Femtosecond Dynamics in Ferromagnetic Metals Investigated with Soft X-Ray Resonant Emission

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(Received 18 January 2005; published 19 December 2005)

We present measurements of the magnetic circular dichroism in x-ray resonant emission in the perpendicular geometry (circularly polarized x rays at normal incidence to the magnetization) for the $L_{2,3}$ absorption region in Fe, Co, and Ni metal. The results show that spin-dependent screening of the core hole takes place within the scattering time scale, which is supported by the absence of the effect in ionic systems. This allows an assessment of the time scale for the screening process (up to a few femtoseconds). The process is almost complete within the scattering time for Fe and Co, but this is not the case for the narrow band metal Ni which shows a much slower dynamics.

DOI: 10.1103/PhysRevLett.95.267402 PACS numbers: 78.70.En, 75.50.−y, 78.70.Ck, 78.70.Dm

The dynamics of ferromagnetic systems involves a variety of time scales characteristic of the different degrees of freedom. The exploration of short time scales is motivated by both fundamental physics and applications [1]. The femtosecond time scale, which is connected to the electronic degrees of freedom, is at the forefront of today's research. Typical experiments are based on fast and intense laser excitation [2,3] exciting the system very far from equilibrium whereby effective electron temperatures of several thousand degrees are reached. The subsequent evolution of the system is probed mainly using photoemission [2] and the magneto-optical Kerr effect [4]. Here we address a completely different scenario. We study the dynamics of the electrons responsible for the magnetism without bringing them very far from equilibrium and obtaining information interesting *per se* and useful to access the ultimate speed of optical reading for future magnetic memory devices [5]. To this end we exploit resonant x-ray scattering, also known as x-ray resonant Raman scattering (RRS) or resonant emission [6]. In this process the incident photon creates a core hole which decays with emission of another photon. The lifetime of the core hole defines the time scale so that the scattering can be used as a stopwatch or core hole clock [7,8]. The application of this approach to magnetism has been considered as a crucial research line for the future [7] but has never been exploited, to the authors' knowledge. The present work is a step forward in this direction. We study the response to a sudden excitation that is the creation of a core hole and represents locally a perturbation. We study the collective reaction of the extended magnetic states screening the core hole, thus obtaining information on the magnetic electronic states without bringing them to high temperature with laser pumping. We show that, in general, during the scattering time the Fermi sea of a ferromagnetic metal (in this case Fe, Co, Ni) relaxes around the core hole giving a spin-dependent screening as observed through the scattering dichroism. This is consistent with recent theoretical work developed for the other decay channel, i.e., Auger emission [9], supporting the present analysis. The most important new result is that in Ni metal this relaxation is far from being complete; i.e., the Ni has insufficient time to fully relax during the scattering. On the other hand, the relaxation is complete in Fe as already pointed out in Ref. [9]. We suggest that the slower screening dynamics is connected with the narrow band nature of Ni metal so that there is a link with the correlation properties. In fact, in Ni we obtain a screening time of 2–3 fsec, while in Fe and Co the upper limit is about 0.7–1 fsec. We believe that the present results can open up an innovative research area with cross fertilization to laser experiments and can stimulate extensive theoretical work.

Since, as shown below, the spin-dependent screening is observed through the scattering dichroism we need genuine scattering dichroism without the undesirable contribution from dichroism in absorption, the so called x-ray magnetic circular dichroism (XMCD) [10,11]. This can be achieved with the dichroism in the perpendicular geometry [12,13] where the circularly polarized incident light is perpendicular to the sample magnetization direction (see Fig. 1, upper panel). In this case there is magnetic circular dichroism in scattering but not in absorption, since the absorption x-ray magnetic circular dichroism requires a magnetization component parallel to the incident photon helicity vector. The perpendicular geometry is crucial to the goal of the present work, i.e., the implementation of the core hole clock in magnetic systems. We use the scattering channel which results in a hole in the $3s$ level. At the absorption edge this is $2p^6 3d^n + h\nu_{\mathrm{in}} \rightarrow 2p^5 3d^{n+1} \rightarrow 2p^6 3d^{n+1} 3s^1 + h\nu_{\mathrm{out}}$, where n is the $3d$ occupation number in the ground state and $h\nu_{\mathrm{in}}$ and $h\nu_{\mathrm{out}}$ are the incident and outgoing photon energies (in this case $h\nu_{\mathrm{out}}$ is about

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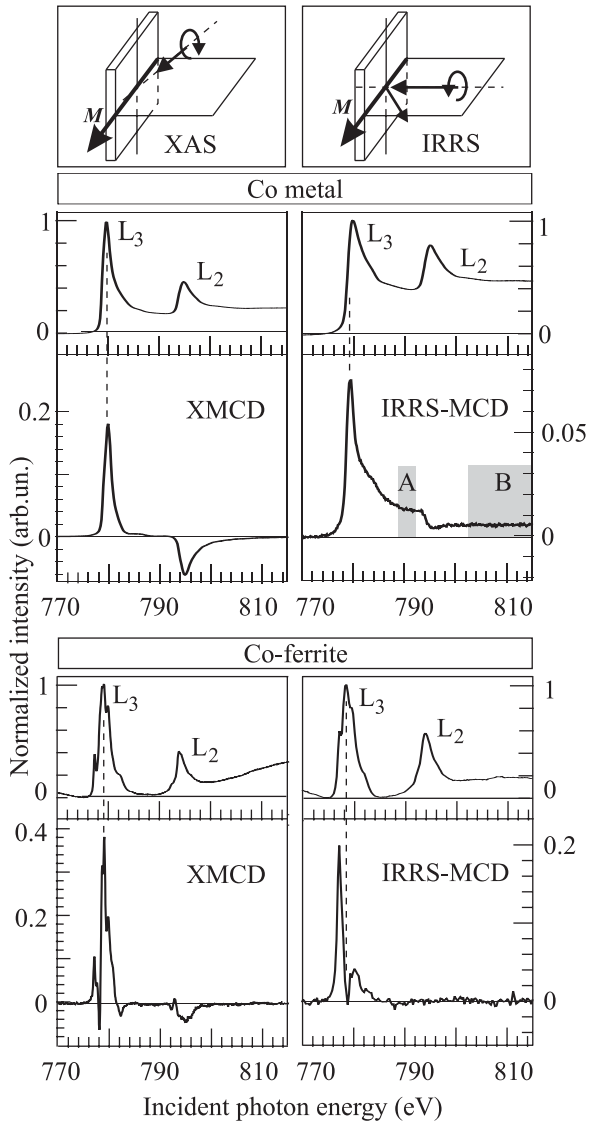

FIG. 1. Geometry of the XMCD and IRRS experiments (upper panel), experimental results for Co metal (middle panels), and Co ferrite (lower panels). Left: $L_{2,3}$ x-ray-absorption spectroscopy (XAS) and corresponding XMCD spectra. Right: $L_{2,3}$ IRRS and corresponding dichroism spectra. To ease the comparison the XAS XMCD is shown to be positive at L_3, contrary to the conventions.

100 eV lower than $h\nu_{\mathrm{in}}$). This is the most appropriate channel, giving the largest L_3 dichroism [14]. Another big advantage of this scattering channel is that the self-absorption of the emitted photons is not resonant, hence not dichroic. Note that in perpendicular geometry the Auger decay channel also displays dichroism as shown in Refs. [9,15–17] where no attempts have been made to use the core hole clock.

The scattering dichroism was measured as in previous work [13,14]. The intensity integrated over the emitted photon energy $h\nu_{\mathrm{out}}$ in the whole scattering channel is measured directly while scanning the incident photon energy $h\nu_{\mathrm{in}}$. This method, which has been called integrated RRS (IRRS), gives the dichroism as a function of $h\nu_{\mathrm{in}}$. The IRRS gives a strong increase in sensitivity compared to traditional RRS since no grating analyzer is used for the scattered beam as opposed to traditional RRS. In the IRRS mode one needs to define a band pass covering the whole $3s$ scattering channel. This is done either by using filters [13,14] or by using a multilayer when filters are insufficiently selective. We have verified for Co metal that both approaches yield the same results. The samples were evaporated films (60 nm Co and Ni on Si, 7.5 nm Fe on MgO, and 1 μm Co ferrite on MgO). Measurements were done at the European Synchrotron Radiation Facility in Grenoble, using $\sim$100% circular polarization from beam line ID08. Further details can be found elsewhere [14]. The scattering angle is 45° (in backscattering) giving the maximum dichroism.

First, we present the evidence for spin-dependent screening of the core hole, i.e., the verification of our diagnostics in the core hole clock experiment. This is done by combining new accurate measurements with the theory of Ref. [9] and also by using published data. Figure 1 gives the IRRS dichroism in perpendicular geometry for Co metal and Co ferrite together with the corresponding XMCD in longitudinal geometry (the peak dichroism is normalized to the peak of the spectra summed over the incident polarizations). As is well known, in both the metal and the ferrite the energy regions corresponding to the $2p \rightarrow 3d$ excitation (L_3 and L_2 regions) show XMCD with vanishing dichroism between L_3 and L_2 and above L_3. In the ionic case the IRRS dichroism is also seen only in the $2p \rightarrow 3d$ excitation region [18] with the additional restriction that the IRRS dichroism must be zero for L_2 [19,20]. In the metal the behavior of the IRRS dichroism is quite different because a clear dichroism signal is also observed in the regions where the $2p \rightarrow 3d$ transitions do not contribute. In Fig. 1 this peculiar IRRS dichroism is labeled with A in the region between L_3 and L_2 and with B in the region above L_2 [21]. This dichroism cannot take place without an evolution of the intermediate state giving a core hole polarization. In fact, in the absence of such an evolution the polarization would be obtained only through $2p \rightarrow 3d$ transitions [19,22]. In the Auger channel it has been demonstrated theoretically [9] that this dichroism is due to the spin-dependent screening of the core hole coupled via exchange to the valence electrons giving a core hole polarization. This theoretical argument is quite general and also applies to the radiative channel, hence explaining our result. This is consistent with the known mechanism for screening of the magnetic impurities and with the spin-dependent dynamics of itinerant magnetic electrons [3]. Another important fact given by the theory [9] is the proportionality of the dichroism to the local magnetic moment on the site of the excited atom, and, in particular, the absence of dichroism for a zero magnetic

moment. Hereafter, the dichroism in regions A and B will be denoted as "L_3 metallic dichroism" and "$L_{2,3}$ metallic dichroism" to emphasize that the effect is typical for the metallic state.

The key issue of the present work is the trend of the metallic dichroism in the sequence Fe, Co, Ni summarized in Fig. 2. The most important result is that the metallic dichroism is seen also in Ni [23]. The dichroism in Ni seen in the present bulk-sensitive, high-quality data shows at a glance that the relaxation around the core hole in Ni is far from being completed during the scattering time, because the metallic dichroism would be almost zero in the case of complete relaxation. In fact, in a fully relaxed situation the screened site of the core hole has an extra $3d$ electron so that the $3d$ shell is locally almost full and essentially without a magnetic moment as confirmed by the supercell calculations in Ref. [9].

A more precise discussion can be given by comparing the measured metallic dichroism with the magnetic moments. For this purpose we use the L_3 metallic dichroism which is stronger and intrinsically simpler than the $L_{2,3}$ metallic dichroism that includes the Coster-Kronig conversion, which in turn is polarization dependent. The crucial information comes from the Z (atomic number) dependence of the flipping ratio (difference to sum ratio of the shaded areas A in Fig. 2) shown in Fig. 3 and normalized to the Fe value. We use the flipping ratio because it is much less sensitive to saturation and self-absorption effects. The experimental trend is compared with that of the $3d$ magnetic moments (both relaxed and unrelaxed) normalized to Fe, taken from Table I of Ref. [9]. The results are interesting in several ways.

(i) Going from Fe to Co the experimental result is close to that of the relaxed magnetic moment. This is a strong indication that in Fe and Co the process takes place via complete or almost complete relaxation of the intermediate state confirming the interpretation of the Auger data in Ref. [9]. The $2p_{3/2}$ core hole lifetime related to the width of the L_3 level is typically 1.5 fsec [24]. The present results for Fe and Co give an upper limit to the screening time constant τ_s due to the sudden creation of an impurity, such as the $2p$ core hole. An almost complete relaxation implies at least $3\tau_s$, so that this upper limit is around 0.5 fsec [see also the analytical arguments of point (iii)]

(ii) As anticipated, the relaxation in Ni is far from being complete because the measured effect is much larger than expected for a relaxed system. Thus the rearrangement in the intermediate state, averaged on the time scale explored by scattering, occurs in the presence of an average moment much larger than the relaxed moment. We suggest that this is linked to the narrow $3d$ hole band of Ni implying that the Fermi sea is slower in building up the screening charge. This is a reasonable conjecture based essentially on the difference in effective mass of the holes in Fe, Co, and Ni.

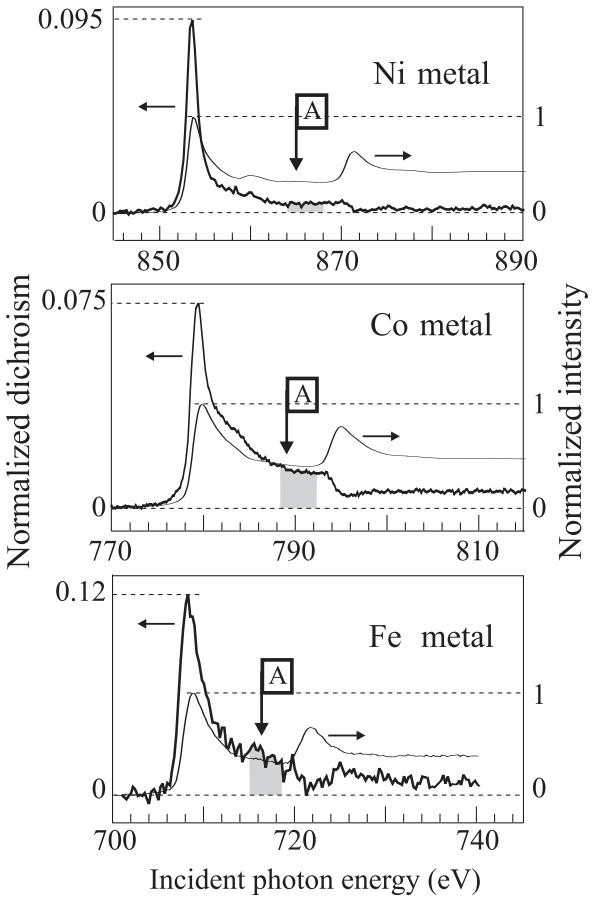

FIG. 2. The IRRS dichroism (thick line) in perpendicular geometry for magnetic $3d$ metals (Fe, Co, Ni). Also shown is the IRRS spectrum summed over the two incident polarizations (thin line).

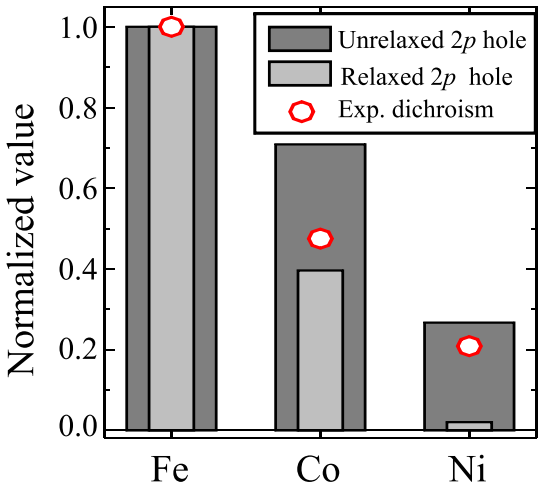

FIG. 3 (color online). Measured flipping ratio (circles) in the L_3 metallic dichroism [energy regions labeled by A in Fig. 2 (shaded areas)] in the Fe, Co, Ni series. Magnetic moments of the $3d$ states with a relaxed and unrelaxed $2p_{3/2}$ core hole. All values are normalized to those of Fe. With this normalization the trend shows the difference between the relaxed and the unrelaxed case in the sequence Fe-Co-Ni.

Future theoretical investigations could be very useful in this respect.

(iii) One can extract useful numbers even without a detailed theory, which is beyond our scope and which could be stimulated by the present results. A simplified model based on a single time constant τ_s describing an exponential screening dynamics yields the value of $x = \tau_s/\tau_c$ where τ_c is the core hole lifetime. For $\tau_c \ll \tau_s$ there is no metallic dichroism because there is no time to develop any screening. For $\tau_s \ll \tau_c$ the relaxation is complete within τ_c. The partial relaxation is between these two extremes. Within a simple exponential approximation and consistently with the proportionality between the dichroism and the magnetic moment, the time dependent dichroism $D(t)$ is approximated as

$$D(t) = C(1 - e^{-t/\tau_s})[\mu_s + (\mu_0 - \mu_s)e^{-t/\tau_s}], \quad (1)$$

where μ_0 and μ_s are the unrelaxed and relaxed moments, respectively, and C is a proportionality constant. The first factor gives the build up of the metallic dichroism and the second the final dichroism which in turn is a function of the screening. The scattering experiment integrates the signal over the core hole lifetime governed by the total decay probability (p_{tot}) and measures a dichroism $D_m = \int_0^\infty D(t)f(t)dt$, where $f(t)$ is the probability of finding the core hole at time t decaying radiatively in competition with the Auger channel ($p_R + p_A = p_{\mathrm{tot}}$), where p_R is the radiative probability, p_A is the Auger probability, and p_{tot} is proportional to $1/\tau_c$ (see Ref. [24]). Introducing the parameter $F = \mu_0/\mu_s$, which is a property of the magnetic sample under investigation, and taking D_m in units of the fully screened dichroism D_s, corresponding to $x \to \infty$, the C drops out and one obtains the universal relation

$$\eta = \frac{D_m}{D_s} = \frac{x(F + 2x)}{(1 + x)(1 + 2x)}. \quad (2)$$

In Ni the parameter F is very large since μ_s is very small ($F = 18$ accordingly to Ref. [9]) and η is about 12–14 (see Fig. 3) so that $\tau_s/\tau_c \simeq 1$ implying $\tau_s \simeq 1.5$–2 fsec.

In conclusion, we have obtained information on the fast dynamics of the Fermi sea in magnetic systems not very far from equilibrium by taking advantage of the core hole clock in scattering and have shown the atomic number dependence of the effect in $3d$ magnetic metals, displaying in Ni a considerably slower screening than in Fe and Co. Moreover, the results demonstrate that this approach can cross fertilize with work in pump-probe mode including future experiments using free electron lasers under construction or in project phase.

The work has been done under the Advanced X-ray Emission Spectroscopy (AXES) contract between the European Synchrotron Radiation Facility (ESRF) at Grenoble and the Istituto Nazionale di Fisica della Materia (INFM-CNR) of Italy.

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