Magnetic Splitting of Image States at Fe(110)

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The exchange splitting of image-induced surface states on Fe(110) is calculated by spin-polarized near-surface embedding. The splitting is 55 meV for the $n=1$ state and is primarily a result of coupling to the spin-polarized substrate potential. The effect of the spin-polarized surface barrier is relatively small and of opposite sign to the substrate contribution. This surprising result is a direct consequence of the negative spin density of surface electrons at the Fermi energy, illustrating the sensitivity of spin-split image states to surface magnetic properties.

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Image-induced surface states which have their origin in the long range image tail of the surface potential have become in recent years a subject of extensive theoretical and experimental studies [1–7]. Up to now most of the work has been concerned with the binding energies, lifetimes, and dispersion of these states. An exciting new topic concerns the interaction of image states with the surface of a ferromagnet which splits the spin degeneracy of these states [8–10]. Very recently, through the technique of spin-polarized inverse photoemission, it has become possible to measure this splitting; the first direct measurements made on the Ni(111) surface give a splitting of 18 meV for the $n=1$ state [11] while indirect measurements, using two-photon photoemission, indicate larger splittings on Fe(110) and Co(111) surfaces [12]. A splitting of majority and minority spin image states larger than their lifetime broadening opens up the possibility of selectively populating the majority $n=1$ image states hence creating an ideal spin-polarized two-dimensional electron gas at the top of a ferromagnetic substrate. In addition, since image states are common to a large number of metal surfaces their magnetic splitting may serve as a probe of magnetic properties at and in the vicinity of magnetic surfaces.

In this Letter we concentrate on Fe(110), which has a relatively high bulk magnetic moment ($2.2\mu_B$ as compared to $0.6\mu_B$ for Ni). We report here our calculated spin splitting of image states at this surface and investigate its origin. The spin splitting is the net result of two effects. First, since the metal is ferromagnetic, spin up and spin down image states are scattered from different substrate potentials. From first-order perturbation theory, the resulting splitting is proportional to the overlap of image state wave functions with the spin polarization of the substrate effective potential $v^{\uparrow}-v^{\downarrow}$ where $v^{\uparrow}$ and $v^{\downarrow}$ are the potentials for spin up and spin down electrons, respectively. On the other hand, in a multiple scattering picture this part of the splitting can be viewed as a bulk band structure effect caused by a difference in the position of spin up and spin down bulk band edges [8,13]. Second, due to the exchange interaction near the crystal surface, the effective surface barrier experienced by electrons outside the metal is also spin dependent.

We take both effects fully into account in our calculations and find that the spin splitting of image states is primarily due to the former effect, i.e., it is a consequence of exchange processes in the substrate. More interestingly, we find that the relatively small contribution of the surface barrier to the splitting has a sign *opposite* to the substrate contribution. Thus, in contrast to the common picture [8,9], the polarization of the surface barrier actually reduces the spin splitting of image states instead of enhancing it. It will be shown that this surprising result is a consequence of a sign reversal in the surface layer magnetization $m(\mathbf{r})=n^{\uparrow}(\mathbf{r})-n^{\downarrow}(\mathbf{r})$ [with $n^{\uparrow\downarrow}(\mathbf{r})$ the spin up (down) charge density] at the Fermi energy which results in a self-consistent way in a sign reversal in the planar average of the surface potential difference $v^{\uparrow}(\mathbf{r})-v^{\downarrow}(\mathbf{r})$ experienced by image states outside the surface.

The calculations are performed using the spin-polarized version of our previously reported near-surface embedding method [14] for calculating image states at realistic metal surfaces. In this method the one-electron Schrödinger equation in a finite region just above the surface—we call this the near-surface region (NSR)—is solved explicitly (see Fig. 1). The scattering of image states from the semi-infinite ferromagnetic substrate is reproduced by a spin-dependent surface embedding potential acting over S_m, while the long range image tail of the surface potential which is crucial for a correct description of image states is replaced by the Coulomb embedding potential acting over S_v. Both the spin-dependent substrate embedding potential and the spin-dependent surface barrier are the inputs of our calculations. These are obtained from a self-consistent spin-polarized full-potential surface embedded Green function (SEGF) calculation [15,16] (using the von Barth–Hedin local spin density approximation [17]) of a single layer of Fe(110) embedded onto the ferromagnetic bulk. From this calculation we find a magnetic moment of $2.75\mu_B$ per surface atom ($r_{MT}=2.35$ a.u.) in good agreement with $2.65\mu_B$ obtained from full-potential augmented linear plane wave slab calculations [18]. The calculated work

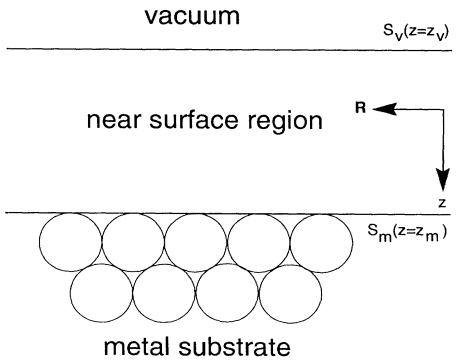

FIG. 1. Calculation geometry for the near-surface region embedded onto the metal substrate and vacuum. In the calculations z_m is located 2.35 a.u. above the last atomic plane. The near-surface region is 10 a.u. thick.

function is 5.30 eV, in good agreement with the experimental value of 5.1 eV [19]. The spin up and spin down potentials in the near-surface region are fully three dimensional with their planar averages smoothly varied through this region to join with continuous derivative to their *common* asymptotic image tail given by [in atomic units (a.u.) with $e=\hbar=m=1$]

$$v(z)=E_v-\frac{1}{4|z-z_0|}, \tag{1}$$

with E_v the self-consistently calculated vacuum level. The position of the effective image plane z_0, which is in principle an adjustable parameter, is fixed in the present calculations at half an interlayer spacing beyond the outermost atomic layer (the jellium edge). Solving the Schrödinger equation in the near-surface region, we find the one-particle Green function from which the density of states is calculated.

In Fig. 2(a) we display the calculated Fe(110) density of states at $\bar{\Gamma}$ for both spin directions, for energies inside the bulk band gaps. The image tail of the surface potential does not affect the density of states at lower energies. Inside the gap, however, it gives rise to the infinite series of magnetically split image states. The spin up states, corresponding to the majority states in the bulk, have slightly lower binding energies and the splitting is strongest for the $n=1$ state. We find a splitting of 55 meV for this state (the binding energy of the $n=1$ spin up state with respect to the vacuum level is -0.71 eV), 3 times larger than the splitting found experimentally for Ni(111) [11] and consistent with the upper limit of 80 meV deduced from high-resolution two-photon photoemission measurements [12]. The splitting, however, is still less than the measured lifetime broadening of image states on *d*-band metals [20] (80 meV on Ni) suggesting that, at least at the clean Fe(110) surface, the use of image states in creating a spin-polarized two-dimensional electron gas might not be feasible.

As can be seen from Fig. 3, the binding energies of image states for both spin directions follow closely the Rydberg-like series:

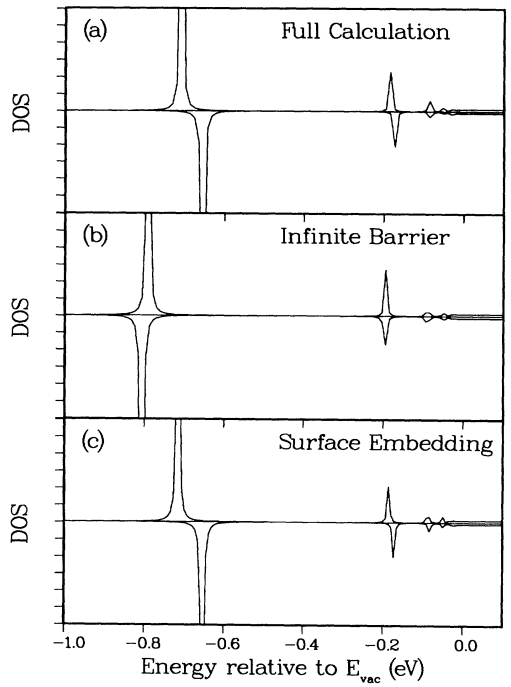

FIG. 2. Fe(110) spin-dependent density of states at $\bar{\Gamma}$ integrated through the near-surface region (imaginary part of energy $=0.0001$ a.u.). The magnetic splitting found from the full calculations (a). The splitting caused by the spin-dependent surface barrier alone (b) and by the spin polarization of the substrate potential alone (c). Note how the splitting changes sign and becomes negative as the substrate magnetism is switched off.

$$E_n^{\uparrow\downarrow}=E_{\rm vac}-\frac{1}{32(n+a^{\uparrow\downarrow})^2}, \tag{2}$$

with $a^{\uparrow}=0.15$ and $a^{\downarrow}=0.22$ the spin-dependent quantum defects. Consequently, the spin splitting $\Delta E_n=E_n^{\downarrow}-E_n^{\uparrow}$ decreases monotonically with n, following an asymptotic $1/n^3$ scaling law:

$$\Delta E_n=\frac{a^{\downarrow}-a^{\uparrow}}{16n^3},\quad n \text{ large}. \tag{3}$$

As described above, the spin splitting may be considered as the net result of a substrate and a surface contribution. To separate these two contributions from each other, we performed a second calculation with the spin-dependent substrate embedding potential replaced with a spin-independent embedding potential corresponding to an infinite barrier. In this way the substrate magnetism is switched off and the only contribution to the exchange splitting comes from the spin dependence of the surface barrier. The result of this calculation is shown in Fig. 2(b). For comparison, we display in Fig. 2(c) the result of a third calculation performed with a spin-independent

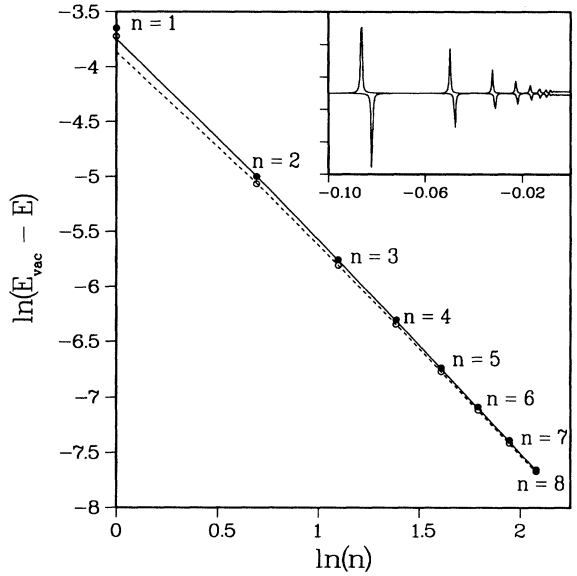

FIG. 3. $\ln(E_n)$ vs $\ln(n)$ for spin up (filled circles) and spin down (open circles) image states at the Fe(110) surface. The functions $-\ln[32(n+a^{\uparrow\downarrow})^2]$ with $a^{\uparrow}=0.15$ (solid line) and $a^{\downarrow}=0.22$ (dashed line) are displayed for comparison. The inset shows the monotonic decrease of the spin splitting for $n>2$ members of the image series on Fe(110). These are resolved by working at a very small imaginary part of energy.

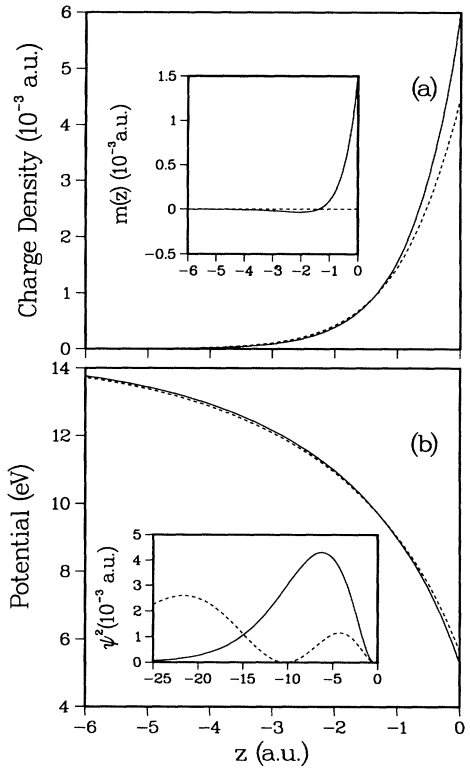

FIG. 4. Planar averaged electron density (a) and the interpolated surface potential (b) for spin up (solid line) and spin down (dashed line) directions in the near-surface region. The insets show the magnetization (a) and the probability densities of the first (solid line) and the second (dashed line) image state (b).

surface barrier (obtained by taking the average of spin up and spin down barriers). It is clearly seen that the splitting caused by the spin dependence of the surface barrier alone is much smaller than the splitting due to the spin-dependent substrate potential, indicating that the exchange splitting of image states is primarily a substrate effect. We note that for this reason, calculations reported in [8] which assume a spin-independent surface barrier but take into account the spin dependence of the bulk band edges yield a spin splitting of the same order as that reported here. The surprising result is that the two contributions have opposite sign (63 vs -14 meV for the $n=1$ state). We are thus dealing with two competing effects: The spin polarization of the substrate potential alone leads to a positive splitting ($E_n^{\downarrow}-E_n^{\uparrow}>0$) while the spin polarization of the surface barrier results in a negative splitting, the net result being positive since the substrate effect dominates.

To understand the physical origin of this result, we display in Fig. 4 the planar averages of the self-consistently calculated majority (spin up) and minority (spin down) charge densities and the surface barrier used in the calculations in the near-surface region, where z is measured from the substrate boundary z_m [which lies 2.35 a.u. outside the outermost atomic layer (see Fig. 1)]. As can be seen from Fig. 4(a), large positive magnetization is found right at the surface but as we move away from the surface the exponential tail of the minority spin down charge density becomes dominant, resulting in a negative spin density in the vacuum region. This behavior is directly followed by the local exchange-correlation potential and the interpolated barrier used in the calculations [Fig. 4(b)]: Right at the surface, the spin up electrons experience a deeper potential but at about 1.5 a.u. away from the surface the potential for spin down states becomes more attractive. Image states have their maximum probability $|\psi_n|^2$ well outside the surface [see inset of Fig. 4(b)]. Therefore, when the substrate magnetism is switched off, the spin up image states experience on average a less attractive potential; hence their binding energy goes up while the binding energy of the spin down states goes down. The net effect is then a negative splitting result in the calculations.

The sign reversal in the local spin density outside the Fe(110) surface found in our one-layer embedding calculations, which gives rise to the above effect, may also be seen in the work of Wu and Freeman (see Fig. 2 of [21]). It can be understood in terms of the band-narrowing effect caused by a lower coordination number at the surface. As a result of the narrowing of the density of states (DOS) at the surface layer, in contrast to the bulk, the

minority spin down states overwhelm the majority states near the Fermi energy [21] and the spin density at this energy is negative. Sufficiently far outside the surface the dominant contribution to the charge density arises from the states near the Fermi energy. Hence the exponential tail of the minority charge density becomes dominant as we move away into the vacuum, resulting in a negative spin density outside the surface. While the effect of this sign reversal spin splitting of image states is masked by the much larger substrate contribution and thus cannot be measured explicitly, it should be possible to measure the sign reversal in the spin density itself directly from the spin scanning tunneling microscopy image of the Fe(110) surface (as a negative difference between tunneling currents for majority and minority spins $I^{\uparrow} - I^{\downarrow}$).

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