Compressive Surface Stress in Magnetic Transition Metals

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Because of the increased electron density within the surface layer, metal surfaces are generally expected to have tensile surface stress. Here, using first-principles density functional calculations, we demonstrate that in magnetic 3d metals surface magnetism can alter this commonly accepted picture. We find that the thermodynamically stable surfaces of chromium and manganese possess compressive surface stress. The revealed negative surface stress is shown to be ascribed to the enhanced magnetic moments within the surface layer relative to the bulk values.

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The residual stress near a free surface is commonly referred to as the surface stress (τ) and is related to the atomic-scale forces acting within the surface plane [1,2]. For solids, τ differs from the surface energy (γ) by the socalled excess surface stress, which for transition metals may have magnitude comparable to γ [3,4]. The surface stress and the surface energy are the two fundamental parameters used for modeling a wide variety of surface phenomena [1,2,5,6].

According to Ibach's model [2], the charge rearrangement at metal surfaces implies a tensile (positive) surface stress. Upon cleaving a bulk metal the electronic charge density of the broken bonds is redistributed between the surface atoms and their backbonds. The accumulated electron density dictates, in general, smaller equilibrium surface lattice constants compared to the bulk values. The positive out-of-plane stress beneath the topmost atomic layer triggers inward surface relaxation. On the other hand, the lattice constraint by the subsurface layers hinders the in-plane relaxation, thus leading to a positive residual stress within the surface plane.

Experimentally, the inward layer relaxation has been confirmed in most of the transition metals, except a few close-packed late transition metal surfaces where a very small outward relaxation was observed [7]. However, the experimental verification of the tensile surface stress has not been feasible [2,8,9]. Techniques are available to establish the polar dependence of τ [10], and the changes in τ due to the deposition of a single monolayer [2], but an accurate determination of its magnitude is not yet possible. The only attempt to measure the surface stress in transition metals was based on the contraction of small metal particles as a result of the surface stress. Unfortunately, these data have a presently unknown large error bar [2].

During the past two decades, a large number of theoretical calculations based on first-principles methods focused on the surface stress of transition metals [3,4,7,11–17]. The surface stress of nonmagnetic series was found to follow closely the parabolic variation of the surface energy with atomic number [3,4]. With two exceptions, the excess surface stress ($\tau - \gamma$) was obtained to be positive for all 4*d* and 5*d* metals. The small negative excess surface stress of Zr and Hf is, however, almost negligible compared to γ and τ . Thus, so far the theoretical data fully confirm that the surface stress on clean transition metal surfaces is tensile, in line with Ibach's model.

In this Letter, we demonstrate that magnetism can overwrite the charge redistribution surface effects in magnetic transition metals resulting in compressive surface stress for some of the close-packed surfaces. The atomic-scale mechanism behind this anomalous surface stress is shown to be the enhanced magnetism near the free surfaces, which favors a larger lattice constant as compared to the bulk.

Calculations were performed using density functional theory [18] in combination with the generalized gradient approximation [19] and the projector augmented wave method [20,21]. The free surfaces were modeled by periodically repeated slabs separated by vacuum layers. At ambient conditions V, Cr, and Fe have the body centered cubic (bcc) structure; Sc, Ti, Co, and Zn have the hexagonal close-packed (hcp) structure, and Ni and Cu are face centered cubic (fcc) metals. For each system, the surface stress was computed for the most stable facet. The corresponding slabs were formed by 8 atomic layers for the fcc (111) surface, 12 atomic layers for the bcc (110) and hcp (0001) surfaces, and 16 atomic layers for the bcc (100) surface. For these systems, the thickness of the vacuum layer was set to 22–23 Å. We considered the antiferromagnetic state for Cr (B2 structure [22]) and the ferromagnetic

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state for Fe, Co, and Ni. Manganese adopts a complex antiferromagnetic structure (α -Mn) with 58 atoms in the unit cell. The (110) surface of α -Mn [23] was modeled by a slab containing 130 atoms separated by a vacuum layer of thickness 12.2 Å. For all slabs, the in-plane lattice constant was fixed to the theoretical bulk equilibrium value, and the interlayer distances, except for the central layers, were allowed to relax to their equilibrium values. The optimization of the atomic structure was performed using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The atoms were relaxed until the remaining forces were less than 20 meV/Å. The Brillouin zone sampling was performed by the Monkhorst-Pack scheme [24]. The chosen plane wave cutoff energy (450–500 eV) and k mesh assured $\sim 1 \text{ meV}$ per atom convergence in the total energy. For each surface, the mean surface stress was determined from the variation of the surface energy upon biaxial in-plane strain [11,25].

The surface energy of 3*d* metals (γ_{3d}) follow a nearly parabolic trend (Fig. 1) and it strongly resembles the trends calculated for 4*d* (Ref. [3]) and 5*d* (Ref. [4]) series. The surface energies are large for the central elements (V, Cr, Mn, Fe, Co) reaching a maximum of 3.06 J m⁻² for Cr. Similar maxima are realized also in γ_{4d} and γ_{5d} for the bcc (110) surface of Mo (2.73 J m⁻²) and W (3.28 J m⁻²). In contrast to γ_{4d} and γ_{5d} , for which shallow local minima for the hcp (0001) surface of Tc and Re can be observed, γ_{3d} exhibits a monotonically decreasing trend for elements with *d* electron number $N_d \ge 4$.

The surface stress of 3*d* metals (τ_{3d}) shows a markedly different behavior (Fig. 1) compared to τ_{4d} and τ_{5d} . For $N_d \leq 3$ and $N_d \geq 7$ the present τ_{3d} and $(\tau_{3d} - \gamma_{3d})$ follow similar trends as those calculated for the 4*d* (Ref. [3]) and 5*d* (Ref. [4]) metals. However, for Cr, Mn, and Fe we can see a deep minimum in τ_{3d} . Most surprisingly, for Cr and Mn the surface stress of the thermodynamically most stable surfaces becomes compressive: -0.32 Jm^{-2} for



FIG. 1 (color online). Calculated surface energy (γ) and surface stress (τ) for 3*d* metal surfaces. Results are shown for the most stable surfaces: (0001) for hcp Sc, Ti, Co and Zn; (100) for bcc V and Cr; (110) for bcc Fe; (111) for fcc Ni and Cu; (110) for α -Mn.

Cr and -0.22 Jm^{-2} for Mn. That is, the thermodynamically stable surfaces of Cr and Mn prefer a larger lattice constant than their bulk counterparts. To our knowledge, these are the only transition metal surfaces where Ibach's model fails.

In order to reveal the origin of the compressive surface stress obtained for Cr and Mn, we repeated our calculations considering two different cases. First, all 3d metals were treated as nonmagnetic (NM), and then Cr, Mn, Fe, Co, and Ni were recalculated for their magnetic ground state (mag). In this study, we kept the surface geometry fixed to the ideal bulk termination in order to exclude the relaxation effects from the magnetic contribution to the surface energy and stress.

We assess the effect of surface relaxation by comparing the unrelaxed magnetic results (Fig. 2) to the fully relaxed magnetic results (Fig. 1). For γ_{3d} the largest changes are obtained for Ti (0.12 J m⁻²), V (0.19 J m⁻²), and Mn (0.12 Jm^{-2}) . The impact of relaxation on the surface stress is much more pronounced, reaching values as high as 1.04 Jm^{-2} for Ti or 2.38 Jm^{-2} for V. The increased sensitivity of τ to the surface geometry is due to the fact that τ varies linearly with the interlayer distance whereas γ has minimum for the equilibrium geometry [3]. Nevertheless, the overall trend of τ_{3d} is not markedly altered by relaxation. In particular, for the unrelaxed surface both Cr and Mn have almost vanishing surface stress (-0.09 and 0.06 Jm^{-2} , respectively). Therefore, we can clearly rule out that the anomalous surface relaxation observed for group VIIB nonmagnetic transition metals [17] is responsible for the compressive surface stress of Cr and Mn.

We define the magnetic contribution to the surface energy (γ^m) and surface stress (τ^m) as the difference between the nonmagnetic (NM) and magnetic (mag) values from Fig. 2. Magnetism was predicted to reduce the surface energy of magnetic metals (viz. $\gamma^m > 0$) [26]. Indeed, γ^m turns out to be sizable for Cr and Mn, for which we obtain $\gamma^m_{Cr} = 0.75 \text{ Jm}^{-2}$ (representing 20% of NM γ_{Cr})



FIG. 2 (color online). Calculated surface energy (γ) and surface stress (τ) for magnetic (mag) and nonmagnetic (NM) 3*d* metal surfaces with unrelaxed geometries. For surface facets, see caption of Fig. 1.

and $\gamma_{Mn}^m = 1.05 \text{ J m}^{-2}$ (28% of NM γ_{Mn}). For Fe, Co, and Ni the average magnetic effect in the surface energy accounts for less than 6%.

In contrast to the magnetic surface energy, the magnetic surface stress for Cr, Mn, and Fe is found to be of order of the corresponding NM surface stress. Namely, $\tau_{\rm Cr}^m = 5.41 \text{ Jm}^{-2}$ (102% of NM $\tau_{\rm Cr}$), $\tau_{\rm Mn}^m = 5.00 \text{ Jm}^{-2}$ (99%), and $\tau_{\rm Fe}^m = 3.88 \text{ Jm}^{-2}$ (71%). That is, surface magnetism drastically reduces the surface stress of Cr, Mn, and Fe. For Co and Ni we have somewhat smaller magnetic effects, $\tau_{\rm Co}^m = 1.11 \text{ Jm}^{-2}$ (30%) and $\tau_{\rm Ni}^m = 0.44 \text{ Jm}^{-2}$ (15%).

The impact of magnetism on the surface stress can be visualized if we realize that the above decrease of the surface stress is associated with the excess magnetic pressure (P_{mag}) around the free surface. Within the Stoner model, the magnetic pressure contribution relative to the nonpolarized case may be estimated as [27]

$$3P_{\rm mag}V \sim \frac{\mu^2 \Delta_d S^2}{N(\epsilon_F)} \bigg[\frac{\alpha}{4\Delta_d S^2} - IN(\epsilon_F) \bigg], \qquad (1)$$

where μ , *I*, $N(\epsilon_F)$, and *S* stand for the magnetic moment, Stoner exchange parameter, density of state at the Fermi level (ϵ_F), and atomic radius, respectively. α describes the decrease of the Andersen bandwidth parameter of the *d* band (Δ_d) with increasing volume (*V*) [27]. For magnetic 3*d* metals $\alpha \approx 4-5$ and $\Delta_d S^2 \approx 0.1$, so that the first term in the square brackets in (1) is typically around 10. This should be compared with the value of $IN(\epsilon_F)$, which is the largest for bcc Fe and usually lies between 1 and 2. Thus, we can generally say that the first term in the expression of P_{mag} is roughly an order of magnitude larger than the second one, which means that the magnetic pressure for magnetic 3*d* metals is always positive and proportional to μ^2 .

Because of the reduced coordination, the surface magnetization is generally enhanced compared to the bulk value, resulting in larger surface magnetic moment (μ_s) than the bulk counterpart (μ_b) . Hence, according to Eq. (1), an excess surface magnetic pressure should appear near free surfaces. Assuming that this excess surface pressure is responsible for the magnetic surface stress, we arrive at $\tau^m \sim \Delta \mu^2$, where $\Delta \mu^2 \equiv \mu_s^2 - \mu_b^2$ represents the surface induced enhancement of the square of the magnetic moment. Comparing the present τ^m values (Fig. 2) to the calculated $\Delta \mu^2$ values, we find an almost perfectly linear relationship between them (Fig. 3). Therefore, the enhanced surface magnetism is the primary factor responsible for the unusually small or negative surface stress of the magnetic 3d metals.

The disclosed anomalous surface stress has an important consequence when comparing the calculated surface energies to the experimental data. The experimental surface energies (γ^{est}) were estimated from the measured liquid surface tensions [28]. γ_{4d}^{est} and γ_{5d}^{est} follow the characteristic parabolic trend with N_d , whereas a pronounced minimum can be seen in γ_{3d}^{est} when going from V to Fe. Namely, the



FIG. 3. Magnetic surface stress (τ^m) versus magnetic moment enhancement $(\Delta \mu^2)$ near the free surfaces of Cr, Mn, Fe, Co, and Ni. The magnetic surface stress refers to nonrelaxed surface geometries (Fig. 2) and $\Delta \mu^2$ represents the difference between surface magnetic moment square and the bulk magnetic moment square.

estimated surface energies for V, Cr, Mn, and Fe are 2.62, 2.35, 1.54, and 2.42 J m⁻², respectively [28]. The local minimum in γ_{3d}^{est} is completely absent from γ_{3d} obtained for the thermodynamically stable structures (Fig. 1). To reduce the effect of surface roughness in the theoretical trend, we also calculated the surface energies for the bcc (100) facet of V, Cr, Mn, and Fe ($\gamma_{3d}^{(100)}$), viz. 2.40, 3.06, 2.14, and 2.50 J m⁻² (Ref. [29]). Although $\gamma_{3d}^{(100)}$ differs significantly from γ_{3d} (Fig. 1), it still does not capture the deep minimum from γ_{3d}^{est} . We note that the trend followed by the present $\gamma_{3d}^{(100)}$ is in line with former theoretical predictions [30]. For the surface stress of the bcc (100) facet of V, Cr, Mn, and Fe ($\tau_{3d}^{(100)}$), we calculated 2.12, -0.32, -2.24, and 1.39 J m⁻², respectively.

It is argued [1,2] that for liquids the excess surface stress disappears so that the liquid surface energy and surface stress are equal. This is because in liquids in the absence of the lattice constraint the surface atoms can easily reorganize to reach their "in-plane" equilibrium density. Increased or decreased surface density, however, implies a different surface energy. In order to estimate the change in the surface energy due to the surface stress, we expand $\gamma(\epsilon)$ as a function of the in-plane lattice strain ϵ , viz. $\gamma(\epsilon) =$ $\gamma + \epsilon(\tau - \gamma) + \cdots$, where we have made use of the Shuttleworth equation (Ref. [2]). Within the continuum model [31], the lattice expansion or contraction caused by the excess surface stress may be expressed in terms of Poisson's ratio (ν) and Young's modulus (E) as $\epsilon \approx (\gamma - \gamma)^2$ τ) $(1 - \nu)/E\lambda$. Here we have omitted the interaction between the surface layer of thickness λ and the underlying bulk [25] in order to mimic the situation from liquids. Within this approximation, upon stress release the surface energy of a bulk crystal changes by $\Delta \gamma \approx -(\tau - \gamma)^2$ $(1 - \nu)/E\lambda$. Hence, in systems where the excess surface

stress is small, $\Delta \gamma$ is negligible, and thus the extrapolated liquid surface tension corresponds to the theoretical surface energy. However, when $|\tau - \gamma|$ is large, the above surface energy correction becomes sizable. Using the calculated $\gamma_{bcc}^{(100)}$ and $\tau_{bcc}^{(100)}$ data, for $\Delta \gamma$ we obtain 2, 224, 515, and 26 mJ m⁻² for V, Cr, Mn, and Fe, respectively. Applying these corrections to γ_{est} [28], we arrive at 2.62, 2.63, 2.15, and 2.45 J m⁻² for the estimated surface energies of V, Cr, Mn, and Fe. These new data are in reasonable agreement with the present $\gamma_{3d}^{(100)}$ values, which shows that the deep minimum in the estimated surface energies for bcc 3*d* metals is, to a large extent, a consequence of the compressive surface stress of Cr and Mn.

Another important implication of the present findings concerns the stability of ideal surfaces. The excess surface stress is known to be the principal driving force for surface reconstruction [31]. For the thermodynamically stable surfaces of Cr and Mn, the obtained large $|\tau - \gamma|$ suggests that these systems might be unstable against reconstruction. Clean $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction on Cr (100) has indeed been observed [32], although later it was shown that a small amount of impurities is needed to observe such superstructure [33].

Previous calculations for nonmagnetic transition metals support the generally accepted picture that transition metal surfaces possess tensile surface stress. Here we demonstrated that surface magnetism can significantly alter the above scenario by overwriting the normal surface behavior and leading to small or negative surface stress values. In particular, we found that the thermodynamically stable (100) surface of bcc Cr and the (110) surface of α -Mn exhibit compressive surface stress. The large negative surface stress in combination with large surface energy indicates instability against reconstruction, and we propose that its effect is also reflected in the surface tension around and beyond the melting point.

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