APPLICATION OF AB INITIO ELECTRONIC STRUCTURE CALCULATIONS TO GRAIN BOUNDARY STRUCTURE

Mojmír Šoba
Ilja Turek
Ligen Wang
Václav Vitek

a) Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic, E-mail mojmir@ipm.cz
b) Solid State Theory Group, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, U.S.A.
c) Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract
State-of-the-art electronic structure methods are briefly characterized and their application to electronic structure of the Σ=5(210)/[001] tilt grain boundary in tungsten, magnetic moments at the Σ=5(310)/[001] tilt grain boundary in iron, and magnetic behaviour of Ru and Rh overlayers at the Ag(001) substrate is shown.

1. INTRODUCTION
Modern electronic structure (ES) calculations are based on first-principles (ab initio) approaches, i.e. on the fundamental quantum theory. Here the atomic numbers of the constituent atoms and, usually, some structural information are the only input data. Such calculations are performed in the framework of the density functional theory [1, 2] in which the complicated many-body motion of all electrons is replaced by an equivalent but simpler problem of a single electron moving in an effective potential. The total energy calculations are now used routinely to evaluate equilibrium lattice parameters, elastic moduli, relative stabilities of competing crystal structures, energies associated with point and planar defects, alloy heats of formation, etc. In such studies, we also obtain information about electronic densities of states and charge densities, which enables us to gain a deeper insight and learn which aspects of the problem studied are important.

State-of-the-art electronic structure calculations have achieved considerable level of reliability in predictions of a variety of physical and chemical properties and phenomena. This is in part due to the continuing rapid development of computing power (both speed and memory) and its increasing accessibility (via networks and workstations). Even more important is advancement of new computational methods and algorithms. They yield highly accurate solutions of the one-electron Kohn-Sham equations [1, 2] and provide information at the atomic and electronic scale with an unprecedented level of detail. In many cases, we are able to design new materials and predict their properties without actually synthesizing them. Computational simulations can also provide data on the atomic scale that are inaccessible experimentally.

Surfaces and/or internal interfaces break the crystal periodicity and introduce thus significant modifications of the ES in their vicinity. They also may be studied by means of the first-principles ES calculational methods.
Since the symmetry of systems with surfaces and interfaces is severely reduced relative to
the bulk, it is necessary to represent the charge density and the potential very accurately.
Therefore, full-potential all-electron versions of the ES methods have usually been used. Here
the full-potential linear augmented plane wave (FLAPW) method [3, 4] and the full-potential
linear muffin-tin orbital (FP-LMTO) method [4] are frequently employed. Plane waves
combined with pseudopotentials are also very popular, especially in simple metals and
semiconductors [5].

An alternative approach for evaluation of the electronic density that provides an elegant
formalism for the treatment of systems characterized by reduced periodicity is based on the
use of Green's functions. An important feature of this formulation is that the Green's function
represents the true solution in the whole space, from which we may project out the part of the
solution that corresponds to the region of interest, e.g. the vicinity of a surface or an interface.
These methods are also called multiple scattering methods, as they effectively treat the
scattering of propagating electrons on individual atoms.

In most applications of the Green's function techniques, the one-electron potentials have
been assumed to have the spherically symmetric muffin-tin form. In this case, it is not
possible to calculate reliably structural energy differences associated with symmetry-lowering
displacements of atoms. However, the band structures, densities of states, non-spheroidized
charge densities (based on the spheroidized electronic potential) are very similar to those
obtained by full-potential calculations, even for low-symmetry configurations [6]. Thus,
having the corresponding atomic configuration (e.g. bcc layer in the grain boundaries in Cu
[7]), the underlying electronic structure characteristics may be calculated quite reliably by
these fast methods. However, we cannot relax, for example, the atomic configuration. At
present, the full-potential KKR technique is being developed by several groups (see e.g. [8]).
This approach has the accuracy of FLAPW and FP-LMTO calculations and uses a correct
geometric model.

Green's functions may be constructed very efficiently within the tight-binding linear
muffin-tin orbital (TB-LMTO) scheme [9, 10]. Namely, a linear combination of the standard
linear muffin-tin orbitals (LMTO's) [11] can be used to construct a new set of basis functions
(so-called screened LMTO's) whose range extends effectively to the second nearest
neighbours [9, 10]; in this way, we obtain a first-principles tight-binding Hamiltonian (this is
the reason we speak about the TB-LMTO method). This is particularly useful for surfaces or
planar interfaces: the perturbation due to the surface or interface couples relatively few basis
functions. The short range of hopping integrals (structure constants) enables us to introduce
the notion of principal layers [12, 13]. Each principal layer contains such a (finite) number of
neighbouring layers that only the nearest principal layers interact. Thus, the whole system
may be considered as a sequence of principal layers, both in the semi-infinite bulks and in the
interfacial region. A detailed description of the approach using principal layers for electronic
structure calculations of surfaces, interfaces and layered systems may be found in [13, 14].

2. APPLICATIONS TO INTERFACES AND SURFACES

The ES techniques discussed above are applicable to calculations of electronic structure of
surfaces, epitaxial interfaces, grain, antiphase and interphase boundaries, multilayers etc. In
this section, we present several illustrative examples of studies of the electronic structure of
grain boundaries and disordered magnetic overlayers.

2.1. Electronic structure of the Σ = 5(210)/[001] tilt grain boundary in tungsten

The atomic configuration of this grain boundary (GB) was determined using interatomic
potentials of the Finnis-Sinclair type [15]. The electronic structure was calculated by the
TB-LMTO Green's function method [14]. Two unperturbed semi-infinite bulks sandwiched the interfacial region consisting of 5 principal layers. Each principal layer contained 4 atomic layers (interactions up to the second nearest neighbours were included). More details about this calculations may be found in [16].

The atomic configuration of the GB obtained using the Finnis-Sinclair type potentials is shown in Fig. 1. Here the atoms numbered 9-14 lie in the most perturbed region.

The analysis of local densities of states (LDOS) at individual atoms shows that away from the “core” of the boundary (atoms 1-7, 17-20) the LDOS is very similar to that of the bulk. However, in the most perturbed GB region, a significant smoothing of the DOS and filling of the gap between bonding and antibonding d-states is observed (Fig. 1). This is the consequence of lower symmetry of the local neighbourhood of atoms in the GB. Similar situation arises in amorphous materials.

Let us note that we have not detected any narrowing of the occupied portion of the d-band due to reduced coordination, as found e.g. in [17]. Namely, in our relaxed GB structure, the coordination is reduced only slightly or not at all. Due to the filling of the pseudogap at the Fermi energy, the bonding d-like peak in the LDOS is broadened for many atoms. On some sites, the whole peak is shifted by the local Madelung potential.

![Fig. 1. Left panel: Atomic configuration of the Σ = 5(210)/[001] tilt grain boundary in tungsten. Open circles represent atoms displaced by ±a[0,0,1/2] with respect to atoms denoted by full circles (a is the lattice constant). Right panel: Local densities of states at atoms 9 and 11 compared with the density of states for ideal bcc tungsten.](image)

2.2. Magnetism in grain boundary regions

Magnetic phenomena are very important, for example, in overlayers and multilayers. However, magnetic behaviour of atoms at grain boundaries in ferromagnetic materials may also be different when compared with the bulk. We illustrate this situation for the Σ = 5(310) tilt grain boundary in iron [14]. The structural model used is identical to that in Ref. [18] (symmetrical unrelaxed structure) and is shown in Fig. 2; explicit numbering of atomic layers is included. This model preserves all bcc interatomic distances between atoms belonging either to the upper or to the lower grain (atomic layers \( n > 0 \) and \( n < 0 \), respectively). The two grains are rigidly displaced along the \( z \) axis so that the resulting distance between the atomic layers \( n = 1 \) and \( n = -1 \) is the same as the nearest-neighbour spacing in the bcc lattice. This procedure increases the volume of the Wigner-Seitz cells for atoms in and near the central atomic layer (\( n = 0 \)). In the present study, screened TB-LMTO structure constants up to second nearest neighbours of the bcc lattice were used. This implies that principal layers...
consist of three neighbouring atomic layers. Self-consistency was attained in the interfacial region consisting of 7 principal layers.

Fig. 2. Structural model of the $\Sigma = 5(310)$ tilt grain boundary in a bcc structure. All coordinates are in units of the bcc lattice constant $a$. The open and full circles refer to atoms with $y = 0$ and $y = a/2$, respectively. The layer numbering in the upper grain starts from the central interface layer, denoted by 0 and marked by the dashed horizontal line. For details, see text.

Fig. 3. Left panel: Local magnetic moments of iron atoms in atomic layers near the $\Sigma = 5(310)$ grain boundary. Right panel: Fe magnetic moments versus atomic sphere radii near the GB (squares) and in the unperturbed bcc Fe (triangles).

It may be seen from Fig. 3 that the local magnetic moments near the grain boundary are enhanced. This is analogous to the effect observed for low-index surfaces (see e.g. [19, 20]). A detailed analysis of the dependence of the local magnetic moments on separation from the
GB has not been made but it appears that most of the difference between the individual local moments and the asymptotic bulk bcc value can be attributed to the magneto-volume effect. The local magnetic moments near the $\Sigma = 5(310)$ boundary versus the atomic sphere (Wigner-Seitz) radius are plotted in Fig. 3 and compared to those in the ideal bcc structures with varying lattice constants. This comparison obviously suggests that the local magnetic moment follows the volume dependence of the global magnetic moment in crystalline bcc iron, as reported by a number of authors (see e.g. Refs. [21, 22]).

It was shown recently that in the ferromagnetic iron the enhanced magnetic polarization in the GB region dramatically reduces the GB energy and its magnitude is in much better agreement with experiments than for the models which do not include magnetic effects [23]. Thus, ferromagnetism affects significantly the inter-granular cohesion and, therefore, it should be incorporated in any realistic description of GB phenomena in ferromagnetic materials.

2.3 Magnetic overlayers on non-magnetic substrates

Epitaxial transition-metal overlayers of monolayer thickness on non-magnetic substrates such as Cu, Ag, Au, Pd, Pt can be considered as two-dimensional itinerant magnetic systems. Recent FLAPW calculations [19, 24] predicted spontaneous magnetic order for 4$d$ and 5$d$ transition-metal monolayers like Ru, Rh, Ir on Ag(001) and Au(001) substrates. This may be induced by the reduced coordination number and hence reduced interatomic hybridization, band-structure effects due to the restriction to two dimensions and, compared to the bulk paramagnetic solid, an increased lattice constant imposed by pseudomorphic film growth. However, experiments using the surface magneto-optic Kerr effect failed to confirm these results [25, 26]. The most probable reason for this discrepancy is the presence of structural imperfections in the samples which are not considered in the calculations. Ample experimental evidence demonstrates that islanding, surface roughness or interdiffusion cannot be neglected in these systems. We have studied the influence of two types of structural imperfections on the ferromagnetism of Ru and Rh monolayers on a Ag(001) substrate [27], using a combination of the surface Green's function approach with the coherent potential approximation [14]. The first case investigated corresponds to a non-integer coverage of the substrate with Ru or Rh varying between 1 and 2 monolayers. This was simulated by surface layers of composition $R_x\text{Vac}_{1-x}/R/\text{Ag(001)}$, $0 \leq x \leq 1$, where R stands for Ru or Rh and Vac denotes a surface vacancy. This model describes a continuous formation of the second R layer on top of the first perfect R layer on the Ag(001) face. The dependence of the local magnetic moments of R atoms on the coverage is shown in Fig. 4.

In the second case, the importance of interdiffusion of Ru (Rh) films one monolayer thick with the Ag substrate was studied by simulating a layer sequence $R_1-x\text{Ag}_x/R/R_1-x\text{Ag}_{1-x}/\text{Ag(001)}$, $0 \leq x \leq 1$, with all atoms occupying the positions of the ideal bulk Ag lattice. This model describes a continuous transition of the R layer from the surface ($x = 0$) to the first subsurface ($x = 1$) position. The corresponding concentration dependence of the local magnetic moments is shown in Fig. 5.

It is seen from both Figs. 4 and 5, that despite the relatively large local magnetic moments in the perfect monolayer ($M_{\text{Ru}} = 1.8 \mu_B$, $M_{\text{Rh}} = 0.9 \mu_B$), the local moments of Ru and Rh atoms are very sensitive to both types of structural imperfections. In the first model, two-dimensional ferromagnetism disappears for coverages higher than 1.5 monolayer (Fig. 4). This is in a reasonably good agreement with FLAPW calculations for perfect double layers [28] yielding nearly negligible local magnetic moments for 4$d$ and 5$d$ transition-metal double layers on a Ag(001) substrate. An even more complicated behaviour transpires from the second model of structural imperfections. A perfect R monolayer in the surface layer ($x = 0$) as well as in the first subsurface layer ($x = 1$) carries a sizable local moment while
ferromagnetic behaviour of monolayers strongly affected by interdiffusion (for intermediate values of $x$) is substantially reduced (Fig. 5). This leads to a magnetic gap for $0.5 \leq x \leq 0.6$ in the Ru case and to a deep minima in both local moments near $x = 0.6$ in the case of Rh.

Fig. 4. Local magnetic moments in Ru (left panel) and Rh (right panel) overlayers on a Ag(001) substrate as a function of coverage. Squares and triangles refer to moments in the complete (S) and incomplete (S+1) transition-metal layers, respectively.

Fig. 5. Influence of interdiffusion on the local magnetic moments in Ru (left panel) and Rh (right panel) overlayers on a Ag(001) substrate. Triangles refer to the moments in the top surface (S) layer, squares refer to the first subsurface (S-1) layer. For details, see text.
The rapid decrease of the local moments with increasing coverage (Fig. 4) and interdiffusion (Fig. 5) can be understood from the shape of the local DOSs of R atoms; a more detailed discussion may be found in [14, 27].

Let us note here that the experiments of Pfandzelter et al [29] have shown that Ru monolayers are ferromagnetic on C(0001) surface below a Curie temperature of 250 K. This is probably due to the fact that the interdiffusion of Ru with the substrate atoms is strongly suppressed and, therefore, the deposited films exhibit a much better quality. The evidence of 4d magnetism has also been found experimentally in free Ru and Rh clusters [30].

3. CONCLUSIONS

In this paper we have demonstrated how the surface first-principles ES methods may be applied to interface problems and how such calculations contribute to a deeper understanding of the underlying physics at interfaces. In this framework, a variety of phenomena may be analyzed, including e.g. surface and interface magnetism. Among the methods listed, the Green's function method within the tight-binding LMTO formalism is particularly convenient since it is computationally very effective and provides reliable results, fully comparable with the more sophisticated approaches. An attractive feature of the Green's function methods is that they may be easily generalized for compositionally disordered systems.

The significance of first-principles calculations is in high reliability of predictions of new properties and phenomena. There are no adjustable parameters and well defined approximations are introduced on the most fundamental level. Nevertheless, similarly as in other atomistic studies, the goal of the ES calculations is not to obtain numbers, but insights. The results include electronic wavefunctions, charge densities, and magnetic moments. On the basis of these results, further material characteristics may be calculated, e.g. cohesive energy, elastic constants, some strength characteristics, magnetic susceptibility, transport coefficients etc. Specifically, in this paper we have shown that the magnetic moment is significantly different at grain boundaries when compared with the bulk. This phenomenon was not considered in previous studies of atomic structure and properties of interfaces, although it may substantially affect the interfacial cohesion and other characteristic quantities [23]. The information available from the first-principles calculations allow us both to test and construct simpler models, which, in turn, may be used in very extensive atomic level studies while the state-of-the-art first-principles calculations can only be made for a relatively small number of atoms (less than ≈100).

The first-principles calculations may also be used for “measurements in the computer”. Thus, computer simulations can substitute a real experiment and, more importantly, provide data on atomic scale that are not accessible experimentally. We expect that in future the first-principles methods will contribute most significantly to studies of electronic structure and atomic configuration of interfaces, especially in systems with covalent bonds, such as non-close-packed metals, non-cubic intermetallics, metal-ceramic interfaces, semiconductor systems etc.

Notwithstanding, simpler methods, such as embedded atom method and N-body central force potentials, will remain essential for studies of very large systems. However, it is imperative to combine simpler methods with the first-principles approaches on one side and experiment on the other.

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REFERENCES