Observation of Spin-Polarized Surface States on Ultrathin bct Mn(001) Films by Spin-Polarized Scanning Tunneling Spectroscopy

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We report the observation of a magnetic contrast of up to 20% in the scanning tunneling spectroscopy dI/dV maps obtained with Fe-coated tips on Mn(001) layers grown on an Fe(001) whisker at 370 K. These nanometer resolution microscopy results show that the layers couple antiferromagnetically. By normalizing the dI/dV curves by tunneling probability functions, we found a spin-dependent peak on the body-centered-tetragonal (bct) Mn(001) surface at +0.8 V, whose high spin polarization gives rise to the dI/dV map contrast. Band structure calculations allow one to identify the +0.8 V peak as due to two spin-polarized d_{z^2} surface states.

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The (001) surfaces of the bcc $3d$ transition metals Cr and Fe are characterized by highly spin-polarized surface states [1–3]. In the periodic table, Mn is not only between Cr and Fe, it is also exactly in the middle of the $3d$ series favoring higher magnetic moments [4]. Although Mn does not exist in a bulk bcc phase at room temperature (RT), previous results showed that body-centered-tetragonal (bct) (001) surfaces can be stabilized by thin film growth at Fe(001) surfaces [5–7]. Recent scanning electron microscopy with polarization analysis results suggested that for films thicker than three layers the ferromagnetic Mn(001) sheets couple antiferromagnetically, whereas the local surface magnetism is unknown [8]. A natural question that arises is whether the magnetization of these artificial bct Mn(001) layers can be related to the existence of highly spin-polarized d-like surface states. Furthermore, the study with local magnetic microscopy with nanometer resolution of a system consisting of an antiferromagnet on top of a ferromagnet is of utmost importance for fundamental understanding of nanomagnetism and possible applications such as spintronical devices. Spin-polarized scanning tunneling microscopy (SP-STM) and spectroscopy (SP-STS) are the most powerful techniques to tackle these issues [9].

In this Letter, we report on the observation of a magnetic contrast in SP-STM and SP-STS measurements on bct Mn(001) layers giving evidence that the layers couple antiferromagnetically. After a careful background correction a peak is found at +0.8 V in the spectroscopic dI/dV curves. Band structure calculations allow us to interpret this peak in terms of spin-polarized d_{z^2} surface states. Problems that arise in determining the sample polarization are discussed.

STM and STS measurements were performed in ultrahigh vacuum (UHV) ($\sim 5\times10^{-11}$ mbar) at RT with an Omicron UHV STM-1. Mn layers were grown on an Fe(001) whisker at 370 K. Details are given in Refs. [7,10]. In the present study, we used two kinds of tips: (1) W tips self-sputtered in UHV by Ar^+ were used as clean W tips [7]. (2) Fe-coated W tips were used as SP tips. A magnetic contrast was reproducibly obtained with relatively blunt W tips covered with 7–10 nm Fe at RT [11]. It is believed that for these tips the magnetization is parallel to the sample surface [9]. The tip was carefully approached to the sample to exclude any mass transport between tip and sample. Furthermore, no voltage pulses were applied during these SP-STS measurements [12]. An external magnetic field was not applied. STS measurements were performed at every pixel of a constant current topographic image by opening the STM feedback loop at a given current and voltage ("set point"). dI/dV curves were obtained by numerical differentiation of the $I(V)$ curves.

Since the growth of Mn layers on Fe(001) changes at coverages above 3 ML (monolayer) from layer-by-layer to layer-plus-islands [7], more than four levels can be exposed at a coverage of 7.2 ML Mn as shown in Figs. 1(a) and 1(c). Previous results showed that from the fourth layer the Fe intermixing in the Mn film can be neglected [7]. At this surface, dI/dV curves were measured at 75×75 pixels. A map of the dI/dV signal at +0.2 V is shown in Figs. 1(b) and 1(d). Numbers in Fig. 1 denote the stacking numbers of the Mn layers, which were estimated by a quartz crystal oscillator calibration and Gaussian fits to the fraction of exposed layers on the surface [7]. Using clean W tips, the dI/dV map shows no contrast [Fig. 1(b)]. All step heights in Fig. 1(a) are 0.16 nm [14]. Furthermore, since the in-plane lattice constant equals that of Fe(001), i.e., 0.287 nm [7], it can be concluded that the Mn films grow in a bct phase. Figures 1(c) and 1(d) show STM and STS measurements, respectively, performed with an Fe-coated W tip. Clearly, the contrast in the dI/dV map oscillates with a period of two layers. From higher resolution images [Figs. 1(e)–1(g)], it can be concluded that the magnetic contrast changes within a lateral length of 1.0 ± 0.5 nm. Although the even layers (> 3 ML), i.e., layers "8" and "10", are darker than the odd layers ("7" and "9") in the dI/dV map, this is not

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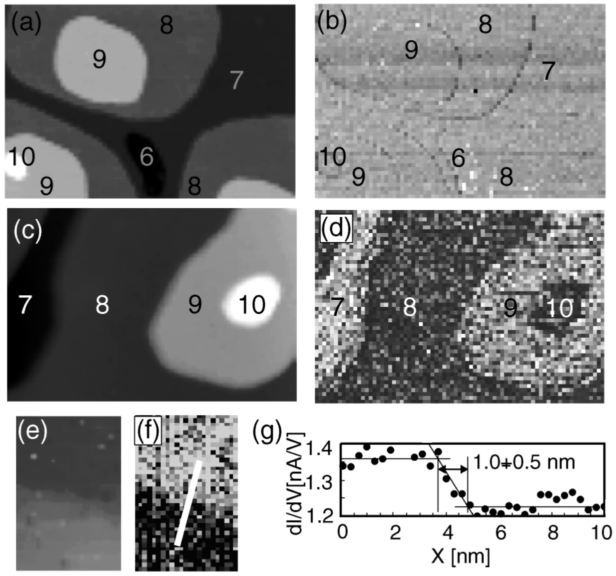

FIG. 1. (a),(b) STM and STS measurements, respectively, obtained with a clean W tip on Fe(001) covered with 7.2 ML Mn at 370 K. (a) A topographic image obtained at a set point of $V_S = -0.5$ V, $I = 0.5$ nA. Scan size is 150×100 nm^2. (b) The dI/dV map at +0.2 V measured at the same area as (a). (c),(e) SP-STM and (d),(f) SP-STS measurements obtained with Fe-coated tips. (c),(e) Topographic images obtained at a set point of $V_S = -0.5$ V, $I = 0.5$ nA. Scan size is 100×67 nm^2 for (c) and 14×20 nm^2 for (e). (e) A hidden Fe step [7], where step height is only 0.02 nm and magnetizations are reversed. (d),(f) The dI/dV map at +0.2 V measured at the same area as (c) and (e), respectively. For (d) black-white scale ranges from 0.75 nA/V to 1.00 nA/V. In (f), one pixel is 0.25 nm. (g) The line profile along the white line in (f).

always the case, i.e., with some Fe-coated tips the odd layers appear darker than the even layers. With the Fe-coated tip also inequivalent step heights are measured for steps from even to odd (0.15 nm) and from odd to even (0.17 nm) layers in Fig. 1(c) [14]. We explain the alternating contrast in the dI/dV maps obtained with Fe-coated tips by the layered antiferromagnetic magnetization of the Mn(001) layers. This explanation is corroborated by the following observations: (i) The alternating contrast in the dI/dV maps has the same onset (> 3 ML) and period (two layers) as previous results obtained with other less local techniques [6,8,15]. (ii) The contrast is observed with the Fe-coated tips only; it is not observed with clean W tips. (iii) Reversed contrasts are also observed using different Fe-coated tips. This indicates the random character of the tip magnetization direction.

The dI/dV curves obtained on the Mn(001) surface do not show peaks (Fig. 2). dI/dV curves normalized by I/V do not show peaks either. Conversely, normalization of the dI/dV curves by the tunneling probability function (T) is more successful. Theoretically, this normalization was shown to lead to the best sample density of states (DOS) recovery [16]. Also, our recent publications show

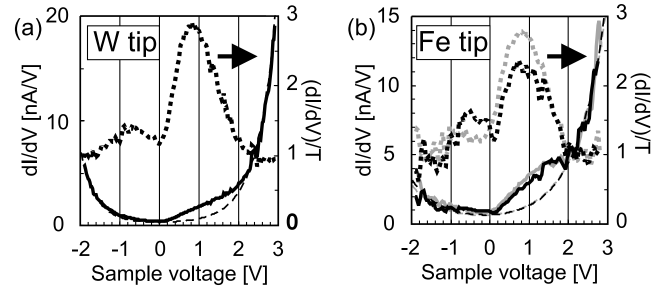

FIG. 2. (a),(b) dI/dV curves normalized by the voltage-dependent tunneling probability functions, which were obtained on Mn films thicker than three layers with clean W tips and Fe-coated tips, respectively. Solid and dotted curves are the dI/dV and the $(dI/dV)/T$ curves, respectively. Tunneling probability functions (dashed curves) were obtained by a fit to the dI/dV curves. In (b), black and grey curves are representative of the odd and the even layers, respectively.

that this method can successfully recover the sample DOS from experimental dI/dV curves [7,10]. In the present work we fitted T multiplied by an offsetted Gaussian line shape (which represents the surface state peak in the DOS) to the dI/dV curves. This fitting procedure was leading only to good fitting results when we used as input work function (ϕ) values 4.0 ± 0.25 eV. For ϕ's varying between those limits the peak amplitude changes $\pm 15\%$ and the width $\pm 5\%$, but the peak energy only ± 10 meV. These changes produce errors in asymmetries $\pm 2\%$ as discussed below [see Fig. 4(d) below]. Figures 2(a) and 2(b) show $(dI/dV)/T$ curves averaged over 30 single curves measured on Mn films thicker than three layers with a clean W tip and an Fe-coated tip, respectively. dI/dV curves were obtained within a large voltage range from -2 V to $+3$ V. Normalized dI/dV curves measured with the clean W tip show two peaks: a strong peak around $+0.8$ V and a weak peak around -0.5 V. In Fig. 2(b), normalized dI/dV curves measured on even layers (grey curve) and odd layers (black curve) show two peaks at the same energies as those obtained with the clean W tips. However, now the amplitude of both peaks oscillates with a period of two layers. The curves measured on even and odd layers cross around the Fermi level. In the approximation of Ref. [16], $(dI/dV)/T$ at positive (negative) voltages is proportional to the sample surface (tip) DOS multiplied by the tip (sample surface) DOS at the Fermi level [17].

To determine the nature of these peaks, band structure calculations were performed using the Vienna Ab initio Simulation Program (VASP) [18,19]. An eight layer slab with the experimental values for the in-plane (2.87 Å) and out-of-plane (2×1.64 Å) lattice constants were used. Furthermore, an antiferromagnetically stacking of the Mn(001) layers was assumed. Peaks are found above the Fermi level in the "minority" band of the surface DOS. To confirm that these peaks are surface states which protrude far enough into the vacuum to be detected by the STM tip, bands with the largest d_{z^2} character at $\bar{\Gamma}$ are selected [1]. These are indicated by thick lines in Fig. 3(a). Three bands are possible candidates for the experimentally observed empty state $(dI/dV)/T$ peak: band α at 0.27 eV, β at 0.50 eV, and γ at 0.87 eV above the Fermi level. A plot of the surface charge density distribution of these three bands shows that the last one has a stronger decay into the vacuum (not shown in Fig. 3). The first two show surface-state-like behavior and their charge densities are plotted in Figs. 3(b) and 3(c). Opposed to the minority band, no surface states were found above the Fermi level for the "majority" band. The width of the $+0.8$ V peak in $(dI/dV)/T$ is about 1 V (Fig. 2). This width is larger than the peak width obtained on Fe(001) (0.13 eV) [1] and Cr(001) (0.2 eV at RT and 0.015 eV at 4.2 K) [2,3]. One reason is that the $+0.8$ V peak in $(dI/dV)/T$ is caused by two surface states: α and β. The difference between the calculated peak energies and the experimental peak energy is attributed to the limitations of our VASP calculations. Nevertheless, based upon the symmetry of the calculated α and β states, these states must be the origin of the experimentally obtained $+0.8$ V peak. Below the Fermi level a weak d_{z^2} state is found at -0.37 eV in the majority band: its charge density does not show a strong vacuum contribution. Nevertheless, since the weak peak around -0.5 V in the $(dI/dV)/T$ curve is reproducibly observed with various tips, we think it is a real feature of the Mn(001) electronic structure.

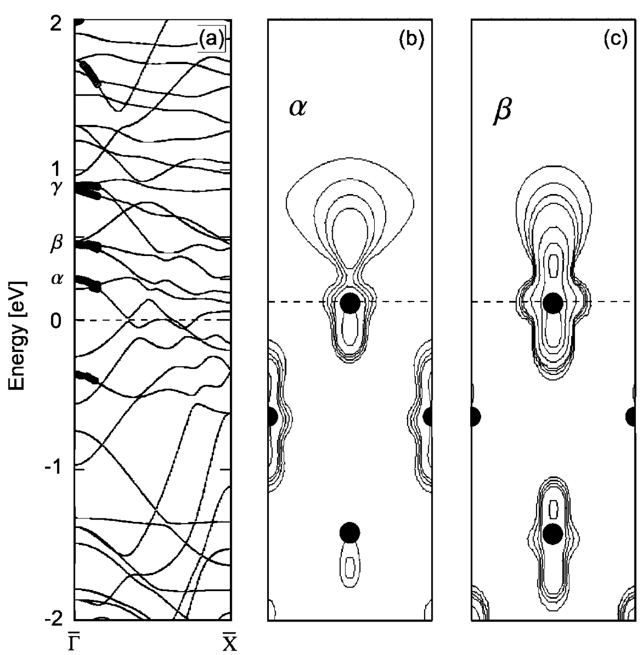

FIG. 3. (a) Band structure of an eight-layer Mn(001) slab. The plot shows both "majority" and "minority" bands, which are equivalent for this even-layered antiferromagnetically ordered slab. The magnetization for each layer is defined by the difference in integrated local DOS of the "majority" and "minority" bands. Thick lines indicate d_{z^2}-like states around $\bar{\Gamma}$, and the dashed line the Fermi level. α, β, and γ could contribute to the experimentally observed $+0.8$ V peak. (b),(c) The isocharge density distributions of the α and the β states at $\bar{\Gamma}$ in a (110) plane. Dots and dashed lines indicate atom positions and the boundary between vacuum and bulk, respectively.

Various methods for extracting the sample polarization from SP-STS were reported [9,20]. However, these methods include a certain ambiguity. For example, when extracting the sample polarization from the SP-STS results one encounters the problem that for a given set point voltage the tip-sample distance (and so the tunneling probability) is different for the even and odd Mn layers. This is due to the SP part of the tunnel current which has different bias voltage dependencies for even and odd layers. Figures 4(a) and 4(b) show dI/dV curves measured on the even and the odd layers (>3 ML) at negative- ($V_S = -0.5$ V) and positive-voltage set point ($V_S = +0.5$ V). The dI/dV curves measured at the positive-voltage set point are clearly different from the ones measured at the negative-voltage set point. Figure 4(c) shows the asymmetry in the dI/dV curves of Figs. 4(a) and 4(b), which is defined as $A_{dI/dV} = [(dI/dV)_{\mathrm{even}} - (dI/dV)_{\mathrm{odd}}]/[(dI/dV)_{\mathrm{even}} + (dI/dV)_{\mathrm{odd}}]$, where $(dI/dV)_{\mathrm{even}}$ and $(dI/dV)_{\mathrm{odd}}$ are dI/dV curves obtained on the even and the odd layers. The asymmetry strongly depends on the voltage set point, whereas it does not depend on the current set point in the range between 0.1 and 1 nA. Strictly speaking, a definition of the asymmetry in terms of dI/dV curves is valid only for low bias voltages where the effects of an increasing background are negligible [21]. The $(dI/dV)/(I/V)$ normalization which was used by Okuno *et al.* [20] cannot exclude the exponential background completely [16] and $(dI/dV)/(I/V)$ is by definition 1 at 0 V, which might influence the asymmetry. On the contrary, the asymmetry ($A_{(dI/dV)/T}$) obtained from the normalized $(dI/dV)/T$ curves does not depend on set points and tips, at least at positive voltages [Fig. 4(d)]. $A_{(dI/dV)/T}$ gives at positive voltages the sample polarization multiplied by the tip polarization at the Fermi level. The asymmetries in Fig. 4(d) are obtained from $(dI/dV)/T$ curves which show a clear spin-dependent peak. The three curves in Fig. 4(d) are similar at positive voltages (+ 10%). The influence of the fitting parameters on the asymmetry can be observed from the error bars in Fig. 4(d). If we assume that the surface states have a 100% polarization and that the tip and sample magnetization are perfectly (anti)parallel, we find a minimum Fermi level tip polarization of 10% which is in agreement with previous results [2]. $A_{(dI/dV)/T}$'s larger than 10% were never observed which makes it likely that the magnetization directions are indeed parallel. Using this tip polarization, the black solid line in Fig. 4(d) is obtained from the calculated spin-dependent sample total states. $A_{(dI/dV)/T}$ has some advantages compared to $A_{dI/dV}$ and $A_{(dI/dV)/(I/V)}$ as used in

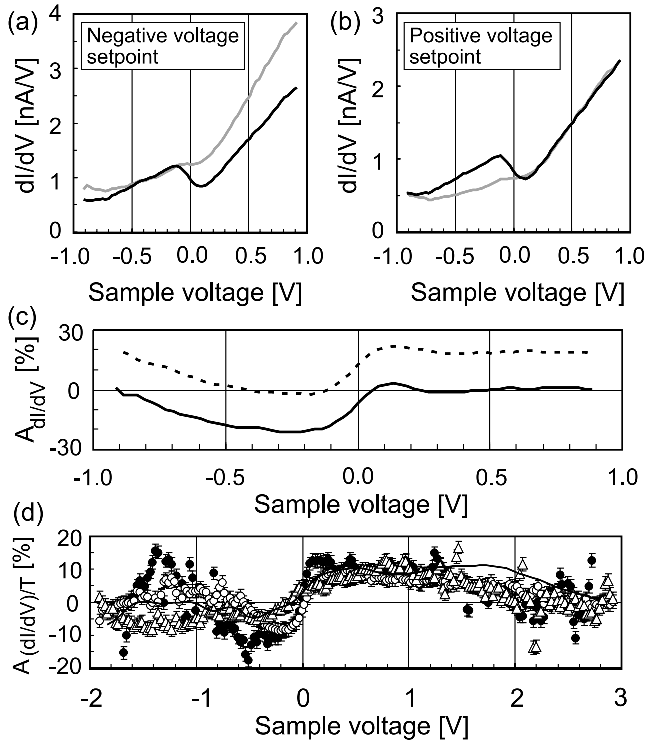

FIG. 4. (a),(b) SP-STS measurements representative of the even (grey curve) and the odd layers (black curve) (>3 ML) at negative- ($V_S = -0.5$ V, $I = 0.5$ nA) and positive-voltage set points ($V_S = +0.5$ V, $I = 0.5$ nA), respectively. (c) The asymmetry in the dI/dV curves. Dotted and solid curves are obtained from (a) and (b), respectively. (d) The asymmetry in the normalized even and odd layer $(dI/dV)/T$ curves with respect to the sample bias voltage. Open circles and triangles were obtained with the same Fe-coated tip using negative and positive voltage set points, respectively. Solid dots were obtained with a different Fe-coated tip ($V_S = -0.5$ V). The black solid curve is obtained from the calculated spin-dependent DOS.

Refs. [9,20]: (1) The exponential background is completely removed. (2) $A_{(dI/dV)/T}$ above the Fermi energy is independent of set points. $A_{(dI/dV)/T}$ obtained at positive and negative set points are shown as open circles and triangles in Fig. 4(d), respectively. (3) Reproducible $A_{(dI/dV)/T}$ values are observed with different Fe-coated tips at the positive-voltage side [Fig. 4(d)]. Scattering of $A_{(dI/dV)/T}$ at the negative-voltage side may be a contribution of the tip DOS [16].

We reported the observation of a magnetic contrast in the dI/dV maps obtained with Fe-coated tips on Mn layers grown on an Fe(001) whisker at 370 K. This contrast was not observed with clean W tips. Therefore, our results give strong evidence that the Mn(001) sheets couple antiferromagnetically even on a nanometer scale. By normalizing the dI/dV curves by the tunneling probability function, we found a spin-polarized peak at +0.8 V on the artificial bct Mn(001) layers. Our band structure calculations confirmed that this peak is possibly related to two spin-polarized d_{z^2} surface states. The asymmetries of the $(dI/dV)/T$ curves are independent of the voltage set points and tips.

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[1] J. A. Stroscio *et al.*, Phys. Rev. Lett. **75**, 2960 (1995).
[2] M. Kleiber *et al.*, Phys. Rev. Lett. **85**, 4606 (2000).
[3] O. Yu. Kolesnychenko *et al.*, Nature (London) **415**, 507 (2002).
[4] B. Heinrich *et al.*, J. Vac. Sci. Technol. A **5**, 1935 (1987).
[5] V. L. Moruzzi and P. M. Marcus, Solid State Commun. **71**, 203 (1989).
[6] S. Andrieu *et al.*, Phys. Rev. B **57**, 1985 (1998).
[7] T. K. Yamada *et al.*, Surf. Sci. **516**, 179 (2002).
[8] D. A. Tulchinsky *et al.*, J. Magn. Magn. Mater. **212**, 91 (2000).
[9] R. Wiesendanger and M. Bode, Solid State Commun. **119**, 341 (2001).
[10] M. M. J. Bischoff *et al.*, Surf. Sci. **501**, 155 (2002).
[11] A tip with a radius > 300 nm was prepared by annealing at 1500 K. The radius of the tip was estimated by field emission spectroscopy.
[12] In order to reshape or clean the tip voltage pulses (± 10 V) were applied between the tip and the sample in our previous results [10]. These pulses likely lead to mass transport from the sample to the tip [13].
[13] T. K. Yamada *et al.*, Appl. Phys. Lett. (to be published).
[14] Using the single step height of bcc-Fe(001) which is 0.143 nm, the apparent step heights of our STM measurements were calibrated. Step heights were measured at large negative bias voltages to exclude electronic effects [7].
[15] T. G. Walker and H. Hopster, Phys. Rev. B **48**, 3563 (1993).
[16] V. A. Ukraintsev, Phys. Rev. B **53**, 11 176 (1996).
[17] The different amplitudes of the $(dI/dV)/T$ curve in Fig. 2(a) and the average of the even and odd $(dI/dV)/T$ curves in Fig. 2(b) are related to the different Fermi level DOS of the Fe-coated tip and the W tip.
[18] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994).
[19] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[20] S. N. Okuno *et al.*, Phys. Rev. Lett. **88**, 066803 (2002).
[21] S. Heinze, Ph.D. thesis, University of Hamburg, 2000.