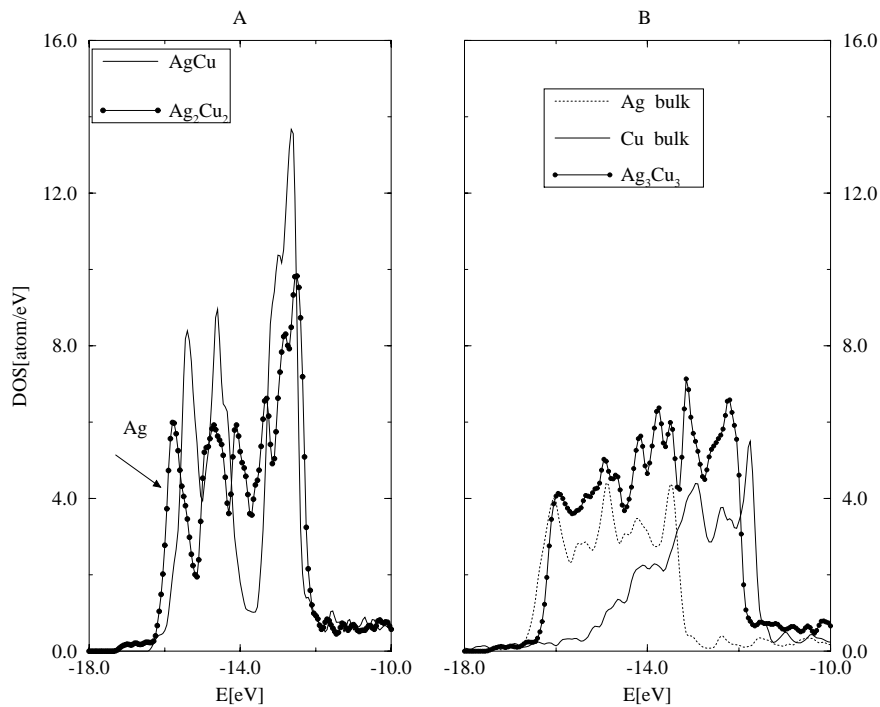


Fig. 5. A: DOS-*vs.*-*E* distribution as a function of *h* for A_nB_n multilayers, $n = 1, 2$. B: comparison of DOS of the crystalline solids with the one of A_3B_3 . Projection on the average atom.

Furthermore the electronic structure found in our calculations reconciles the divergence between [1–3]. In [2] this divergence is attributed to the critical dependence of DOS on *h*. In agreement with this suggestion, the plots in Figure 3 show a sharp rise of the bandwidth for *h* in the range 2, 3. The calculations, however, add a further element of complexity to the evaluation of the properties of multilayers. As illustrated by Figure 5, a drastically different picture is obtained when using a layer-by-layer rep-

resentation (Fig. 5A) or a charge averaged among layers (Fig. 5B). Experiments leading to the one or the other of charge distributions, produce, by necessity, contradictory results.

The second significant aspect of this study is that the properties of DOS are insensitive to the magnetic or non-magnetic nature of the multilayer components. This might be an artifact of the non-spin polarized calculations adopted in this study. However FLAPW spin-polarized

calculations for analogous systems [7, 9, 12, 15] show an interlayer coupling whose main features are, as in our case, the absence of hybridization and intermixing. This leads to the conclusion that non-spin polarized calculations lead to a simplified structure of the bands without altering their fundamental properties.

References

1. G.J. Mankey, K. Subramanian, R.L. Stockhauer, R.L. Kurtz, *Phys. Rev. Lett.* **78**, 1149 (1997).
2. C. Pampuch, O. Rader, R. Klaesges, G. Carbone, *Phys. Rev. B* **63**, 153409 (2001).
3. P. Srivastava, N. Haack, H. Wende, R. Chauvistre', K. Baberschke, *Phys. Rev. B* **56**, R4398 (2001).
4. D.S. Wang, A.J. Freeman, H. Krakauer, *Phys. Rev. B* **24**, 1126 (1981).
5. S. Ohnishi, A.J. Freeman, M. Weinert, *Phys. Rev. B* **28**, 6741 (1983).
6. X.Y. Zhu, J. Hermanson, *Phys. Rev. B* **27**, 2092 (1983).
7. C.L. Fu, A.J. Freeman, T. Oguchi, *Phys. Rev. Lett.* **54**, 2700 (1985).
8. R. Richter, J.G. Gay, J.R. Smith, *Phys. Rev. Lett.* **54**, 2704 (1985).
9. R.H. Victora, I.M. Falicov, *Phys. Rev. B* **31**, 7335 (1985).
10. J.T. Wang, Z.Q. Li, Y. Kawazoe, *J. Phys. Cond. Matt.* **9655** (1988).
11. G.W. Fernando, B.R. Cooper, *Phys. Rev. B* **38**, 3016 (1988).
12. T. Kraft, P.M. Marcus, M. Scheffler, *Phys. Rev. B* **49**, 11511 (1994).
13. D. Sanchez-Portal, E. Artacho, J. Junquera, P. Ordejon, A. Garcia, I.M. Soler, *Phys. Rev. B* **83**, 3884 (1999).
14. J. Izquierdo, A. Vega, L.C. Sanchez Porta, J. Junqueras, E. Artacho, J.M. Soler, P. Ordejon, *Phys. Rev. B* **61**, 13639 (2000).
15. X. Yin, K. Hermann, *Phys. Rev. B* **63**, 1154 (2001).
16. A.M. Mazzone, *Modeling Simul. Mater. Sci. Eng.* **9**, 171 (2001).
17. P. Blaha, K. Schwarz, J. Luitz, WIEN97-A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties (K. Schwarz, Tech. Universität Wien, Austria 1999) ISBN: 3-9501031-0-4.
18. J.G. Tobin, S.W. Robey, J.E. Klebanoff, D.A. Shirley, *Phys. Rev. B* **28**, 6169 (1983).
19. A.P. Sutton, *Electronic Structure of Materials* (Clarendon Press, 1993).
20. G. Fuster, J.M. Tyler, N.E. Brenner, J. Callaway, D. Bangkoko, *Phys. Rev. B* **42**, 7322 (1990).