X-ray resonant magnetic scattering from surfaces

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We show that the magnetic structure of surfaces can be successfully investigated by combining x-ray surface diffraction and x-ray resonant exchange scattering. The resonant x-ray surface diffraction spectra of linearly polarized radiation are shown to be sensitive to the magnitude and direction of the surface magnetic moments by explicit calculations for different magnetic structures of the (001) surface of antiferromagnetic UAs and of the (0001) surface of ferromagnetic Gd.

I. INTRODUCTION

The magnetic properties of surfaces and thin films are of great technological interest; more fundamentally, the determination of their magnetic behavior is of importance for testing the predictions of model systems. Several experimental observations,[1-3] making use of electrons as a probe, have detected surface magnetic order and critical behavior different from the bulk, as suggested by theoretical models.[4]

In this paper, we show that surface magnetism can be successfully investigated using polarized x rays; the method we propose combines two techniques, each well established in its own domain: x-ray resonant exchange scattering[5-8] (XRES) and x-ray surface diffraction.[9-11]

Besides determining long-range magnetic ordered structures, resonant x-ray surface diffraction can provide information about the relative magnitude and direction of the surface and bulk magnetic moments; moreover, contrary to electronic probes, it allows the use of an external magnetic field to align magnetic domains. The only limitation of the technique is that the transitions associated with XRES must correspond to photon wavelengths suitable for diffraction while fulfilling the selection rules and the requirement of a spin-orbit split core level. Among the materials of interest for magnetism, only the $3d$ transition metals do not meet this condition.

We present detailed calculations for two paradigm cases: the (001) cleavage surface of antiferromagnetic (AF) UAs and the (0001) surface of ferromagnetic (FM) Gd. In these systems, bulk magnetic properties have been studied experimentally and theoretically using XRES (Refs. 8 and 12) and circular dichroism.[13,14] In addition, for Gd(0001), spin-polarized low-energy electron diffraction (SPLEED) (Ref. 1) and electron capture spectroscopy[2] indicate a surface critical temperature higher than that of the bulk. These experiments have also revealed other puzzling features, tentatively attributed to enhanced surface magnetic moments and to surface moments antiparallel to bulk ones. Our results show that the latter case could clearly be discriminated with x rays. Conversely, no studies of the UAs surfaces have been performed.

II. RESONANT MAGNETIC SCATTERING FROM SURFACES

It has recently been shown that very precise information on the surface structure and relaxation[9-11] can be obtained by the wave-vector dependence of the diffuse surface x-ray scattering, the so-called crystal truncation rods (CTR's). This method can be extended to the study of the surface magnetic structure by studying at resonance the CTR's associated to magnetic reflections. The resulting spectra are sensitive to both direction and magnitude of the surface magnetic moments. The modeling required to obtain these quantities from experiments, in analogy to structural CTR studies, is simplified by the fact that multiple scattering can be neglected (kinematical approach).

To leading order in the weakly relativistic limit,[15] the total amplitude for coherent elastic scattering of x rays is given by

$$f=-Zr_0\hat{\epsilon}_f^*\cdot\hat{\epsilon}_i+f'+if'' , \tag{1}$$

where, in the electric dipole approximation and neglecting crystal field effects,[6]

$$\begin{aligned} f'+if''=\frac{3\lambda}{8\pi}\{&[F_{11}+F_{1-1}]\hat{\epsilon}_f^*\cdot\hat{\epsilon}_i\\ &-i[F_{11}-F_{1-1}](\hat{\epsilon}_f^*\times\hat{\epsilon}_i)\cdot\hat{\mathbf{u}}\\ &+[2F_{10}-F_{11}-F_{1-1}](\hat{\epsilon}_f^*\cdot\hat{\mathbf{u}})(\hat{\epsilon}_i\cdot\hat{\mathbf{u}})\} , \end{aligned} \tag{2}$$

with, at $T=0$,

$$F_{L,M}(k)=\frac{4}{\lambda}\frac{L+1}{L}\frac{e^2k^{2L}}{[(2L+1)!!]^2}\times\sum_{\alpha'J'M'}\frac{\left|\left\langle\alpha'J'M'\left|\sum_j r_j^L Y_{L,M}(\hat{\mathbf{r}}_j)\right|\alpha JM\right\rangle\right|^2}{E_{\alpha'J'M'}-E_{\alpha JM}-\hbar\omega+i\Gamma/2} .$$

$\hat{\epsilon}_i$ and $\hat{\epsilon}_f$ represent, respectively, the ingoing and outgoing photon polarization, $\hat{\mathbf{u}}$ denotes the (local) quantization axis of a given ion, and j runs over all electrons. In what follows, $\hat{\epsilon}_\pi$ and $\hat{\epsilon}_\sigma$ represent the linear polarizations in the plane of scattering and perpendicular to it, respectively, with $\hat{\epsilon}_\pi = \hat{k} \times \hat{\epsilon}_\sigma$.

The quantities $F_{1,M}$ have appreciable value only near an absorption edge. The shape of the spectra is determined by the (virtual) transitions between the ground state $|\alpha JM\rangle$, with $M=-J$, and the excited state $|\alpha' J' M'\rangle$, under the dipolar selection rules $\Delta J = 0, \pm 1$. In magnetic systems, the $\hat{\mathbf{u}}$-dependent resonant processes yield the XRES reflections. When magnetic and charge reflections overlap, the magnetic contribution is singled out by measuring the asymmetry ratio[7] $(I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)$.

For a semi-infinite crystal, the cross section per unit in-plane cell is proportional to[10]

$$I(\mathbf{Q}) = \left| \sum_{l=0}^{-\infty} e^{-iq_z la} \sum_m e^{-i\mathbf{Q}\cdot\tau_m} f_{l,m} \right|^2 , \tag{3}$$

where $\mathbf{Q} = (\mathbf{q}_\parallel, q_z) = \mathbf{k}_f - \mathbf{k}_i$ is the scattering wave vector, l labels the unit cell of length a in the z direction orthogonal to the surface, m runs over the atoms in the unit cell; f is also l dependent as the magnetization may change in proximity to the surface. A finite x-ray penetration depth μ is taken into account by writing $q_z = q_z + i/\mu$, μ being estimated from the absorption spectra. We impose Laue conditions on the in-plane transferred momentum $\mathbf{q}_\parallel = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2$, with $\mathbf{b}_1$ and $\mathbf{b}_2$ the two-dimensional reciprocal lattice vectors. For each reflection (m_1, m_2), the dependence of the scattered intensity on q_z, the scattered wave vector perpendicular to the surface, yields the associated CTR. For a single monolayer the CTR's are featureless, whereas for a semi-infinite ideal crystal the intensity peaks at values of q_z satisfying bulk Laue conditions, and decays as $\sin(q_z a)^{-2}$.[10] For a semi-infinite crystal with nonideal truncation, the decay of the CTR's away from bulk Bragg peaks depends on the interference between surface and bulk contributions. The interpretation in terms of kinematical diffraction theory of the CTR's shape leads to a very precise determination of the surface structure in relation to the underlying bulk.[10,11] This method can be extended to the study of the surface magnetic structure by considering the magnetic reflections as a function of q_z, with linearly polarized light at resonance (XRES CTR's). The shape of the XRES CTR's is sensitive to the differences in the magnetic properties of bulk and surface. Here we limit ourselves to consider the magnetic effects and therefore, in the following, we will consider surfaces with ideal crystalline structure but either the same or a different magnetic structure than the bulk. In favorable cases, the resulting XRES diffracted intensities are only two orders of magnitude weaker than those due to charge scattering and are therefore observable. However, care has to be taken in surface preparation since it has been shown[16] that surface disorder can further reduce the scattered intensity up to 2–3 orders of magnitude.

III. DISCUSSION OF SELECTED EXAMPLES

First, we consider an AF material. We distinguish two cases. (i) Only the in-plane unit cell is modified by the AF order, while the magnetic and charge periodicity coincide in the z direction. In this case, by analogy with structural surface reconstructions, new values (m_1, m_2) become allowed (due to the larger magnetic unit cell in real space) and the effect of the surface on the associated CTR's is readily identified. (ii) The AF order changes the unit cell perpendicular to the surface. In this case, new bulk magnetic reflections appear along the CTR's masking the effect of the surface.

Let us now specify to UAs. The AF type-I phase of UAs ($T_N = 127$ K) has alternating FM sheets along one of the (100) directions;[8] therefore three types of domain may be present. A magnetic field, applied along the z direction, can suppress the domain with magnetization along z. We take the Fourier component of the magnetization to be either (1, 0, 0) with moments along (100) or (0, 1, 0) with moments along (010). This corresponds to a doubling of the in-plane unit cell due to magnetic moments antiferromagnetically aligned along either the x or the y direction. The z direction is unaffected.

We calculate $I(\mathbf{Q})$ at the M_4 edge of U^{3+} ($E = 3728$ eV, $\lambda = 3.3$ Å). The $F_{1M}(k)$ matrix elements are obtained using Cowan's Hartree-Fock (HF) and multiplet programs (with relativistic corrections).[17] The calculation is performed in intermediate coupling, considering transitions from the $5f^2$ configuration lowest state to the full $3d^9 5f^3$ multiplet. The electrostatic and exchange parameters are scaled down to 80% of their HF values[18] and a $\Gamma = 4$ eV core-hole width is assumed. The magnetic resonance, associated with the $F_{11} - F_{1-1}$ term, is essentially Lorentzian with a peak value of $\sim 10 r_0$. We use a penetration length $\mu = 1.1 \times 10^{-4}$ cm for β greater than the critical angle $\beta_c = 0.79°$ and $\mu = \lambda / [2\pi(\beta_c^2 - \beta^2)^{1/2}]$ otherwise.

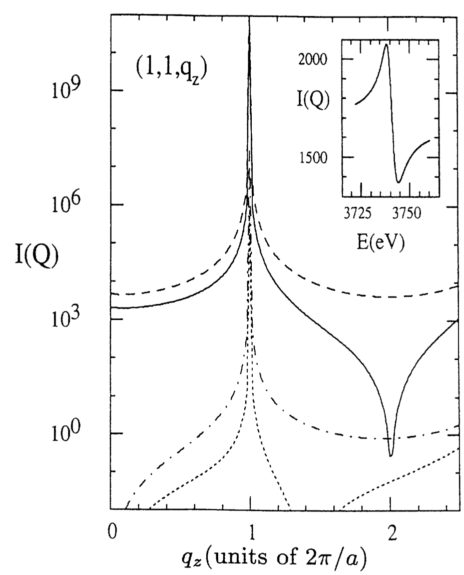

FIG. 1. $(1,1,q_z)$ charge CTR's for UAs(001) at $E = 3738$ eV, where the intensity at resonance is highest. Solid line: $I_{\pi\to\pi}$; dashed line: $I_{\sigma\to\sigma}$; dotted line: $I_{\sigma\to\pi}$; dot-dashed line: $I_{\pi\to\sigma}$. Inset: $I_{\pi\to\pi}$ vs E at $q_z = 0$.

Since we have no *a priori* knowledge of either the magnitude or the direction of the magnetic moments at the surface, we have calculated the scattered intensity for several directions and magnitudes of the surface moments.

In Fig. 1 we show the CTR's associated with the charge $(1,1,q_z)$ reflection for incoming and outgoing σ and π polarizations. The calculated spectrum, dominated by charge scattering, is the same for the two magnetic domains. The Laue conditions on $\mathbf{q}_{\parallel}$, at $q_z=0$, correspond to an angle $2\theta=48°$ between incoming and outgoing photons and a zero incidence angle β. To match the Laue conditions, while changing β and scanning the q_z component at the fixed frequency of the resonance, the angle 2θ has to be varied. At $q_z=2.5(2\pi/a)$, $\beta=46°$ and $2\theta=111°$. In particular, $2\theta\sim90°$ for $q_z\sim2(2\pi/a)$, whence the dip in the intensity for the $\pi\rightarrow\pi$ channel. Following Ref. 10 we estimate the count rates at $q_z=0$ to be $\sim10^6$ photons $\sec^{-1}$ if we assume an incident intensity of 6×10^{11} photons $\sec^{-1}\,\mathrm{mm}^{-2}$. Notice that at $q_z=0$ we are away from bulk Bragg peaks and that the intensity at this point is comparable with that of a single monolayer.[10] The intensities of magnetic reflections we show next are about 2 orders of magnitude weaker, so that the experiment we propose should remain feasible.

The CTR's associated with the (charge forbidden) $(2,1,q_z)$ XRES reflection are shown in Fig. 2; only the term $(\hat{\epsilon}_f^*\times\hat{\epsilon}_i)\cdot\hat{\mathbf{u}}$ contributes to the scattered intensity. In the $\sigma\rightarrow\sigma$ channel, the intensity is identically zero, whereas in the $\pi\rightarrow\pi$ channel it is zero at $q_z=0$ and then rises rapidly. When the directions of the surface and bulk moments coincide, consider their moduli ratio γ taken with a positive (negative) sign if they are parallel (antiparallel). This quantity determines the shape of the CTR's between the Bragg peaks; notice, however, that γ and $1-\gamma$ lead to the same behavior. The shape of the CTR's is also affected when surface and bulk moments point in different directions; this case is depicted in Fig. 3. We have considered a single q bulk magnetic structure which goes over to a $2q$ magnetic structure at the surface, to account for possible surface anisotropies. This amounts to having an AF surface layer with moments along either the (110) or the $(1\bar{1}0)$ directions, on a bulk with moments along either the x or the y direction. The total scattered intensity, with a 90% π polarization of the incoming photon, is shown in Fig. 3. It is worth noticing that information on the surface is also obtained without a polarization analysis of the outgoing photon.

The intensities at the (2, 1) and $(-2,-1)$ reflections, related by $\boldsymbol{k}_i\leftrightarrow\boldsymbol{k}_f$, are not the same for polarized radiation, since the components $I_{\pi\rightarrow\sigma}$ and $I_{\sigma\rightarrow\pi}$ are interchanged. A comparison of equivalent reflections should allow a separate determination of the components of the scattered intensity.

The above analysis shows that, whenever surface and bulk moments do not coincide, anomalous profiles of the CTR's may appear. This should be the case on approaching T_N, as the critical behavior of bulk and surface is not expected to be the same.

Second, we consider a FM system. We present results for the Gd(0001) surface, at the L_2 edge ($E=7930$ eV, $\lambda=1.56$ Å). The matrix elements F_{1M} and $\mu=5.7\times10^{-4}$ cm are determined on the basis of the band-structure calculation of Ref. 14. The $F_{11}-F_{1-1}$ term contributes a peak amplitude of $\sim r_0$.

For ferromagnets, the behavior of the asymmetry ratio, as a function of q_z, yields information on the surface; to maximize it, charge scattering has to be reduced. The Laue conditions for the $(1,3,q_z=0)$ reflection imply $2\theta\sim84°$ so that the $\pi\rightarrow\pi$ charge scattering is reduced to about 1% of the $\sigma\rightarrow\sigma$ component, as shown in Fig. 4(b). The asymmetry ratio is therefore enhanced by having possibly complete π polarization.

The Gd metal does not possess an easy axis of magnetization, due to the spherical symmetry of the atomic $^8S_{7/2}$ configuration of the Gd^{3+} ion, which remains a good

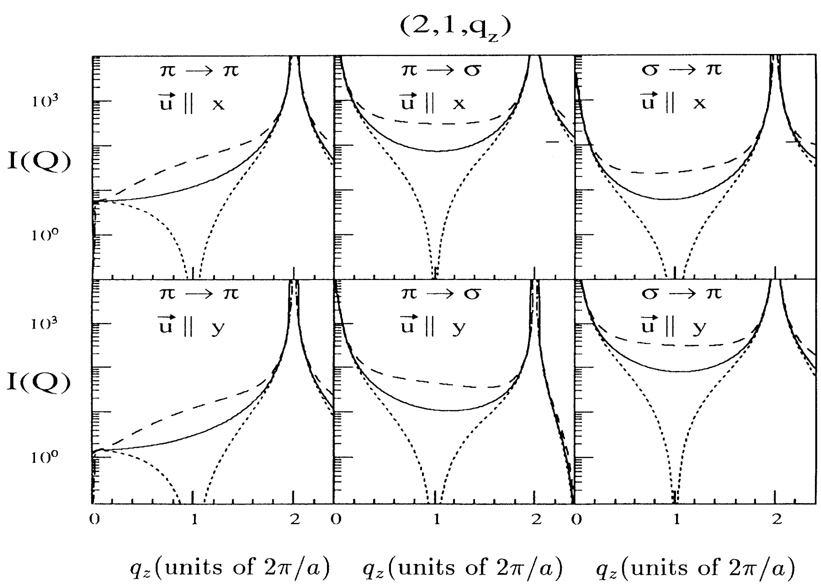

FIG. 2. $(2,1,q_z)$ magnetic CTR's of UAs(001) at $E=3741$ eV (at the maximum of the Lorentz-shaped intensity) for x (top panels) and y (bottom panels) domains and for several values of γ. Solid line: $\gamma=1$ or 0; dashed line: $\gamma=-0.5$ or 1.5; dotted line: $\gamma=0.5$.

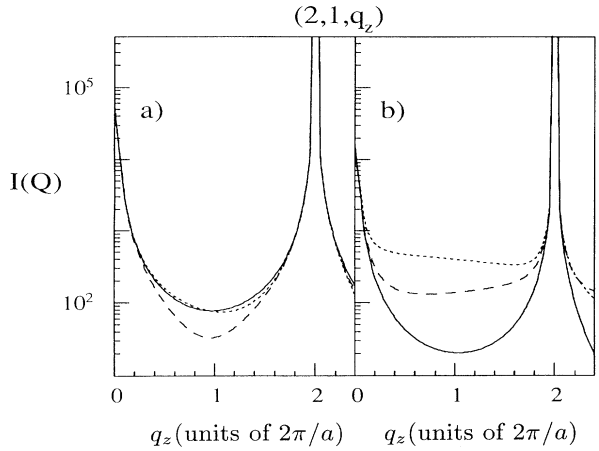

FIG. 3. $(2,1,q_z)$ magnetic CTR's of UAs(001) at $E=3741$ eV for the x (a) and y (b) domains and for several directions of the surface moments. We show the total $I(\mathbf{Q})$, for 90% π-polarized light. Solid line: $\hat{\mathbf{u}}_s=\hat{\mathbf{u}}_b$; dashed line: $\hat{\mathbf{u}}_s=(1,1,0)/\sqrt{2}$; dotted line: $\hat{\mathbf{u}}_s=(1,-1,0)/\sqrt{2}$.

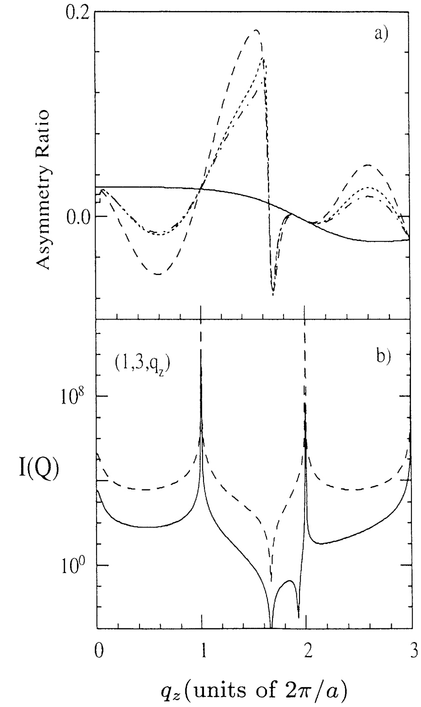

FIG. 4. (a) Asymmetry ratio $(I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)$ of the $(1,3,q_z)$ reflection of Gd(0001) at $E=7959$ eV with 98% π polarization of the incoming photon; $I_\uparrow$ is calculated with $\hat{\mathbf{u}}_b=(0,0,1)$ and $\hat{\mathbf{u}}_s$ in several possible directions and $I_\downarrow$ for all $\hat{\mathbf{u}}$'s reversed. Solid line: $\hat{\mathbf{u}}_s=\hat{\mathbf{u}}_b$; dashed line: $\hat{\mathbf{u}}_s=-\hat{\mathbf{u}}_b$; dotted line: $\hat{\mathbf{u}}_s=(0.866,0.5,0)$ (b axis); dot-dashed line: $\hat{\mathbf{u}}_s=(1,0,0)$ (a axis). (b) Thomson charge scattering for the $(1,3,q_z)$ reflection of Gd(0001). Solid line: $I_{\pi\to\pi}$; dashed line: $I_{\sigma\to\sigma}$.

description also in the metal. We take advantage of this fact and present results obtained with the magnetization along the z direction, to maximize the XRES contribution at grazing incidence.

The calculated asymmetry ratios, for different orientations of the surface moments, are shown in Fig. 4(a). It can be seen that the curves clearly discriminate between surface moments which are parallel or antiparallel to those in the bulk. Furthermore, if the moments are not all aligned along z, sensitivity to those surface moments lying in the surface plane is brought about by the asymmetry between $I_{\pi\to\sigma}$ and $I_{\sigma\to\pi}$. We notice that the sign of the asymmetry ratio is determined by the sign of $\hat{\mathbf{k}}_i \times \hat{\mathbf{k}}_f \cdot \hat{\mathbf{u}}$; the charge (Thomson) part of the $I(\mathbf{Q})$, shown in Fig. 4(b), provides an intensity scale at each q_z. The calculations are performed assuming 98% π polarization of the incoming photon, a value currently attainable, and summing over all outgoing polarizations.

IV. CONCLUSIONS

We have shown, by means of detailed calculations, that it should be possible to probe the magnetic properties of surfaces by combining XRES and x-ray surface diffraction. Sensitivity to direction and magnitude of the surface moments can be achieved for both AF and FM order. In the case of AF order, as shown for UAs(100), even in the presence of domains, an analysis of the CTR's associated with the magnetic reflections can discriminate between different possible orientations and magnitude of the surface moments, as compared to bulk ones. For FM order, as in Gd(0001), the asymmetry ratio is the relevant quantity; we have shown that, for surface moments antiparallel to bulk ones,[1,2] the asymmetry ratio in Gd(0001) strongly depends on q_z and attains large values, even with radiation of nonvanishing ellipticity. These magnetic effects are estimated to be observable for clean, well-ordered surfaces and to be enhanced in case of surfaces with different magnetic properties than the bulk.

Note added. We note that specular reflectivity experiments to detect surface magnetic scattering are presently underway at Brookhaven National Laboratory, following preliminary calculations by D. Gibbs.

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