Quadratic X-Ray Magneto-Optical Effect upon Reflection in a Near-Normal-Incidence Configuration at the M Edges of 3d-Transition Metals

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(Received 29 September 2009; published 3 May 2010)

We have observed a quadratic x-ray magneto-optical effect in near-normal-incidence reflection at the M edges of iron. The effect appears as the magnetically induced rotation of $\sim 0.1^\circ$ of the polarization plane of linearly polarized x-ray radiation upon reflection. A comparison of the measured rotation spectrum with results from x-ray magnetic linear dichroism data demonstrates that this is the first observation of the Schäfer-Hubert effect in the x-ray regime. *Ab initio* density-functional theory calculations reveal that hybridization effects of the $3p$ core states necessarily need to be considered when interpreting experimental data. The discovered magneto-x-ray effect holds promise for future ultrafast and element-selective studies of ferromagnetic as well as antiferromagnetic materials.

DOI: 10.1103/PhysRevLett.104.187401

PACS numbers: 78.20.Ls, 78.70.Dm

X-ray magneto-optical spectroscopy techniques are widespread, sensitive methods for element-selective characterization of magnetic systems [1]. In particular, the great sensitivity of resonant magnetic scattering methods has been demonstrated in many experiments exciting the $L_{3,2}$ edges ($2p \rightarrow 3d$ transitions) of 3d transition metals (TM) in magnetic nanostructures with system sizes down to the atomic scale [2]. These experiments have recently been extended from static investigations towards magnetization dynamics [3]. While the temporal structure of synchrotron radiation restricted the time resolution to nanoseconds in the past, studies on the ultrafast magnetization dynamics have nowadays become feasible using femtosecond x-ray pulses provided, e.g., by novel femto-slicing facilities at third generation synchrotron radiation sources such as the ALS (Berkeley, U.S.), BESSY (Berlin, Germany), and the SLS (Villigen, Switzerland) [4]. Much higher photon flux and thus improved experimental sensitivity in magneto-optical experiments will become available with the advent of soft x-ray free electron lasers (FEL). However, the existing FEL facility FLASH (Hamburg, Germany) is designed to provide photon energies of up to 200 eV; that is, the $L_{3,2}$ edges of 3d TM (in the range of 650 to 950 eV) are currently not accessible.

An alternative is provided by resonant $3p \rightarrow 3d$ transitions, i.e., the M edges (at 50 to 65 eV), where the observable magneto-optical effects possess the same order of magnitude when compared to the $L_{3,2}$ edges (see, e.g., Refs. [5–7]). Moreover, the importance of the M edges for the investigation of TM compounds might soon reach beyond large scale facilities. Berlasso *et al.* [8] have recently demonstrated the feasibility of performing ultrafast, tabletop experiments at the M edges of TM through the higher order harmonic generation (HHG) of femtosecond

laser pulses. Consequently, ultrafast, element-selective magneto-optical techniques exciting the $3p$ core level electrons can become accessible to many laboratories. A first such study was reported very recently [9]. Despite these promising properties, the M edges have rarely been investigated thus far and their capabilities for the above described experiments have not yet been explored. To fully profit from current FEL capacities and future HHG possibilities for element-specific static and time-resolved magnetization studies, it is then necessary to further explore magneto-optical techniques in this promising energy range.

In this Letter we report the discovery of a novel quadratic x-ray magneto-optical effect at the M edges of TM occurring upon reflection of linearly polarized radiation in near-normal incidence. By comparison with additional x-ray magnetic linear dichroism (XMLD) measurements and *ab initio* calculations, we show that the reported effect is the x-ray analogue to a similar observation made by Schäfer and Hubert (SH) in the 1990s using visible light [10] which subsequently proved to be a valuable tool for the visualization of magnetic domains [11].

The Schäfer-Hubert effect results from the symmetry breaking that occurs due to the preferred magnetization axis in a magnetically ordered material. As a consequence, the indices of refraction are different for linearly polarized light propagating with electric polarization $\mathbf{E}$ parallel to $\mathbf{M}$ ($n_{\parallel}$) and perpendicular to $\mathbf{M}$ ($n_{\perp}$), respectively. Light traversing the material with $\mathbf{E}$ and $\mathbf{M}$ at an angle of 45° contains equal components $E_{\parallel}$ and $E_{\perp}$. In near-normal incidence reflection the magnetic modification embodied in $n_{\parallel}$ and $n_{\perp}$ leads to the magnetic Schäfer-Hubert rotation of the polarization plane upon reflection, which, using Fresnel theory, can be expressed as

$$\theta_{\text{SH}} \approx \text{Re} \left[\frac{(n_{\parallel} - n_{\perp})n_0}{n_{\parallel}n_{\perp} - n_0^2} \right] \approx \text{Re} \left[\frac{(\epsilon_{\parallel} - \epsilon_{\perp})n_0}{(n^2 - n_0^2)n} \right], \quad (1)$$

where $n = (n_{\parallel} + n_{\perp})/2$, $\epsilon_{\parallel}$, $\epsilon_{\perp}$ are the permittivities for $\mathbf{E} \parallel \mathbf{M}$, $\mathbf{E} \perp \mathbf{M}$, respectively, and n_0 is the refractive index of the cap layer. The dominating quantity for the effect is $\Delta = \epsilon_{\parallel} - \epsilon_{\perp}$, which also is essential to the XMLD and the x-ray Voigt effect that are both observable in transmission [12]. Earlier investigations proved that $\epsilon_{\parallel} - \epsilon_{\perp}$ is to lowest order proportional to $\langle M^2 \rangle$ [13]. Therefore the Schäfer-Hubert effect can be observed for ferromagnetic as well as antiferromagnetic materials.

The experiments were performed at the U125/PGM beam line of the synchrotron radiation source BESSY [14]. The spectral resolution $E/\Delta E$ was set to 5000. The degree of linear polarization of the incident light was $P_{\text{lin}} = 0.99$ [14]. The BESSY polarimeter chamber [15] was used for acquisition of the data. In order to guarantee a solely magnetic origin for Δ , i.e., $\Delta = \epsilon_{\parallel} - \epsilon_{\perp} \propto \langle M^2 \rangle$ [cf. Eq. (1)], the sample must necessarily be cubic, amorphous, or polycrystalline [16]. The investigated sample was a magnetron-sputtered 50 nm thick polycrystalline Fe layer deposited on a 100 nm thick Si_3N_4 membrane. A 3 nm Al cap layer was deposited to prevent oxidation. The incoming radiation was set at an angle of incidence of $\phi = 10^\circ$ with respect to the sample normal as shown in Fig. 1(a). Two magnetic coils allowed magnetic saturation of $\mathbf{M}$ along two orthogonal directions in the sample plane. The polarization state of the reflected light was analyzed using a rotatable gold mirror analyzer and measuring its reflected intensity using a GaAs : P photodiode detector.

In the present experiments a differential detection scheme was employed in order to detect the rotation of the polarization plane of the radiation upon reflection, i.e., the Schäfer-Hubert effect. We profit from the general property of quadratic MO effects which in the present

case can be expressed by $\theta(\alpha) = \theta_{\text{SH}} \sin 2\alpha$, where α is the angle between the incident polarization and the magnetization as stated above. The measured rotation is thus maximized when setting the magnetization at angle of $\pm \pi/4$ with respect to the polarization. The respective experimental orientations are denoted by m_T and m_L , respectively, in Fig. 1(a). Subtracting the corresponding rotation angles of the polarization plane then yields $2\theta_{\text{SH}}$. Note that, due to the deviation of 10° from normal incidence, an additional small linear MO Kerr rotation may be present in the data. It is eliminated by reversing the magnetization at each orientation and averaging the measurements.

The near-normal reflectivity of the sample in the vicinity of the M edges is depicted in Fig. 1(b). It shows a peak at about 55 eV that accounts for the resonant $\text{Fe } 3p \rightarrow 3d$ transitions. Contrary to the well studied $L_{3,2}$ edges, the core level spin-orbit interaction is much smaller and does not allow us to resolve the M_2 and M_3 edges separately. The reflectivity is of the order of 10^{-2} . At the $L_{3,2}$ edges the reflectivity in near-normal incidence would be several orders of magnitude smaller, and hence, be below current detector capabilities. Therefore the only feasible detection of an element-selective SH effect is the M edges. Figure 1(c) shows the intensity at the detector when rotating the analyzer by an angle of γ from 0 to 2π (open circles) at an off-resonant energy. Any additional magnetically induced rotation θ of the polarization plane causes a shift of this curve according to $I(\gamma) = R_0[1 + P \cos 2(\gamma + \theta)]$, where R_0 denotes the product of the reflectivity of the sample with that of the Au analyzer and P is the product of the polarizing power of the Au layer and the degree of linear polarization of the reflected radiation. Here we can set $P = 1$ [13]. Fitting the above equation to the data [cf. the red line in Fig. 1(c)] we obtain θ for each photon energy and magnetization. The SH rotation is finally given by $\theta_{\text{SH}} = [\theta(m_T) - \theta(m_L)]/2$. The resulting SH rotation spectrum θ_{SH} is given in Fig. 2. It shows a resonant behavior with a twofold sign reversal close to the M edges and maximum values of about $\pm 0.1^\circ$.

For comparison we have measured the corresponding XMLD effect in transmission geometry [13]; no earlier XMLD measurements at the M edges have been reported. Figure 3(a) shows $\text{Im}\Delta$ (open circles) being directly deduced from the transmission data and $\text{Re}\Delta$ (solid circles) obtained from a Kramers-Kronig transformation. The expected Schäfer-Hubert rotation can be computed from the experimental Δ values by means of Eq. (1). For the permittivity ϵ and refractive index n we use reported data [8]. As depicted in Fig. 3(b), the calculated (upper white triangles) and measured θ_{SH} (solid circles) spectra agree nicely. It is worth mentioning that the XMLD data also allow us to deduce a maximum x-ray Voigt rotation in transmission of $8^\circ/\mu\text{m}$ at the M edges, which is remarkably similar to that measured at the Co L edges ($7.5^\circ/\mu\text{m}$) [13]. This is surprising, since, in the conventional under-

FIG. 1 (color online). (a) Experimental setup for the detection of the Schäfer-Hubert effect. (b) Reflectivity in the vicinity of the iron M edges at near perpendicular incidence. (c) Normalized detector signal when rotating the analyzer by an angle of γ .

FIG. 2. Photon energy dependent Schafer-Hubert rotation of the polarization plane of linearly polarized x rays in the vicinity of the Fe M edges.

standing, it is the larger spin-orbit splitting of the core $j_{3/2}$ and $j_{1/2}$ levels, being nearly a factor of 10 larger at the L edges than at the M edges, that is believed to be responsible for the large L edge magneto-x-ray effects. As we will show below through *ab initio* calculations, the microscopic mechanism leading to the XMLD at the M edges is actually quite different from that at the L edges. The size of the rotation demonstrates that quadratic magneto-optical effects at the M edges can serve as an equal alternative to respective experiments at the L edges.

In addition, our experiments confirm a previously predicted relation [17] between the Schafer-Hubert rotation and the XMLD effect occurring in reflection. The corresponding asymmetry is given by $A_R = (R_{\perp} - R_{\parallel}) / (R_{\perp} + R_{\parallel})$ with $R_{\perp}$ and $R_{\parallel}$ being the reflectivity for the magnetization perpendicular or parallel to the polarization plane [12]. At near-normal incidence it has been predicted that $A_R = 2\theta_{SH}$ [17]. A respective θ_{SH} spectrum computed from the experimentally determined A_R data is given in Fig. 3(b) [gray (red) triangles]. The agreement with the measured θ_{SH} rotation is again excellent as it reproduces the experimentally measured rotation spectrum both in shape and magnitude. A small difference visible at about 57 eV could be related to interference effects, which are not included in Eq. (1).

Ab initio density-functional theory calculations have been performed using a full-potential linearized augmented plane wave method in the WIEN2K implementation [18]. We may note that a particular difficulty for the theoretical description of the $3p$ semicore states is related to the relative sizes of the exchange splitting and spin-orbit splitting of the $3p$ levels. Whereas at the L edges the exchange splitting of the $2p$ states is quite small and, consequently, can be treated as a perturbation to the spin-orbit split $j_{3/2}$ and $j_{1/2}$ levels, this can no longer be done for the $3p$ states. In our relativistic calculations exchange and spin-orbit splitting were therefore included on an equal footing. Also, a considerable hybridization of the $j_{1/2}$ and

FIG. 3 (color online). (a) Imaginary and real part of the x-ray magnetic linear dichroism measured at the Fe M edges. (b) Calculated Schafer-Hubert rotation θ_{SH} based on (i) the XMLD transmission data of Fig. 3(a) (open triangles) and (ii) the XMLD asymmetry measured in reflection [gray (red) triangles]. Both data are compared to the experimentally determined θ_{SH} values (solid circles, cf. Fig. 2).

$j_{3/2}$ states can be expected at the $3p$ level. To allow for this, the $3p$ states of iron have been treated as valence states in our calculations. The combined effect of the exchange and spin-orbit interaction as well as of hybridization on the $3p$ states is illustrated in Fig. 4(a), where we show the computed $3p$ density of states (DOS) of bulk Fe. Clearly, the $3p$ states are no longer separate $j_{1/2}$ and $j_{3/2}$ levels, but are mixtures of all $|jj_z\rangle$ components, a situation which is markedly different from that of the $2p$ levels. Our relativistically calculated energies of the $3p$ levels are in good agreement with values reported in Ref. [19], which, however, did not consider the hybridization of the $|jj_z\rangle$ components.

FIG. 4 (color online). (a) j, j_z resolved density of states (DOS) of the $3p$ core levels of Fe. (b) Calculated Schafer-Hubert rotation spectrum at the Fe M edge, with j, j_z hybridization included (solid curve) or without (dashed curve).

To obtain the Schäfer-Hubert rotation spectrum we first calculated the complex dielectric tensor of bcc Fe and subsequently applied the four-vector Yeh formalism [20] to obtain θ_{SH} . The theoretically derived θ_{SH} spectrum shown in Fig. 4(b) agrees well with the experimental one [21]. Respective simulations show that the smaller magnitude of the experimental data relative to the theory is due to the Al capping layer, which has been neglected in our calculations given in Fig. 4(b). Note that in the experimental procedure of reversing the magnetizations m_T and m_L we cancel out a constant background signal. The corresponding background has accordingly been subtracted for the theoretical θ_{SH} rotation.

To evaluate the influence of j, j_z mixing in the $3p$ states we have computed θ_{SH} also without the j, j_z hybridization. As shown in Fig. 4(b) this leads to significant deviations from both the experimental as well the calculated data with hybridization. Apart from the different spectral shape, the magnitude of θ_{SH} is about 5 times larger than the one with j, j_z mixing included. This demonstrates that, for proper description and interpretation of x-ray magneto-optical effects at the M edges, it is essential to take the hybridization of the j, j_z levels into account.

In conclusion, we have detected a novel quadratic magneto-x-ray effect occurring upon reflection of linearly polarized x rays in near-normal incidence. A comparison with x-ray magnetic linear dichroism data and *ab initio* calculations confirms that this effect is the x-ray analogue of the SH effect in the visible light regime. Our calculations also show that the hybridization of the $3p$ core level states has to be considered for a proper description of magneto-optical effects at the M edges of the $3d$ transition metals. The x-ray Schäfer-Hubert effect offers promising opportunities with the recent advances of short wavelength optics [22] and the increasing availability of ultrashort UV and x-ray pulses [23]. Thereby the detection of polarization effects has particular advantages over related intensity effects, e.g., for ultrafast pump-probe studies, where strong nonmagnetic intensity effects mask the actual magnetization dynamics [24]. Polarization detection also allows ultimately shot-noise limited sensitivity for investigations on supported ferromagnetic or antiferromagnetic nanostructures [25]. The x-ray analogue of the Schäfer-Hubert effect may therefore enable element-specific studies on static and dynamical interactions in complex nanostructures as, e.g., spin valves and spin torque devices. Respective experiments are further promoted by current developments of novel polarization detectors [26].

We gratefully acknowledge financial support by the German Federal Ministry of Education and Research (BMBF) Grant No. 05 KS4HR2/4, the Swedish Research Council (VR), STINT, the European Community's Seventh Framework Programme (FP7/2007-2013) under Grant No. 214810, "FANTOMAS," and Grant No. NMP3-SL-

2008-214469, "UltraMagnetron," and the Swedish National Infrastructure for Computing (SNIC).

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