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Anomalous surface relaxation in hcp transition metals

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First-principles total-energy calculations indicate anomalously large surface relaxations for groups IVA and VIIA hcp metals. In addition, for group VIIA elements the magnitude of the layer relaxation exhibits an unusually slow decay with the distance from the surface. We argue that the above phenomena can be traced back to the peculiar Fermi surface of groups IVA and VIIA hcp metals. Namely, the anomalous surface relaxation appears as a consequence of low-energy excitations with near $2k_F$ wave vectors, which is also reflected by the flat and degenerate d bands located close to the Fermi level in the L-A-H plane of the hcp Brillouin zone.

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I. INTRODUCTION

Establishing the thermodynamically stable surface geometries for solids 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 different 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.

Several former theoretical works focused on the surface structure of transition metals[8–14] including some that focused on the appearance of localized surface phonons with altered symmetry as a consequence of symmetry breaking along the direction perpendicular to the surface.[15–17] Today, there is a general consensus that transition-metal surfaces exhibit inward relaxation, and the size of this relaxation increases with surface roughness.[18] Exceptions are some of the close-packed surfaces of the late transition metals, which show small outward relaxations. The origin of the surface relaxation was suggested to be the depletion of *sp* electrons in the surface layer relative to the bulk.[9] This mechanism results in a gradually decreasing inward relaxation with increasing d occupation number across the transition series. Unfortunately, the proposed model[9] is unable to explain the anomalous relaxations obtained for some of the $4d$ hexagonal metals.[8]

In this work, using density-functional calculations, we show that the layer relaxation for the close-packed surfaces of $5d$ transition metals follows a trend similar to that of the $4d$ metals.[8,9] Using these theoretical results, we carry out a systematic analysis of the surface relaxation in nonmagnetic transition metals and reveal the electronic origin of the observed anomalous relaxation for the (0001) surface of the hexagonal-close-packed (hcp) Zr, Tc, Hf, and Re. We demonstrate that these anomalies can be explained by the particular shape of the Fermi surface for these metals, which are also reflected by the flat and degenerate d bands close to the Fermi level in the L-A-H plane of the hcp Brillouin zones. We mention that the same peculiar behavior of the electronic band structure is responsible for the observed unusually soft [001] longitudinal optical (LO) phonons in the above hcp metals.[19–21] We call attention to the fact that these phenomena are related to the particular response of the bulk electronic system to external perturbations, regardless whether these perturbations are displacements of atoms in a lattice or creation of a surface. This response is determined mainly by the bulk electronic structure, and the characteristic behavior of the screening charge density can be traced back to the topology of the Fermi surface (similar to the "nesting condition" in the theory of charge-density waves). For hcp metals, especially for Tc and Re, for the screening of perturbations along the (0001) direction, the special shape of the Fermi surface results in a screening charge which can explain the observed anomalous behavior for both kinds of phenomena.

The rest of this article is organized as follows: in Sec. II the density-functional method used to calculate the surface geometry is described. Results are presented in Sec. III, and in Sec. IV we give the explanation for the electronic origin of the anomalous relaxations obtained for groups IVA and VIIA hcp transition metals. This article ends with Conclusions (Sec. V).

II. CALCULATIONAL METHOD

The calculations were performed with the Vienna *ab initio* simulation package (VASP) (Ref. 22) employing the Perdew-Burke-Ernzerhof generalized gradient approximation.[23] The projector augmented-wave method was applied using a 350 eV plane-wave cut-off energy. The surface (layer) relaxations were performed for the (111) facet of the face-centered-cubic (fcc) lattice, for the (110) facet of the body-centered-cubic

TABLE I. Comparison of the multilayer relaxation of the hcp (0001) surfaces of Re and Os for 10- and 20- layer slabs (d_{ij} are in percent).

Layers	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}	d_{67}	d_{78}	d_{89}	d_{910}	d_{1011}
Re 10	−6.23	3.94	−2.72	2.93	−2.19					
Re 20	−6.17	3.86	−2.42	2.29	−1.36	1.17	−0.85	0.74	−0.67	−0.03
Os 10	−3.79	0.04	0.89	−0.04	−0.47					
Os 20	−3.82	0.01	1.04	−0.31	−0.30	0.43	0.03	−0.06	0.10	0.00

(bcc) lattice, and for the (0001) facet of the hcp lattice. We define the layer relaxation as the percentage change in the layer distances relative to the bulk value, i.e., $d_{ij} \equiv 100(\lambda_{ij}^{s} - \lambda_{ij}^{b})/\lambda_{ij}^{b}$ with $j = i+1$ and λ_{ij}^{s} and λ_{ij}^{b} as the equilibrium surface and bulk interlayer distances, respectively. For the Brillouin-zone sampling, a $25 \times 25 \times 25$ k-point grid was used in bulk calculations and a $55 \times 55 \times 1$ k-point grid was used in surface calculations (with the surface being in the xy plane). This k-point density was found to assure an accuracy better than $\pm 0.1\%$ in d_{ij}.

In the present calculations, the free surfaces were modeled by slab geometries containing N_a atomic layers and a vacuum layer of width equivalent to five atomic layers. It is important to note that the layer relaxation of the innermost layers is very much dependent on the slab thickness ($\sim N_a \lambda^b$). The magnitude of the innermost layer distance in a thin slab will, in principle, never be quantitatively correct. This is because the central layers of the slab do not exactly reproduce the bulk geometry. For instance, an increase in the slab width can significantly alter the deepest layer relaxation (d_{56}) obtained from a calculation using a ten-layer slab. To illustrate this effect, we performed test calculations on the (0001) surfaces of the hcp Re and Os, comparing the multilayer relaxations obtained for $N_a = 10$ with those obtained for $N_a = 20$. In this test, all the other numerical parameters (e.g., k-point density) were kept fixed. The results are summed up in Table I. As can be seen, the outer layer relaxations for the ten-layer Re slab agree well with those obtained for the wider slab, while the innermost layer changes significantly upon increasing the width of the slab. In fact, it is found that in Re the layer relaxation decays very slowly with the distance from the surface. The effect is less pronounced in the case of Os, where d_{56} is already very small, and the layer relaxation falls off rapidly. Since most of the metal surfaces examined here exhibit similar behavior as Os (see Sec. III), and since we are not primarily interested in the quantitative evaluation of the deep layer relaxations (i.e., d_{ij} for $i \gtrsim 3$), all results presented in Sec. III were obtained for $N_a = 10$ except for Re, where $N_a = 20$ was used.

TABLE II. Calculated layer relaxations (in percent) for single-layer (d_{12}^{s}) and multilayer (d_{ij}) relaxations of the close-packed surfaces of 5d transition metals. For Re 20 layers were used, otherwise 10 layers were used in the slab calculation.

		Single layer	Multilayer				
	Surface	d_{12}^{s}	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
La	Hcp(0001)	−4.22	−4.77	4.33	−1.99	1.06	−0.91
Hf	Hcp(0001)	−6.40	−6.86	3.49	−1.03	0.68	0.09
Ta	Bcc(110)	−4.91	−4.87	0.24	0.01	0.11	0.31
W	Bcc(110)	−3.71	−3.76	0.45	0.02	0.18	−0.16
Re	Hcp(0001)	−5.33	−6.17	3.86	−2.42	2.29	−1.36
Os	Hcp(0001)	−3.72	−3.79	0.04	0.89	−0.04	−0.47
Ir	Fcc(111)	−2.05	−2.09	−0.51	0.32	−0.02	0.10
Pt	Fcc(111)	1.19	0.99	−0.49	−0.12	0.11	0.12
Au	Fcc(111)	1.92	1.67	0.04	0.22	0.38	0.29

In all calculations, the in-plane lattice constants were fixed to the theoretical bulk equilibrium values, and all interlayer distances (λ_{ij}, where i and j are the layer indices) were allowed to relax. In addition to the full multilayer relaxation, we also carried out single-layer relaxations where only the top interlayer distance (λ_{12}) was relaxed. Finally, 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.

III. RESULTS

In Table II, we list the present results for the layer relaxations obtained for the close-packed surfaces of 5d transition metals. Examining the calculated multilayer relaxations seen in Table II, we see that for most 5d metals the relaxation decays relatively fast with the distance from the surface. The only striking exception is the aforementioned Re, where d_{56} has a similar magnitude as the top-layer relaxation (d_{12}). A similar anomalous behavior was found in the case of hcp Tc.[8]

Another important feature of the layer relaxation for the 5d metals is the absolute size of the top-layer relaxation (d_{12}). Before investigating the electron occupation number dependence of d_{12}, we observe that the top-layer relaxations agree well with those obtained by relaxing only the outermost layer (d_{12}^{s}). Therefore, in Fig. 1, we compare the present values for d_{12}^{s} obtained for the 5d metals with those reported in the case of 4d metals (inset). It has been shown that the top-layer surface relaxation for nonmagnetic transition metals follows a generic trend across the series with decreasing relaxation as we approach the noble metals.[9] In general, both the 4d and 5d series follow this trend. For Pd, Pt, and Au, the surface relaxation changes sign, and the surface atoms exhibit a slight outward displacement. Beyond this generic trend, however, for some hcp metals an anomalous behavior can be observed. In particular, groups IVA (Zr and Hf) and VIIA (Tc and Re) show significantly larger re-

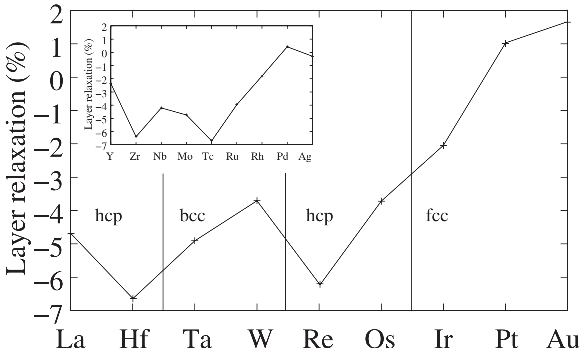

FIG. 1. Top-layer relaxations for the close-packed surfaces of 5*d* transition metals. The inset shows results obtained for the 4*d* transition metals (Refs. 8 and 9) In both series, an anomalous behavior is found for groups IVA (Zr and Hf) and VIIA (Tc and Re) metals.

laxation than groups IIIA (Y and La) and VIA (Ru and Os), respectively.

Regarding the slow decay of the layer relaxation of Re, one may suspect that this effect is merely caused by using an insufficient number of layers in the slab. But this is not the case. As mentioned earlier in Sec. II, the layer relaxation in Re does not fall off even if a 20-layer slab is used (see Table I).

In the following, we will investigate the electronic origin of the obtained anomalous surface relaxations for Zr, Hf, Tc, and Re. Furthermore, we will point out that the slow decay of the relaxation for Tc and Re is connected to the unusually soft optical phonons in these metals.

IV. ORIGIN OF ANOMALOUS LAYER RELAXATION

One possible way to approach the problem of surface relaxations is by looking at the surface as a two-dimensional defect with a potential which is screened toward the bulk metal. It is well known that free surfaces cause Friedel oscillations in the charge density toward the bulk metal.[24] The periodicity of the Friedel oscillation is twice the Fermi wave vector k_F, and it is generally incommensurate with the relevant lattice constant (interlayer distance) of the metal. This causes the layer relaxation to fall off quickly toward the bulk. However, if the lattice constant and $2k_F$ are commensurate, then the layer relaxation and the Friedel oscillation strengthen each other, which results in a slowly decaying layer relaxation toward the bulk.

We can find the periodicity of the Friedel oscillation for the (0001) surface of groups IVA and VIIA hcp metals by investigating their Fermi surfaces. The Fermi surfaces of elementary metals are available from various databases.[25,26] The Fermi surfaces from Fig. 2 were obtained from density-functional calculations[26] and correspond to the zone-edge bands of Zr, Tc, Hf, and Re, respectively. In all cases, small hole pockets appear at the zone edge. In the cases of Zr and Hf, the hole pockets are located at the *H* point (the corner of the hexagonal Brillouin zone), while in the cases of Tc and Re they are located at the *L* point (the half point of the line connecting the neighboring corners of the hexagon). The presence of these hole pockets allows for low-energy excitations in the k_z direction, as marked by the arrows in Fig. 2. As the hole pockets are at the edge of the zone, the wave vectors connecting them correspond to the periodicity of the lattice along the *z* axis, i.e., to the *c* lattice constant of the hexagonal lattice. This is especially prominent for Tc and Re as their hole pockets are located extremely close to the zone boundary. In the case of the other 4*d* and 5*d* transition metals, there are no similar hole pockets in the Fermi surface,[25,26] and therefore, the wave vector of the low-energy excitations responsible for the Friedel oscillations is always incommensurate with the lattice periodicity perpendicular to the surface.

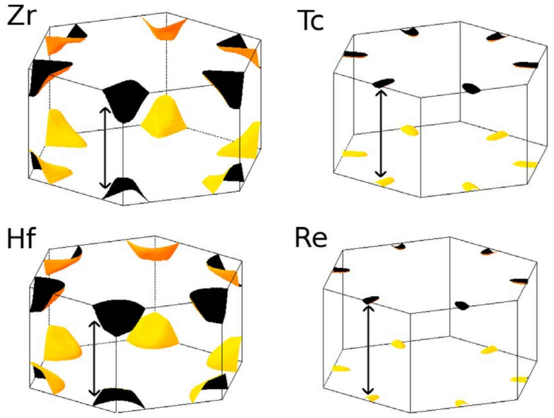

FIG. 2. (Color online) Fermi surface pieces obtained from the zone-edge bands of Zr, Tc, Hf, and Re, as taken from the database of Ref. 26. These hole pockets are not present in Ru and Os. Arrows indicate the characteristic *k* vectors of the possible low-energy excitations in the k_z direction. In the case of Tc and Re, where a nesting condition is nearly satisfied, the wavelength of the charge-density oscillations corresponding to these wave vectors is close to the *c* lattice constant of the bulk metal. For Zr and Hf, the hole pockets are wider, and the electron-hole excitations between the extremal surfaces result in a somewhat shorter wave vector.

Our results from Table II show that the layer relaxation falls off very slowly in the case of Re and relatively slowly in the case of Hf. For all other 5*d* metals, the relaxation vanishes rapidly with the distance from the surface. This correlates perfectly with the topology of the Fermi surfaces described above. Therefore, we conclude that the shape of the Fermi surface, specifically the presence of small hole pockets at the zone edge, is responsible for the anomalously slow decay of the layer relaxation at the (0001) surfaces of groups IVA and VIIA hcp metals.

As mentioned in Sec. I, the characteristic behavior of the screening charge density in the response of the bulk electronic system to an external perturbation is mainly determined by the bulk electronic structure and the topology of the Fermi surface, regardless of the type of perturbation we are dealing with. In the following, we will turn to a different kind of perturbation, which is the longitudinal optical zone-center phonon. In Tc and Re, and to a somewhat less extent also in Zr and Hf, the [001] longitudinal optical phonon branches have anomalously low frequency and show anomalous temperature dependence.[20,21] Similarly to the layer re-

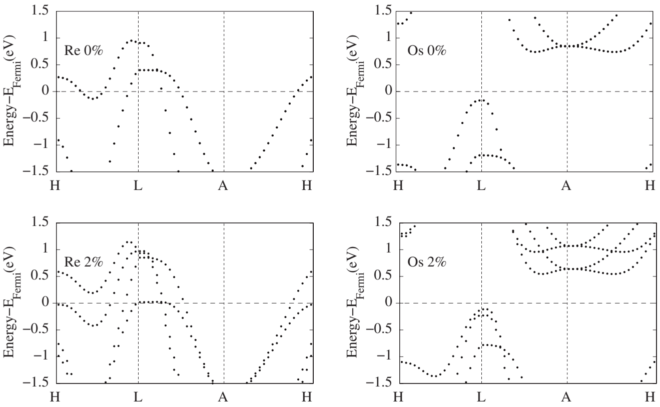

FIG. 3. Electronic band structures for bulk Re and Os near the Fermi level along the *H-L-A-H* line (note that there are no states crossing the Fermi level for Os in this part of the Brillouin zone). A flat electronic band appears in the undistorted hcp lattice near the *L* point (upper panels). When one of the atoms is displaced along the hexagonal *c* axis, the degenerate bands near the *L* point split. With a displacement of 2%, one of these bands crosses the Fermi level in the case of Re (lower-left panel) but both of them remain below the Fermi level for Os (lower-right panel).

laxation discussed above, the origin of these anomalies was ascribed to the electronic structure of the bulk—in this case through the electronic bands near the Fermi level.[19]

We have calculated the bulk electronic band structures of all hexagonal 4*d* and 5*d* transition metals along the *H-L-A-H* line in the hcp Brillouin zone. The top panel of Fig. 3 shows the electronic band structure for Re and Os. For Re (and Tc, not shown), there is a doubly degenerate flat electronic band with high density of states at ~0.4 eV above the Fermi level around the *L* point. These states correspond to the hole pockets near the *L* point from Fig. 2. Motivated by the works of Liu *et al.*[19] on the [001] LO phonons in Zr, Tc, and Hf, we 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. The results in the case of 2% distortion for Re and Os are shown in the bottom panel of Fig. 3. It can be seen 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. The bands for Hf, Zr, and Tc (not shown) split in a similar way. For Os (and Ru), this band remains completely below the Fermi level during the distortion, and thus, no flat band is shifted across the Fermi level by lattice distortion. Since the anomalous layer relaxation among the transition metals appears exactly for groups IVA and VIIA elements, there seems to be a clear connection between the presence of the degenerate flat band at the Fermi level (Fig. 3) and the anomalous layer relaxations (Fig. 1).

TABLE III. Calculated frequencies of the Γ-point [001] longitudinal optical phonons for the 4*d* and 5*d* hcp metals. Convergence was achieved at a 25×25×25 *k*-point grid in all cases except Tc, which required a 35×35×35 *k*-point grid.

	Y	Zr	Tc	Ru	La	Hf	Re	Os
$\omega_{\mathrm{LO}}(\mathrm{cm}^{-1})$	153	146	16	252	71	94	76	212

The band splitting near the Fermi level is expected to be reflected by a sizable change in the total energy and thus by the LO phonons. In Table III, we compare the [001] longitudinal optical phonon frequencies (ω_{LO}) obtained by VASP calculations for the eight hcp 4*d* and 5*d* transition metals. The obtained frequencies are in reasonable agreement with the available measured phonon frequencies (and extrapolated to low temperatures), such as Hf and Zr.[20,21] The most striking feature of the calculated phonon frequencies is the anomalously low values for Tc and Re. This anomalous behavior has been established from experiments[20] and it is qualitatively reproduced by our calculations. We note, however, that the present calculations overestimate the magnitude of the phonon softening, especially for Tc. We ascribe this deviation to the temperature broadening on the electronic structure, which has been neglected in our calculations. Both Tc and Re are in the middle of the transition series, where the cohesion energy shows a maximum and thus one would expect high phonon frequencies. It is worth noting that in accordance with the Fermi-surface-based explanation of the anomalous layer relaxation, the phonon softening can be interpreted as a Kohn anomaly caused by the low-energy $2k_F$ excitations between the hole pockets at the upper and lower zone boundaries.

Finally, 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[27] with $\lambda_{12}=(\sqrt{3}/6)a$, where *a* is the hexagonal lattice constant. Since there is no known anomaly in the [100] LO phonon branches, one would expect no anomaly in the layer relaxation based on the results above. The results are summarized in Table IV. It can be seen that for these surfaces the relaxations are significantly larger than those for the close-packed surfaces (Table II) but at the same time they decay fast with increasing distance from the surface. This finding confirms that indeed in Re the anomalous relaxation along the hexagonal *c* axis originates from the peculiar electronic structure near the zone edge.

TABLE IV. Calculated multilayer relaxations (d_{ij} in percent) for the $(10\bar{1}0)$ surfaces of Re and Os. It can be seen that the relaxation decays much faster for Re in the case of this surface than in the case of the close-packed surface (see Table II). The relaxation for Os decays similarly as for the close-packed (0001) surface.

		Multilayer relaxation				
	Surface	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
Re	$(10\bar{1}0)$	−16.44	0.12	−1.85	1.79	−1.35
Os	$(10\bar{1}0)$	−17.20	0.63	−2.41	1.54	−1.32

V. CONCLUSION

We have performed first-principles calculations for the surface relaxation of 5*d* transition metals. Anomalous behavior has been found for hcp Hf and Re, and similarly for Zr and Tc in the 4*d* series. We have demonstrated that these anomalies can be traced back to the presence of small hole pockets in the Fermi surface at the boundary of the hcp Brillouin zone. These lead to slowly decaying Friedel oscillations and thus to slowly decaying surface relaxations toward the bulk. Alternatively, the surface anomalies can be understood from the particular topology of the bulk electronic structure close to the Fermi level, which is also responsible for the anomalous temperature dependence and softening of the [001] longitudinal optical phonon branches of some hcp transition metals.

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