## Reduction of the Ni(110) surface spin- and orbital-magnetic moment by a $c(2 \times 2)$ S overlayer

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The modification of the room-temperature surface magnetic moment of Ni(110) by a  $c(2 \times 2)$ S overlayer has been investigated using spin-polarized inverse photoemission (SPIPE) and magnetic circular dichroism (MCD) in core-level photoemission. SPIPE measurements, which are mostly sensitive to the spin contribution, indicate a reduction of the spin polarization to  $(44 \pm 19)$ % of the clean surface value. The MCD, which is mostly sensitive to the orbital moment, is reduced to  $(25 \pm 3)$ %. This apparent difference in the sensitivity to the S overlayer can in part be explained by considering the different sampling depths of the two techniques. The results provide support for theoretical predictions that the clean surface magnetic moment of Ni(110), in both the spin and orbital contributions, is enhanced compared to the bulk.

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Magnetic thin films, surfaces, and multilayers of transition metals have attracted much interest due to theoretical predictions<sup>1</sup> and experimental evidence<sup>2</sup> of strongly enhanced magnetic moments at their surfaces and interfaces. The enhanced magnetic moments tend to be modified by adsorbates, and there have been a number of studies that have investigated this phenomenon.<sup>3–9</sup> In some cases it has been possible to relate this to adsorbate-induced changes to the electronic structure.<sup>7,8</sup> For nickel surfaces, attention has focused on the effects of oxygen<sup>3–6,8</sup> and sulfur<sup>6,8,9</sup> adsorption. Ni(110)(2×1)O photoemission data indicate that the overlayer has a spin polarization parallel to that of the substrate.<sup>5</sup>

Bonding of S to Ni is expected to be more covalent than that of O to Ni on electronegativity grounds. This increased covalency should result in a greater reduction of the substrate surface magnetic moment, and indeed spin-polarized inverse photoemission (SPIPE) results for Ni(110) $c(2 \times 2)$ S,<sup>8,9</sup> compared to those for Ni(110)(2×1)O, <sup>10</sup> seem consistent with this picture. This earlier S adsorption work investigated the behavior of two S-induced features in SPIPE data recorded in the  $\overline{\Gamma X}$  azimuth.<sup>8</sup> One exhibits characteristics of adsorbate-induced umklapp processes involving a bulk electron band with an exchange splitting of  $240 \pm 30$  meV, while the other has an exchange splitting of  $85 \pm 20$  meV. The latter shows dispersion with  $\mathbf{k}_{\parallel}$  leading to its assignment to transitions into hybridized Ni-S electronic states. This result also suggests a strong adsorbate-substrate magnetic coupling.<sup>8</sup> In addition to the sulfur-induced states, an imagepotential state was observed which has an exchange splitting of  $32 \pm 13 \text{ meV.}^9$ 

Many magnetic circular dichroism (MCD) measurements have been carried out on Ni, although these have usually been in x-ray absorption mode.<sup>11–13</sup> There have, however, been measurements of Ni(110) using magnetic linear dichroism angular distribution<sup>14</sup> and MCD in photoemission.<sup>2</sup> The latter study focused on a comparison between experimental results and theoretical calculations for the clean surface.

Here we examine the effect of a  $c(2 \times 2)$ S overlayer on the surface magnetic moment of Ni(110) using SPIPE measurements in the  $\Gamma Y$  azimuth, and MCD. Since SPIPE is mostly sensitive to the spin contribution and MCD is mostly sensitive to the orbital moment,<sup>2</sup> these are largely measured separately using the two techniques. A reduction of the MCD to about 25% of the clean surface value is observed on forming the  $c(2\times 2)$ S overlayer, while the asymmetry in the SPIPE data is reduced to around 44% of the clean surface value.

The SPIPE measurements employed an apparatus,<sup>15,16</sup> geometry, and methodology,<sup>17,18</sup> that are described in detail elsewhere. Briefly, spin-polarized electrons are generated by photoemission from a negative-electron-affinity GaAs(100) photocathode at room temperature, with the electron spin being selected by the helicity of circularly polarized irradiation. Measurements were made at room temperature in the isochromat mode, with emitted photons being counted by a solid-state bandpass detector.<sup>16</sup> This has a detection energy centered at 9.8 eV and a resolution of 0.73 eV full width at half maximum (FWHM). Figure 1 shows the experimental geometry employed for SPIPE measurements.

The MCD photoemission experiments were carried out on beamline 4.1 at the SRS, Daresbury Laboratory. Circularly polarized light ( $h\nu = 150 \text{ eV}$ ) was selected using an aperture



FIG. 1. Experimental geometry used for the SPIPE measurements, showing the Ni picture frame and magnetizing coil. A normal-incidence geometry was employed (i.e.,  $\theta = 0^\circ$ ). The direction of magnetization *M* is indicated.

in the beamline,<sup>19</sup> which was modified to allow through only the top 12% of the beam. An angle of incidence of 40° was employed, with photoemission detected at normal emission using a Scienta 200 SES electron energy analyzer. The MCD difference spectrum was obtained from a spectrum recorded with magnetization along  $[1\bar{1}1]$  and a spectrum with the magnetization vector reversed. The position of the Fermi level was recorded immediately after each scan to act as an energy reference. For two consecutive scans the shift was typically  $\leq 0.02$  eV.

Experiments were carried out using a picture frame Ni(110) single crystal, on which repeated cycles of 500 eV  $Ar^+$  sputtering and annealing to 975 K were employed to obtain a clean and structurally ordered surface. Magneto-optic Kerr effect measurements were performed *in situ* to ensure that the sample stayed magnetically saturated in remanence during data acquisition and to confirm that the magnetization direction could be reversed. The Ni sample was magnetized by passing a short pulse (approx. 1 ms) of around 400 A through a coil that encircled one of the legs of the picture frame. The order and cleanliness of the sample were confirmed using low-energy electron diffraction (LEED) and Auger electron spectroscopy.

An exposure of about 4 L at  $1 \times 10^{-8}$  mbar H<sub>2</sub>S was used to form the  $c(2\times 2)$ S overlayer with subsequent heating to 400 K in order to remove residual hydrogen. LEED was employed to monitor the  $c(2\times 2)$ S overlayer growth during H<sub>2</sub>S exposure.

Figure 2(a) shows normal-incidence SPIPE data from both clean Ni(110) and Ni(110) $c(2 \times 2)$ S. There is only one detectable feature in the clean Ni(110) data, labeled  $B_1$ .  $B_1$ arises from transitions into empty 3d bulk bands.<sup>17</sup> These observed bands lie just above the Fermi level, and are only seen in the minority-spin channel. The  $B_1$  feature is also observed in the Ni(110) $c(2 \times 2)$ S data, but here it is substantially reduced. This is consistent with a downward shift of the minority-spin band so that more states become occupied, which consequently leads to a reduction in the magnetic moment. Additional features are observed on forming the c(2) $\times 2$ )S overlayer, denoted A and I in Fig. 2(a). A is an adsorbate-induced feature, which originates predominantly from the topmost layer according to one-step calculations performed using a layer Korringa-Kohn-Rostoker method,<sup>20</sup> and I is an adsorbate-enhanced image-potential state.<sup>8,9</sup> The image-potential state I appears at 4.6 eV above the Fermi level, and has maximum intensity in the normal-incidence scans. A and I do not occur near the Fermi level and hence do not contribute to the magnetic moment.

The spin polarization of the SPIPE spectra is shown in Fig. 2(b). In addition to the spin polarization of  $B_1$  there is also a substantial spin polarization of the inelastic background. It is widely accepted that this arises in Ni(110) SPIPE due to an extreme spin asymmetry in the density of states (DOS) just above the Fermi level ( $E_F$ ), as these energy levels serve as the final states for inelastic SPIPE processes.<sup>10,21</sup> Since the inverse photoemission signal is sensitive only to the uppermost layers of the sample this provides evidence of a strong surface magnetic moment.



FIG. 2. (a) SPIPE normal-incidence spectra  $(h\nu=9.8 \text{ eV})$  of clean Ni(110) and the Ni(110) $c(2\times2)$ S spectra at room temperature. Open (closed) circles refer to the data recorded with minority-(majority-) spin electrons. The lines between points represent a function fitted to the data. (b) The asymmetry of the spectra and fitted functions in (a). The asymmetry is defined as  $(I_{\uparrow}-I_{\downarrow})/(I_{\uparrow}+I_{\downarrow})$ , where  $I_{\uparrow}(I_{\downarrow})$  are the intensities of emitted photons, normalized for an equivalent 100% polarized beam, from electrons parallel (antiparallel) to the  $[1\overline{10}]$  direction, while also accounting for the 35.3° angle between this direction and the  $[1\overline{11}]$  magnetization direction (Ref. 12).

The background spin asymmetry decreases to about half its clean surface value on forming the  $c(2\times 2)S$  overlayer. This is caused by a reduction in the spin asymmetry in the DOS just above  $E_F$  that evidences a decrease in the surface magnetic moment. Further evidence of the reduced surface magnetic moment is obtained from the comparison between the overall spin polarization for the clean surface and the  $c(2\times 2)S$  overlayer. This was estimated by integrating the normalized spin asymmetries over the full energy range in Fig. 2(b) so as to account for both direct transitions and transitions involving inelastic scattering processes. The values obtained indicate a reduction to  $(44\pm 19)\%$  of the clean surface value by formation of the  $c(2\times 2)$  overlayer, the error being derived simply from the statistical uncertainty.

Figure 3 shows the MCD as measured by Ni 3p photoemission from clean Ni(110) and Ni(110) $c(2 \times 2)$ S. There is clearly a large dichroism from Ni(110), which evidences a strongly enhanced orbital moment at the surface.<sup>2</sup> It is now widely accepted that the surface magnetic moment will be larger than that in the bulk because of the reduction in neighboring atoms, the 3d band narrowing, and the enforced up-



FIG. 3. (a) Ni 3*p* photoemission spectra ( $h\nu = 150 \text{ eV}$ ) at normal emission of clean Ni(110) and Ni(110) $c(2 \times 2)$ S. The spectra were first normalized to the photon flux and secondly to background intensity. Filled (empty) triangles refer to data recorded with the projected light helicity antiparallel (parallel) to the  $[1\overline{1}1]$  magnetization direction. (b) The magnetic circular dichroism  $I^- - I^+$  of the spectra in (a). The dichroism spectra have been expanded for clarity, and are displayed with the same arbitrary units as in (a).

ward electrostatic shift which serves to maintain charge neutrality.<sup>2,22</sup> The dichroism in Fig. 3(b) is shown as  $I^ -I^+$ , which at its maximum is about 12% of the photoemission peak height. If the different experimental geometries employed here and in the work by van der Laan *et al.*<sup>2</sup> are accounted for, then agreement is found within the errors of both experiments.

The  $c(2 \times 2)$ S overlayer causes the Ni 3*p* MCD to decrease to  $(25\pm3)$ % of the clean surface value, where again the error is derived from the statistical uncertainty. The implication of this change is, again, that the surface magnetic moment is reduced. This reduction, which is in line with that obtained from the SPIPE data, can be explained by considering the interaction of the S orbitals with Ni orbitals at the Ni(110) surface. To do so, we draw an analogy with the picture for O on Ni(110) derived from electronic structure calculations. These point to a decrease in the occupancy of minority-spin states and an increase in the occupancy of minority-spin states associated with Ni atoms bound to O. This arises from hybridization of Ni 3*d* and O 2*p* states, and results in a local decrease in the magnetic moment.<sup>23</sup>

The apparent discrepancy between the adlayer-induced reductions in surface magnetic moment derived from MCD and SPIPE can at least in part be ascribed to a difference in their sampling depths. In the MCD experiment, which monitors approximately 80 eV electrons, the mean free path (MFP) is about 5 Å.<sup>24</sup> In contrast the MFP is about 10 Å for the approximately 10 eV electrons used in the SPIPE experiments.<sup>24</sup> Since the magnetic moment is expected to be enhanced at the clean surface,<sup>1</sup> MCD data should reflect a greater adsorbate-induced reduction in the magnetic moment than that derived from the SPIPE results.

Our results support a strong surface enhancement of the magnetic moment, since the overlayer-induced reduction is too large to be explained in its absence. Take the MCD results, for instance; even if it is assumed that the overlayer completely removes the magnetic moment of the top two layers, the MCD would only be reduced to 65% of the clean surface value in the absence of an enhanced clean surface magnetic moment. A 65% value is obtained by assuming an equal but MFP-weighed contribution to the MCD signal from each of the top 10 Ni layers of the clean surface. By analogy, under the same conditions we would expect a reduction of the SPIPE spin asymmetry to 75% of the clean surface value.

A clean surface enhancement is consistent with calculations for Ni(110) that predict an enhancement of 60% for the orbital moment and 26% for the spin moment.<sup>25</sup> However, a much larger clean surface enhancement is necessary to explain an overlayer-induced reduction of the MCD to 25% and the SPIPE polarization to 44% of the clean surface values. For instance, if again we take ten contributing layers, nine with the bulk moment and the surface layer moment increased by 100%, four or more magnetically dead layers would be required at the adsorbate-covered surface to account for the observed decrease in the spin and orbital moments. This seems unlikely in light of calculations for CO on Ni(110) which suggest that only the moments in the top layer are affected by the adsorbate.<sup>26</sup> The corollary is that the clean surface spin and orbital moments must be enhanced by several hundred percent to explain our observations. Any overlayer-induced antiferromagnetic coupling mechanism to reduce the surface moment can be ruled out by the observation of an unoccupied adsorbate-induced state which is exchange split with the same sign as the substrate.<sup>8</sup>

In principle, the surface sampling depth could be investigated further by varying the incidence and emission angles. However, in SPIPE this is not straightforward because additional exchange-split *s*-*p*-like states contribute to the Ni(110) spectra for electron incidence angles off normal.<sup>17</sup> These exhibit a small contribution to the magnetic moment near the *L* point of the Brillouin zone but are not detected for normal incidence on Ni(110).<sup>17</sup> As for MCD, the response depends critically on the experimental geometry.<sup>2</sup> For these reasons we limited the experiment to the simplest geometry with normal electron incidence and emission, respectively.

Although the difference between the SPIPE and MCD results could be explained qualitatively on the basis of sampling depth, three other factors should be considered in a complete analysis. The first is the SPIPE and MCD sensitivity to spin and orbital moments discussed above. The second is the effect of photoelectron diffraction on the MCD data. This will arise from a change in the angular distribution occasioned by the  $c(2 \times 2)$ S overlayer, but is unlikely to be significant because of the relatively large acceptance angle  $(\pm 8^{\circ})$  of the analyzer. However, calculations of the radial

cross section for Fe 3p, which should be almost identical to that of Ni 3p, show that at a kinetic energy of 80 eV the emission to the *s* and *d* continua is very similar.<sup>27</sup> This results in the two contributions partially canceling and could therefore lead to enhancement of any anomalies due to photoelectron diffraction. The third factor to be considered in a full analysis is electron localization associated with surface roughness, steps, and other defects. This can also contribute to a strongly enhanced clean surface magnetic moment.<sup>28</sup>

In summary, we have shown using two techniques, SPIPE and MCD, that the surface magnetic moment of Ni(110) is strongly reduced by a  $c(2 \times 2)$ S overlayer. This reduction is apparent in both the spin and orbital contributions. SPIPE measurements, which are mostly sensitive to the spin contribution, indicate a reduction of the spin polarization to (44  $\pm$ 19)% of the clean surface value, while the MCD, which

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measures primarily the orbital moment, is reduced to  $(25 \pm 3)\%$ . This difference between these results can in part be ascribed to the different sampling depths of the two techniques. Nevertheless, both techniques indicate an enhancement of the magnetic moment at the clean surface compared to the bulk, consistent with the predictions of local spin density functional calculations. Moreover, the extent to which this enhancement is observed supports the suggestion that there is a large orbital contribution to the clean surface magnetic moment as well as a strongly enhanced spin moment. Our observations can only be explained if both the spin and orbital moments are enhanced by several hundred percent at the clean Ni(110) surface.

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