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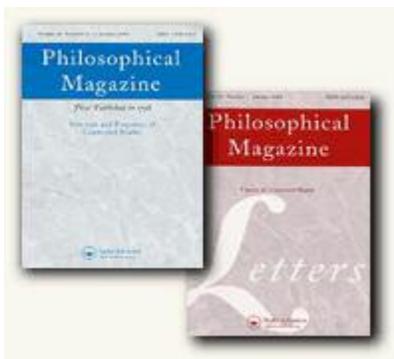
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RESEARCH ARTICLE

On the surface relaxation of transition metals

V. Zólyomi^{a,b}, J. Kollár^{a *}, L. Vitos^{a,c,d}

^aResearch Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, P. O. B. 49, H-1525, Budapest, Hungary ^bDepartment of Biological Physics, Eötvös University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary ^cApplied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden ^dDivision for Materials Theory, Department of Physics and Materials Science, Uppsala University, SE-75121 Uppsala, Sweden

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First principles band structure calculations are presented for the layer relaxation of the close-packed surfaces of $5d$ transition metals. Anomalously large relaxations are found for group IVA and VIIA hcp metals. For these elements, the size of the layer relaxation exhibits an unusually slow decay with the distance from the surface. We argue that this phenomenon can be attributed to the peculiar flat and degenerate d -bands located close to the Fermi level in the L-A-H top-plane of the hcp Brillouin zone, and which are also responsible for the anomalously low [001] longitudinal optical phonon frequencies observed in these hcp metals.

Keywords: surface relaxation; transition metals; density functional theory

1. Introduction

The determination of the surface geometry is one of the basic questions in surface physics. Transition metal surfaces are of particular interest, since they act as catalysts in different chemical reactions [1] and control the epitaxial growth mechanism in metallic multilayers [2, 3]. Many basic surface properties are especially sensitive to the surface geometry. The simplest change in the crystal geometry at the surface is the layer relaxation. In particular, the surface stress [4–6], being a fundamental parameter in surface reconstruction [4, 7], varies nearly linearly with the interlayer distance [8, 9]. Since the experimental determination of the surface relaxation involves a relatively high uncertainty [9], first principles calculations on the surface geometry are of primary importance.

In this work, we report on a density functional investigation of the layer relaxation for the most close-packed surfaces of $5d$ transition metals. Using the present results together with our previous theoretical data obtained for the $4d$ series [8, 9], we carry out a systematic analysis of the layer relaxation in transition metals. We show that there is a remarkable inward relaxation at the beginning and in the middle of the series, which decreases gradually with increasing d electron number and ends up in a small outward relaxation for the late transition and noble metal surfaces. We find that some of the hexagonal close-packed (hcp) metals (Zr, Tc, Hf, and Re) exhibit anomalously large inward layer relaxation. We demonstrate that this anomaly can be attributed to the presence of the flat and degenerate d -bands

*Corresponding author. Email: jk@szfki.hu

	Surface	Layer relaxation				
		d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
La	hcp(0001)	-4.77	4.33	-1.99	1.06	-0.91
Hf	hcp(0001)	-6.86	3.49	-1.03	0.68	0.09
Ta	bcc(110)	-4.87	0.24	0.01	0.11	0.31
W	bcc(110)	-3.76	0.45	0.02	0.18	-0.16
Re	hcp(0001)	-6.23	3.94	-2.72	2.93	-2.19
Os	hcp(0001)	-3.79	0.04	0.89	-0.04	-0.47
Ir	fcc(111)	-2.09	-0.51	0.32	-0.02	0.10
Pt	fcc(111)	0.99	-0.49	-0.12	0.11	0.12
Au	fcc(111)	1.67	0.04	0.22	0.38	0.29

Table 1. Calculated layer relaxations (d_{ij} in percent) for single layer and multilayer relaxations of the close-packed surfaces of $5d$ transition metals.

close to the Fermi level in the L-A-H plane of the hcp Brillouin zone, which split during the contraction of the hcp crystal planes. This peculiar behavior of the band structure is also reflected in the unusually soft [001] longitudinal optical phonons in the above hcp metals [10–12].

2. Method

The calculations were performed with the Vienna *ab initio* Simulation Package (VASP [13]) employing the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) parameterization [14]. The projector augmented-wave method was applied using a 350 eV plane-wave cutoff energy. A $25 \times 25 \times 25$ k -point grid was used for bulk calculations, and a $55 \times 55 \times 1$ k -point grid was used for surface calculations (with the surface being in the xy plane). The surface relaxations were performed for the (111) facet of the face centered cubic (fcc) lattice, for the (110) facet of the body centered cubic (bcc) lattice, and for the (0001) facet of the hcp lattice. The free surfaces were modeled by slab geometries. Each slab contained 10 atomic layers and a vacuum layer of width equivalent with 5 atomic layers. In all calculations, the in-plane lattice constants were fixed to the theoretical bulk equilibrium values and only the inter-layer distances (λ_{ij} , i and j are the layer indices) were allowed to relax. The band structure calculations for the bulk hcp metals were performed using the fully self-consistent electron charge density obtained for the $25 \times 25 \times 25$ k -point grid, and scanning the electronic bands along the H-L-A-H line with 60 inequivalent k -points. The band structure for the hcp Re slab was calculated for 1000 inequivalent k -points along the H-L-A line using the self-consistent charge density obtained for the $55 \times 55 \times 1$ k -point grid.

3. Results

In Table 1, we list the present results for the layer relaxations obtained for the close-packed surfaces of $5d$ transition metals. Here the layer relaxation is defined as $d_{ij} \equiv (\lambda_{ij}^s - \lambda_{ij}^b)/\lambda_{ij}^b$ where λ_{ij}^s and λ_{ij}^b are the equilibrium surface and bulk inter-layer distances, respectively. The multilayer relaxations show that for most $5d$ metals the relaxation decays relatively fast with the distance from the surface, the only exception being Re. A similar anomalous behavior was found in the case of hcp Tc [8].

Another interesting feature of the layer relaxations can be seen if we compare the present values for d_{12} obtained for the close-packed surfaces of $5d$ metals (Table

1) with those reported in the case of $4d$ metals [9]. It has been shown that the top-layer surface relaxation for the nonmagnetic transition metals follows a generic trend across the series, with decreasing relaxation as we approach the noble metals [9]. In general, both $4d$ and $5d$ metals follow this trend. For Pd, Pt, and Au, the surface relaxation changes sign, and the surface atoms exhibit a slight outward displacement. Beyond the generic trend however, an anomalous behavior for group IVA and group VIIA hcp metals can be observed. In particular, Hf (Zr) and Re (Tc) show significantly larger relaxation than La (Y) and Os (Ru).

It is quite natural to relate the contraction of surface layers to the periodic contraction of bulk lattice planes, i.e. the [001] longitudinal optical phonon excitations. It has been known for a long time that in Tc and Re, and to a somewhat less extent in Zr and Hf as well, the [001] longitudinal optical phonon branches have anomalously low frequency and show anomalous temperature dependence [11, 12]. The origin of these anomalies was ascribed to the electronic bands near the Fermi level [10]. Here we show that similar band structure effects are responsible for the anomalous layer relaxation for the hcp transition metal surfaces as well.

In order to understand the electronic origin of the anomalous layer relaxation, we have calculated the bulk electronic band structures of all $4d$ and $5d$ hcp transition metals along the H-L-A-H line in the hcp Brillouin zone. Results for La and Hf are displayed in the top panel of Figure 1. A doubly degenerate electronic band appears at the Fermi level near the A point, which lies very close to the Fermi level for Hf and Zr (not shown), but lies well above the Fermi level for La and Y (not shown). The lower panel of Figure 1 shows the electronic band structure for Re and Os along the same high-symmetry lines. For Re and Tc (not shown), there is a doubly degenerate flat electronic band with high density of states near the Fermi level around the L point. The corresponding bands in Os and Ru (not shown) are situated well below the Fermi level. Since the anomalous layer relaxation among the transition metals appears exactly for group IVA and group VIIA elements, there seems to be a clear correlation between the appearance of the degenerate flat band at the Fermi level (Figure 1) and the anomalous layer relaxations (Table 1).

Motivated by the works of Liu *et al* [10] on the [001] LO phonons in Zr, Tc and Hf, we have examined the splitting of the bands for all four anomalously behaving hcp metals. In these calculations, the distance between the two hexagonal planes within the hcp unit cell was distorted slightly, while keeping the a and c lattice constants unchanged. This distortion simulates the [001] LO phonon, and it also corresponds to the direction of the surface layer relaxation for the close-packed (0001) surface. Calculations were carried out for 1% and 2% distortions. We have found that in the case of Re, the doubly degenerate flat electronic band above the Fermi level (near the L point from the Brillouin zone) splits in such a way that one of the bands with a relatively high density of states shifts onto the Fermi level at 2% distortion. The bands for Hf, Zr, and Tc (not shown) split in a similar way. For Os and similarly Ru (not shown), this band remains completely below the Fermi level during the distortion, and thus no flat band is shifted across the Fermi level. We have also examined the splitting of the bands in terms of atom localization, and found that both bands are equally localized on the two atoms in the hcp unit cell in all cases.

4. Discussion

It is clear that the band splitting near the Fermi level should have a sizable effect in the total energy as well. We have calculated the [001] longitudinal optical phonon frequencies (ω_{LO}) with VASP for the eight hcp $4d$ and $5d$ transition metals. Convergence was achieved at a $25 \times 25 \times 25$ k -point grid in all cases except Tc, which

required a $35 \times 35 \times 35$ k -point grid. We obtained 153 cm^{-1} , 146 cm^{-1} , 16 cm^{-1} , and 252 cm^{-1} for the ω_{LO} of the $4d$ hcp metals Y, Zr, Tc, and Ru, respectively, while in the case of the $5d$ hcp metals, we obtained 252 cm^{-1} , 71 cm^{-1} , 94 cm^{-1} , and 76 cm^{-1} for La, Hf, Re, and Os, respectively. These obtained frequencies are in line with measured phonon frequencies (and extrapolated to 0 K) [11, 12]. The most striking feature of the calculated phonon frequencies is the anomalously low values for Tc and Re, especially when compared to those obtained for Ru and Os. All of these elements are in the middle of the transition series, where the cohesion energy shows maximum and thus one would expect high phonon frequencies. We suggest that the origin of the phonon anomaly is similar to that of the anomalous surface relaxation observed for these hcp metals: namely, the splitting of the doubly degenerate flat electronic bands near the Fermi level driven either by surface relaxation or by lattice distortion corresponding to the zone-center [001] longitudinal optical phonon mode.

A natural question that arises is whether the above band-splitting scenario remains valid for the electronic structure near free surfaces. To answer this question, we have calculated the electronic band structure of the fully relaxed 10-layer slab Re along the H-L-A line from the hcp Brillouin zone (Figure 2). At the L point, a more-less flat band can be seen at the Fermi level, reminiscent of the bands for bulk Re at the L point (Figure 1). There is however some notable distortion in the slab bands. For comparison, we have calculated the band structures of bulk Re in planes parallel to the L-A-H plane, but deeper into the Brillouin zone along k_z . Figure 2 shows the full comparison between the bulk and slab electronic structures for Re. It can be seen that as we go deeper in k_z , the bands near the Fermi level split, and some mixing occurs as well. At $k_z = 0.45$ (in units of reciprocal lattice constant), one of the split bands lies almost exactly at the Fermi level. A similar flat band with high density of states occurs for the metallic slab, which in the fully relaxed case gets just below the Fermi-level, thus stabilizing the large inward layer relaxation. Clearly, the origin of the large inward layer relaxation lies in the particular topology of the bands near the Fermi-level, similarly to that of the longitudinal optical phonon softening in the [001] direction.

To give a further support that there is a correlation between the anomalous layer relaxation on the (0001) surface and the softening of the LO phonon branch, we have calculated the multilayer relaxation for hcp Re and Os along the less close-packed (10 $\bar{1}$ 0) facets. The hcp structure has two (10 $\bar{1}$ 0) surfaces depending on the first interlayer distance λ_{12} . Here we consider the more stable (10 $\bar{1}$ 0) facets [15] with $\lambda_{12} = (\sqrt{3}/6)a$, where a is the hexagonal lattice constant. Since there is no known anomaly in the temperature dependence of the [100] LO phonon branches, one would expect no anomaly in the layer relaxation based on the results above. We have found that for this surface the relaxation decays fast in both Re and Os: it starts at roughly -17% relaxation for d_{12} , and drops to around 1-2 % in the subsequent layer distances. This finding indicates that indeed in Re the anomalous relaxation along the hexagonal c axis has a bulk rather than a surface origin, and the surface relaxation is not an isotropic property of the transition metals. These results further support that the presence of flat bands at the Fermi level is responsible for the anomalous layer relaxation in the close packed surface.

5. Conclusion

In summary, we have performed first principles calculations on the surface relaxation of hcp transition metals. We have found an anomalous behavior around the

1 center for both the $4d$ and $5d$ series, especially for Tc and Re. We have concluded
2 that the anomaly can be attributed to the particular topology of the electronic
3 bands close to the Fermi level, similarly to the electronic origin of the anomalous
4 temperature dependence and softening of the [001] longitudinal optical phonon
5 branches of some hcp transition metals. The present findings have substantial effect
6 on a wide field of surface science and nanotechnology. In particular, the anomalous
7 surface relaxation has significant impact in catalytic applications, in nano-pattern
8 fabrication, surface-tailoring in metal-clusters as well as in epitaxial heterostruc-
9 tures.

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References

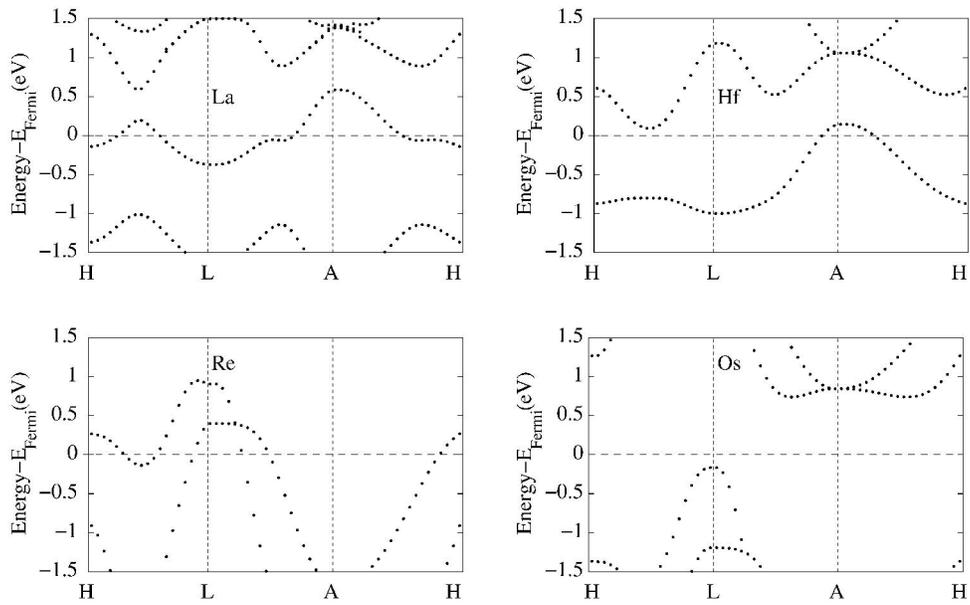
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25 [1] T. Bligaard and J.K. Norskov, A. Nilsson, L.G.M. Pettersson and J.K. Norskov, eds., Elsevier, 2007.
26 [2] R.F.C. Farrow, IBM J. Res. Develop. 42 (1998), p. 43.
27 [3] J.J. Miguel and R. Miranda, J. Phys.: Condens. Matter 14 (2002), p. R1063.
28 [4] H. Ibach, Surf. Sci. Rep. 29 (1997), p. 193.
29 [5] D. Sander, Current Opinion in Solid State and Materials Sciences 7 (2003), p. 51.
30 [6] P. Müller and A. Saúl, Surf. Sci. Rep. 46 (2004), p. 157.
31 [7] R.C. Cammarata, Prog. Surf. Sci. 46 (1994), p. 1.
32 [8] S.K. Kwon, Z. Nabi, K. Kádas, L. Vitos, J. Kollár, B. Johansson, and R. Ahuja, Phys. Rev. B 72
33 (2005), p. 235423.
34 [9] K. Kádas, Z. Nabi, S.K. Kwon, L. Vitos, R. Ahuja, B. Johansson, and J. Kollár, Surf. Sci. 600 (2006),
35 p. 395.
36 [10] S.H. Liu, C. Stassis, and K.M. Ho, Phys. Rev. B 24 (1981), p. 5093.
37 [11] H.G. Smith and N. Wakabayashi, Solid State Commun. 39 (1981), p. 371.
38 [12] C. Stassis, D. Arch, O.D. McMasters, and B.N. Harmon, Phys. Rev. B 24 (1981), p. 730.
39 [13] G. Kresse and J. Furthmüller, Phys. Rev. B 54 (1996), p. 11169.
40 [14] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77 (1996), p. 3865.
41 [15] L. Vitos, A. Ruban, H. Skriver, and J. Kollár, Surf. Sci. 411 (1998), p. 186.
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Figure 1. Electronic band structures for bulk La, Hf, Re, and Os near the Fermi level along the H-L-A-H line of the hcp Brillouin zone.

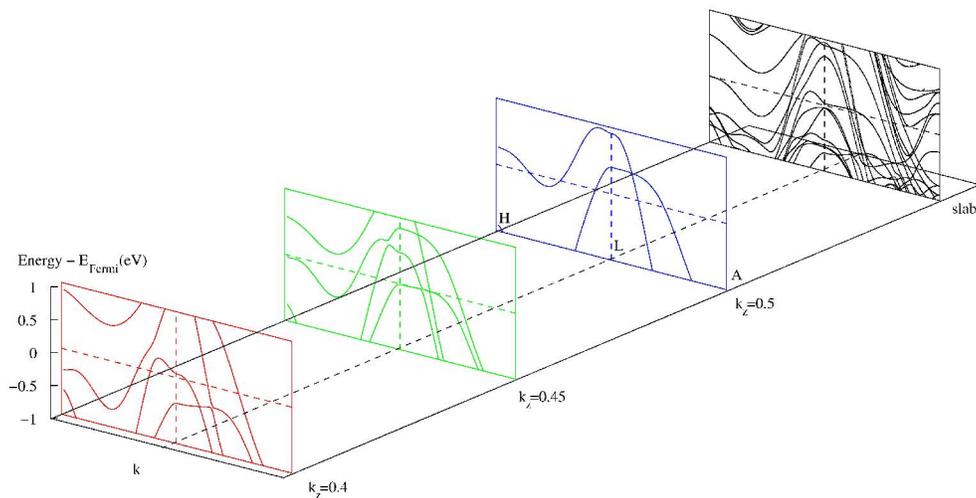
Figure 2. Comparison of the electronic band structure of a 10-layer Re slab and bulk Re. For the slab, the bands along the H-L-A line in the $k_z = 0.5$ (in units of reciprocal lattice constant) plane are plotted. For the bulk, we show the bands along the H-L-A line in the $k_z = 0.5$ plane, as well as the bands along parallel lines within the $k_z = 0.45$ and $k_z = 0.4$ planes. It can be seen that the distortion of the bands near the Fermi level in the slab geometry is similar to the way the zone boundary bands of bulk Re are distorted as we go deeper into the Brillouin zone along k_z .

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