## Spin Density at the Fermi Level for Magnetic Surfaces and Overlayers

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Results of calculations of the spin density at the Fermi energy for several illustrative examples—the clean Fe(110) surface and the O/Fe(110), Fe/Ni(111), and Ru/Ag(001) overlayer systems—using the full potential linearized augmented plane wave method demonstrate that this energy-sliced spin density differs substantially from the total spin density previously given in the literature. The difference of the density of states at  $E_F$  between the two spin parts is found to play the key role. Its negative sign in the surface-vacuum region for Fe(110) and its sign reversal when oxygen is added as an overlayer explain the experimental results obtained by using spin-polarized metastable atom deexcitation spectroscopy.

PACS numbers: 75.30.Pd, 75.70.Ak

In the exciting field of low-dimensional magnetic systems including surfaces, interfaces, and ultrathin films [1], local spin density functional (LSDF) *ab initio* electronic structure calculations, especially those using the full potential linearized augmented plane wave (FLAPW) method, have played a key role [2,3]. Extensive calculations concluded that an environment with weakened interatomic interaction (e.g., at the interfaces with the vacuum or an inert substrate) gives rise to strong magnetic moment enhancement [3].

The verification of these theoretical predictions has been one of the main goals for experimentalists in the past decade. Many spin-polarized (SP) experimental techniques, e.g., SP photoemission, surface magneto-optic Kerr effect (SMOKE), SP Auger spectroscopy, SP-LEED, scanning electron microscopy with polarization analysis (SEMPA), Lorentz electron microscopy, etc., have been developed and have interplayed strongly with theoretical investigations [1,3-5]. Recently, the scanning tunneling microscopy (STM), which has emerged as a powerful means to study surface atomic structure [6], has also been introduced to investigate surface magnetism by using a magnetic tip (like CrO<sub>2</sub>) and was successfully applied to observe the antiferromagnetic (AFM) coupling of ferromagnetic terraces at the Cr(001) surface [7]. Since STM has a high spatial resolution on the atomic scale, it is uniquely able to identify in-plane AFM coupling [e.g., as predicted for Fe/Ru(0001) [8]] from the paramagnetic state ("magnetically dead").

According to Bardeen's equation [9], the tunneling current is

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} [f(E_{\mu}) - f(E_{\nu} + eV)] |M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\nu}), \quad (1)$$

where the tunnel matrix is given by  $M_{\mu\nu} = (\hbar^2/2m) \times \int_{S_0} d\mathbf{S}(\Psi^*_{\mu} \nabla \Psi_{\nu} - \Psi_{\nu} \nabla \Psi^*_{\mu})$ ,  $S_0$  denotes the surface of the tip, f(E) is the Fermi distribution function, V is the bias voltage, and  $\Psi_{\mu}$  ( $E_{\mu}$ ) and  $\Psi_{\nu}$  ( $E_{\nu}$ ) stand for the eigen-

functions (eigenenergies) of the sample and the tip, respectively. Obviously, unlike other usual techniques, STM is highly spatially and energy sensitive, i.e., only states in a narrow energy window ( $\sim 0.2 \text{ eV}$  around  $E_F$ for small V) with their wave-function tails extending into the tip region contribute to the tunneling current [10]. With a simplified model (spherical tip and only s-type orbital), Tersoff and Hamann [11] obtained an expression  $I = VN(\mathbf{R}, E_F)$  where  $N(\mathbf{R}, E_F)$  is the local density of states at  $E_F$  of the sample at the tip region **R**. Thus, STM images of the magnetic structure (reflected by the difference between tunneling currents for majority and minority spins, i.e.,  $I_{\uparrow} - I_{\downarrow}$ ) over metal surfaces actually correspond only to the spin density at the Fermi energy,  $m(\mathbf{r}, E_F)$ , rather than the total spin density,  $m(\mathbf{r})$ , as usually given in the literature.

In addition, another newly developed technique, spinpolarized metastable atom deexcitation spectroscopy (SPMDS) [12,13] is also dominated by the magnetization at  $E_F$  if the ionization of He(2<sup>3</sup>S) takes place far enough (> 2.0 Å, i.e., the same place where the STM image is taken) away from the metal surfaces. Based on the theory developed by Penn and Apell for SPMDS [13], the  $m(\mathbf{r}, E_F)$  was found to be negative for Fe(110), differing in sign compared to the calculated  $m(\mathbf{r})$  [14]. However, the negative sign of  $m(\mathbf{r}, E_F)$  in the vacuum region can be reversed by oxygen adsorption [15]. Therefore, calculations of  $m(\mathbf{r}, E_F)$  in the vacuum region are needed for direct comparison with the STM and SPMDS results which, in turn, are helpful to develop reliable theories for these techniques.

Here, we report the calculated  $m(\mathbf{r}, E_F)$  for several selected systems such as the clean and oxygen-adsorbed Fe(110) surfaces, and the Fe/Ni(111) and Ru/Ag(001) overlayer systems. The FLAPW method is employed in all the calculations;  $m(\mathbf{r}, E_F)$  is obtained by taking account of states only lying in a 0.25-eV-wide energy window just below  $E_F$ . Integrations over k space are substi-

tuted by summations over sixteen special k points in the  $\frac{1}{4}$  irreducible 2D Brillouin zone [16]. It is clearly demonstrated that  $m(\mathbf{r}, E_F)$  depends mainly on the difference of the density of states (DOS) at  $E_F$  between the two spin parts and usually differs in sign from  $m(\mathbf{r})$ .

As the first example,  $m(\mathbf{r})$  and  $m(\mathbf{r}, E_F)$  of the bcc Fe(110) clean surface (seven-layer slab) are presented in Figs. 1(a) and 1(b), respectively. As is typical of  $m(\mathbf{r})$ for the 3d metal surfaces, large positive spin polarization is found around the atomic sites while small negative spin density pockets ("dog bones") occupy the interstitial region; the spin polarization in the surface region is enhanced pronouncedly especially toward the vacuum side. Note that in the surface vacuum region,  $m(\mathbf{r}, E_F)$  in Fig. 1(b) becomes *negative*—i.e., opposite in sign from  $m(\mathbf{r})$  in Fig. 1(a). Thus, despite the enhancement of the surface magnetic moment over the bulk value  $(2.4\mu_B \text{ vs})$  $2.1\mu_B$ ;  $r_{MT} = 2.0$  a.u.), STM (as did SPMDS [15]) experiments are expected to see a negative spin polarization on the Fe(110) surface. Quantitatively, we plot the planar average of the spin densities [both  $m(\mathbf{r})$  and  $m(\mathbf{r}, E_F)$ ] and the spin polarization [defined as  $P(z) = m(z)/\rho(z)$ ] in Fig. 2, where z starts from the Fe(S) plane,  $d_0$  denotes the place of the vacuum boundary [2.31 a.u. and 4.76 a.u. for Fe(110) and O/Fe(110), respectively]. Clearly, both  $m(\mathbf{r})$  and  $m(\mathbf{r}, E_F)$  decay quickly to zero at only 3-4 a.u. away from the vacuum boundary, so both STM and



FIG. 1. (a) The total spin density  $m(\mathbf{r})$  and (b) the spin density from states at  $E_F$ ,  $m(\mathbf{r}, E_F)$ , for Fe(110). Contours shown on the vertical (110) plane start from  $\pm 1 \times 10^{-4} e/a.u.^3$  and increase successively by a factor of  $\sqrt{2}$ . The solid and dashed lines indicate positive and negative spin density, respectively.

SPMDS should be taken within the region  $z - d_0 < 3.0$ a.u. Unexpectedly, neither P(z) nor  $P(z, E_F)$  shows asymptotic behavior even out to 10 a.u. away from the vacuum boundary [where  $\rho(z) < 10^{-10} e/a.u.^3$ ]. Corresponding to Fig. 1, P(z) is positive for  $z - d_0 < 3.5$  a.u. and increases with decreasing z, whereas  $P(z, E_F)$  is negative (from -45% at the vacuum boundary to -60% at  $z - d_0 = 3.5$  a.u.). Unfortunately, there are no SPMDS spin-polarization results available for Fe(110). However, Penn and Apell [13] determined that  $P(z, E_F)$  is about -23% for Ni(110). Since the detected spin asymmetry for Fe(110) [15] is 1.5-1.8 times larger than that for Ni(110) [13] at higher retarding potential (e.g., 12 eV), its measured  $P(z, E_F)$  value should be about -40%—i.e., close to the calculated  $P(z, E_F)$ .

Physically,  $m(\mathbf{r}, E_F)$  depends strongly on the DOS and wave-function character of these states at  $E_F$ . The DOS curves for Fe(110) for both the majority (solid lines) and the minority (dashed lines) spins are plotted in Fig. 3. For the bulklike Fe(C) atom, the Fermi level falls on a weak majority spin antibonding peak and in the minority spin nonbonding valley. Fewer minority spin states contribute to the charge density at  $E_F$ , and thus  $m(\mathbf{r}, E_F)$  is dominated by the majority spin states. By contrast, the surface layer DOS curves are significantly narrowed due to the lowered coordination number. This results in (i) an almost complete occupation for the majority spin band and a reduced  $N_{\uparrow}(E_F)$ , and (ii) a substantially increased  $N_1(E_F)$  because of surface states and surface resonances in the minority spin band. Subsequently, the minority spin overwhelms the majority spin contributions at  $E_F$  for the surface Fe layer. In the vacuum, the tails of these minority spin states (e.g., the peak at -0.5 eV) becomes dominant especially in the region close to or above  $E_F$ . This explains why  $m(\mathbf{r}, E_F)$  in Fig. 1(b) becomes negative in the surface-vacuum region.

Since the surface band narrowing is a general phenomenon, the conclusion that  $m(\mathbf{r}, E_F)$  is negative in



FIG. 2. Planar average of P(z) for, curve a, Fe(110) and b, O/Fe(110);  $P(z, E_F)$ , for curve c, Fe(110) and d, O/Fe(110) — right scale. Planar average of m(z), for curve e, Fe(110) and f, O/Fe(110);  $m(z, E_F)$ , for curve g, Fe(110) and h, O/Fe(110) — left scale.



FIG. 3. The density of states in each muffin-tin sphere and vacuum for FM Fe(110). Solid and dashed lines stand for majority spin and minority spin, respectively.

the vacuum region can be easily extended to all Fe, Co, and Ni surfaces. For example, we also get the same result for the Fe(111) surface [17]. Unlike the case of Fe,  $m(\mathbf{r}, E_F)$  should be also negative in bulk Co and Ni since their majority spin bands are fully occupied. This inference is clearly demonstrated by the  $m(\mathbf{r}, E_F)$  plot for Fe/Ni(111) in Fig. 4(b), where  $m(\mathbf{r}, E_F)$  becomes negative around all Ni atoms despite the strong positive  $m(\mathbf{r})$ in these regions shown in Fig. 4(a).

Usually, the DOS (even "local" DOS) given in the literature represents an integration in some region (e.g., muffin-tin spheres or vacuum), and the question now arises whether the sign of  $m(\mathbf{r}, E_F)$  [i.e.,  $\Delta N(\mathbf{R}, E_F)$ ] can be estimated solely from these "integrated" DOS curves. Clearly, the answer is yes when the difference between the integrated  $N_1(E_F)$  and  $N_1(E_F)$  is large enough. As listed in Table I, the differences between  $N_{\uparrow}(E_F)$  and  $N_1(E_F)$  are distinct for the Fe(C) atom in Fe(110) and Ni atoms in Fe/Ni(111); thus the sign of  $m(\mathbf{r}, E_F)$  is unambiguous [positive for Fe(C) in Fig. 1(b), and negative for Ni in 4(b)]. For Fe(S) (and vacuum region) in Fe(110) and in Fe/Ni(111), the  $N_{\uparrow}(E_F)$  becomes closer to  $N_1(E_F)$ , and so  $m(\mathbf{r}, E_F)$  is small in value but still negative. Of course, the actual profile of  $m(\mathbf{r}, E_F)$  depends on the details of their wave functions for states at  $E_F$  in this case. From Fig. 1(b), we can see that the states at  $E_F$  are mainly  $d_z^2$ -like for the majority spin, while those for minority spin have  $d_{xz}$  character around the surface atom for Fe(110). Unlike  $m(\mathbf{r})$  in Fig. 4(a),  $m(\mathbf{r}, E_F)$ becomes structureless in the vacuum region for



FIG. 4. (a) The total spin density  $m(\mathbf{r})$  and (b) the spin density from states at  $E_F$ ,  $m(\mathbf{r}, E_F)$ , for Fe/Ni(111). Contours start from  $\pm 1 \times 10^{-4}$  e/a.u.<sup>3</sup> and increase successively by a factor of  $\sqrt{2}$ . The solid and dashed lines indicate positive and negative spin density, respectively.

Fe/Ni(111) in Fig. 4(b). Thus it would be hard to observe the magnetic configuration on Fe/Ni(111) using SP-STM. Furthermore, if the  $N_1(E_F)$  and  $N_1(E_F)$  become almost equal, as for the Ru atom in Ru/Ag(001),  $m(\mathbf{r}, E_F)$  shown in Fig. 5(b) contains both positive and negative contributions. Although the  $N_1(E_F)$  is slightly larger than the  $N_1(E_F)$  listed in Table I,  $m(\mathbf{r}, E_F)$  is negative in the vacuum region. Compared to  $m(\mathbf{r})$  in Fig. 5(a), the corrugation of  $m(\mathbf{r}, E_F)$  becomes very small — which also makes observation of 4d magnetism of Ru/Ag(001) using SP-STM difficult. In this case,  $m(\mathbf{r}, E_F)$  cannot be estimated simply from the DOS curves even in sign, but have to be calculated specially (as was done in the present work).

Finally, to check the effects of oxygen adsorption, results were also obtained for  $p(1 \times 1)$  O/Fe(110). Quite strikingly, the oxygen adsorption *enhances* the magnetic moment at the interfacial Fe site by 6% (from  $2.40\mu_B$  to

TABLE I. The calculated density of states at  $E_F$  for the majority spin  $[N_1(E_F)]$  and minority spin  $[N_1(E_F)]$  (in states/eV spin atom).

System	Layer	$N_{\uparrow}(E_F)$	$N_{\downarrow}(E_F)$
Fe(110)	Fe(S)	0.40	0.59
	Fe( <i>C</i> )	0.72	0.18
Fe/Ni(111)	Fe	0.48	0.60
	Ni(1)	0.06	0.99
	Ni( <i>C</i> )	0.05	2.02
Ru/Ag(001)	Ru	0.90	0.85



FIG. 5. (a) The total spin density  $m(\mathbf{r})$  and (b) the spin density from states at  $E_F$ ,  $m(\mathbf{r}, E_F)$ , for Ru/Ag(001). Contours start from  $\pm 1 \times 10^{-4} \ e/a.u.^3$  and increase successively by a factor of  $\sqrt{2}$ . The solid and dashed lines indicate positive and negative spin density, respectively.

2.54 $\mu_B$ ). In addition, the positive induced oxygen magnetic moment is as large as  $0.7\mu_B$  ( $r_{\rm MT}$  = 1.85 a.u.). As seen in Fig. 2, while P(z) remains small and positive [(5-10)%] after oxygen adsorption, the sign of  $P(z, E_F)$  is now reversed to positive, from 51% at the vacuum boundary to 30% at  $z - d_0 = 3.5$  a.u.—which confirms the SPMDS measurement [15].

The work at Northwestern University was supported by the National Science Foundation (Grant No. DMR 89-06935 and by a grant of computer time at the Pittsburgh Supercomputing Center through its Division of Advanced Scientific Computing) and at Argonne National Laboratory by the Department of Energy. We thank S. D. Bader for helpful discussions and comments on the manuscript.

- See the review by L. M. Falicov, D. T. Pierce, S. D. Bader, R Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, J. Mater. Res. 5, 1299 (1990), and references therein.
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