Magnetic X-Ray Dichroism in Core-Level Photoemission from Ferromagnets

L. Baumgarten and C. M. Schneider
Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-1000 Berlin 33, West Germany

H. Petersen and F. Schäfers
Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) GmbH, Lentzeallee 100, D-1000 Berlin 33, West Germany

J. Kirschner
Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-1000 Berlin 33, West Germany
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We report on the novel effect of magnetic x-ray dichroism in core-level photoemission from ferromagnets with circularly polarized radiation. Depending on the relative orientation of photon spin and sample magnetization (parallel or antiparallel), a single emission line may be resolved into two lines, due to exchange splitting of the core level. The mechanism is explained in terms of spin-selective dipole transitions in the presence of spin-orbit coupling. Possible applications of magnetic x-ray dichroism in photoemission from magnetic samples are pointed out.

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The transmission or reflection of circularly polarized light interacting with magnetic matter may depend on its helicity, i.e., the sense of rotation of the electric vector of the electromagnetic wave. A familiar example for this "magnetic dichroism" is the magneto-optic Kerr effect. The coupling between the aligned electron spins ($s = \frac{1}{2}$) and the photon spin ($s = 1$) is in this case, as well as in all others to be discussed below, provided by the spin-orbit interaction of the electronic states—either in the initial or in the final state, or in both. A counterpart to the optical polar Kerr effect was recently reported in the x-ray region.[1,2] It was found that the absorption cross section for x-ray photons at core levels of ferromagnets depends on the relative orientation of the photon spin and the sample magnetization. This was successfully interpreted in terms of the spin-split density of states at and above the Fermi level.[3] As shown earlier by van der Laan *et al.*,[4] magnetic x-ray dichroism may in special cases even be observed with linearly polarized radiation. A general theoretical treatment of linear and circular dichroism in absorption was very recently given by Carra and Altarelli.[5]

The new phenomenon we report on here is distinct from all the above in that it occurs in *emission* of electrons from core levels into free-electron states, rather than absorption of photons at core-level edges. The basic observation is that a single core-level emission peak from a ferromagnet may be resolved into two energetically separated lines, if excited by circularly polarized x rays with the photon spin aligned with the sample polarization. The relative intensity of these lines reverses when the magnetization of the sample or the helicity of the photons is reversed. Since the final energy of the electrons is far above the Fermi level, we basically probe the spin-split electronic structure of the core levels, rather than the spin-split empty density of states in the valence band. "Magnetic x-ray dichroism in photoemission" may find wide application in the study of the element-specific local magnetic structure on the atomic scale in ferromagnets, ferrimagnets, and antiferromagnets in the near-surface region. Our observations also shed new light on a long-standing issue of the interpretation of exchange splittings in the x-ray photoelectron spectrum of iron.

A number of proposals for the production of circularly polarized light have been made,[6-8] but up to now no circular polarized light in the soft-x-ray region was available. In this Letter we report on the first use of the high degree of circular polarization of off-plane synchrotron radiation in combination with a grazing-incidence monochromator. This technique has before only been exploited in the normal-incidence regime, at photon energies ≤ 35 eV,[9] where depolarization due to the optical components is known to be negligible, and where the separation of the polarization components is easier due to the larger vertical divergence of the radiation. The circularly polarized radiation was provided by the monochromator SX-700-3 at BESSY,[10] which is equipped with a movable premirror to accept the synchrotron radiation above or below the plane of the electron orbit. Its position was set according to extensive calculation of optical ray tracing and of polarization properties of the optical elements, using known optical constants and the known emission characteristics of the bending magnet. The precise degree of circular polarization is not known, but the good agreement between predicted and measured photon intensity behavior for different mirror settings gives us confidence in estimating the circular polarization as 60%–80%.

A clean Fe(110) single crystal was irradiated by circularly polarized x rays of about 800 eV energy. Photoelectrons were excited from the iron L_2 ($2p_{1/2}$) and L_3

($2p_{3/2}$) shells. These were chosen because of their high photoionization cross section and the large spin-orbit interaction in the initial state. The electrons were analyzed by a hemispherical analyzer with a transport lens. The crystal was held remanently in a single-domain state by a soft iron yoke with a current winding. We used grazing incidence of the photons with respect to the surface, such that photon spin and magnetization were nearly parallel. For a given photon helicity, photoelectron spectra were recorded alternatingly with reversed sample magnetization, and added up in a computer. The experiment was repeated for the opposite photon helicity and at different photon energies.

Some typical experimental results are shown in Fig. 1, taken at $h\nu = 850$ eV. The angle of incidence of the photons was 10° with respect to the target surface; the electron takeoff angle was 55°. Figure 1(a) shows the total intensity curve I in the region of the spin-orbit-split $2p$ lines of iron, averaged over the two magnetization states of the sample. The inset displays, on enlarged scales, the peaks of the partial intensities I^+ and I^- for the two magnetization states separately. Figure 1(b) shows the asymmetry A of the partial intensities, being defined as the difference of the intensities for the sample spin orientation parallel and antiparallel to the photon spin divided by the sum of the two intensities: $A = (I^+ - I^-)/(I^+ + I^-)$. Coming from low binding energy, the asymmetry is seen to show a plus-minus feature at the $2p_{3/2}$ line, and a weaker and broader minus-plus feature at the $2p_{1/2}$ line. We found experimentally that reversing the helicity reverses the asymmetry curve, but not an instrumental background due to slight intensity changes upon reversing the magnetization. This instrumental background may consequently be removed by measuring the asymmetries for the two helicities separately and taking their difference. The result is shown in Fig. 1(b). The partial intensities in Fig. 1(a) have been obtained from a separate measurement at twice the monochromator resolution over limited energy ranges. They were formed from the corresponding asymmetry according to $I^{\pm} = I \times (1 \pm A)/2$. We show them on enlarged energy and intensity scales with zero suppression to emphasize the energetic splitting. The peaks are split by 0.3 ± 0.2 and 0.5 ± 0.2 eV for the $2p_{1/2}$ and the $2p_{3/2}$ lines, respectively. Comparing the intensity curves in dashed and solid lines we note that the apparent energetic shift goes in opposite directions for the two components of the $2p$ spin-orbit doublet. This is explained below. To see whether the final state plays a major role, we varied the kinetic energy of the photoelectrons from 80 to 180 eV by changing the photon energy. We did not find significant changes of the asymmetry except the trivial one of decreasing asymmetry with increasing secondary-electron background. The essential result of the experiment is that the shape and intensity of photoelectron spectra from core levels excited by circularly polarized x rays depend on the relative orientation of photon spin and sample magnetization.

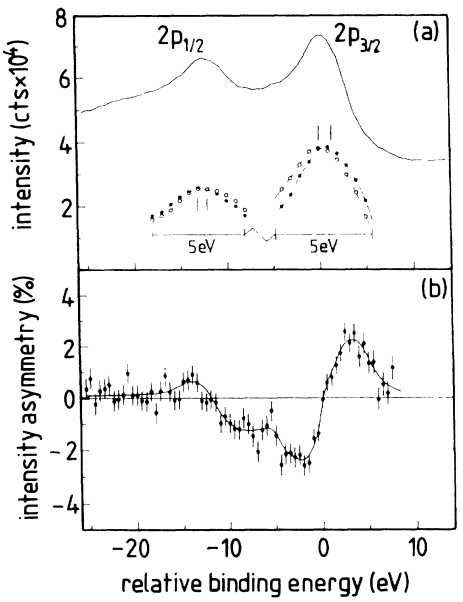

FIG. 1. The effect of magnetic x-ray dichroism in photoemission. (a) The upper part shows the total intensity spectrum in the region of the spin-orbit-split Fe $2p$ levels. The lower curves show, on enlarged scales, the partial intensities in the peak regions for photon spin parallel (solid lines) and antiparallel (dashed lines) to the sample magnetization. Note the apparent energetic peak shift in opposite directions (intensity zero suppressed). (b) Asymmetry A of the measured intensity for photon spin and sample magnetization parallel (I^+) and antiparallel (I^-). $A = (I^+ - I^-)/(I^+ + I^-)$. The asymmetry curve was obtained from two separate runs with opposite photon helicity.

For the explanation of these results we make reference to Fig. 2, which shows in a highly schematic way the energy-level splittings and the expected photoemission intensities when using circularly polarized light. First, consider the spin-orbit-split $2p_{1/2}$ and $2p_{3/2}$ core levels in a paramagnet, being occupied by two and four electrons, respectively. Exciting these electrons by completely circularly polarized light into free-electron states leads to preferential emission of up electrons from $2p_{1/2}$ and down electrons from $2p_{3/2}$ due to spin-orbit interaction. This is well known from atomic physics.[11] The assumption of free-electron final states is justified since the kinetic energy is some 100 eV above the Fermi level (the photon energy is well above the binding energy). If the light helicity is reversed, electrons with opposite spin are excited. The emitted intensity is exactly the same in both cases (i.e., no asymmetry), but the emitted electrons are highly polarized along the photon spin orientation. Neglecting spin-orbit interaction in the final states, the polarization is $+100\%$ for $2p_{1/2}$ and -50% for $2p_{3/2}$.[12] This is indicated by the length of the arrows in the respective Lorentz-type lines. Now we consider a ferromagnet and introduce an exchange splitting $\Delta_{ex} \ll \Delta_{so}$ of the core levels, which means that the spin-

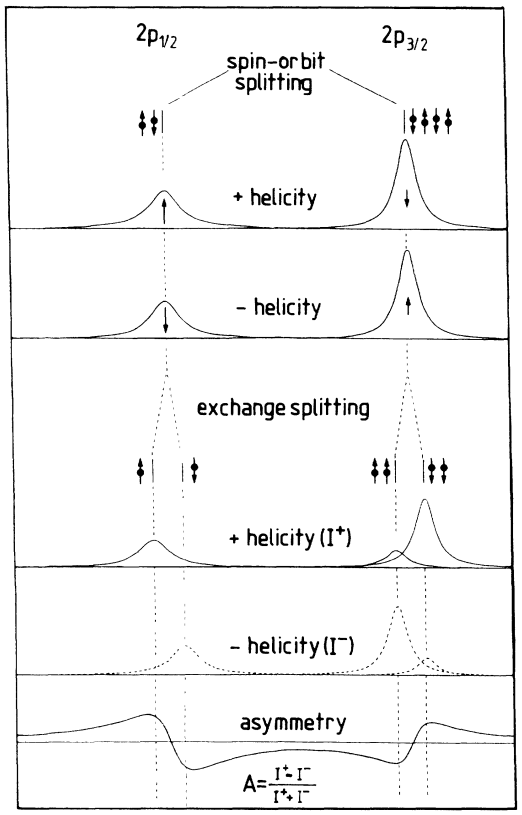

FIG. 2. Schematic explanation of the origin of magnetic x-ray dichroism in photoemission. The effect comes from the interference of spin-orbit interaction in the core levels and exchange interaction with the $3d$ valence electrons, together with the dipole selection rules for circularly polarized light. From top to bottom the figure shows the expected relative intensities of Lorentz-type photoelectron lines when excited by circularly polarized light in the presence of spin-orbit splitting only (top), and with additional exchange splitting (bottom). The low-intensity satellite in the $2p_{3/2}$ is not resolved in the experiment. For details see text.

orbit-split $2p$ levels are further split into minority and majority states. If we now send in circularly polarized x rays of positive helicity, the same dipole operator works as above in the nonmagnetic case, exciting preferentially majority electrons from $2p_{1/2}$ and minority electrons from $2p_{3/2}$. The essential condition is that the spin orientation of the sample must be aligned with the photon spin—hence our glancing-incidence geometry. Reversing the helicity reverses the spin orientation, as before, but now the energetic positions of minority and majority electrons in the emission spectrum are interchanged. If we now form the asymmetry function $A=(I^+-I^-)/(I^++I^-)$ from the two intensity curves (Fig. 2, bottom), we end up with a plus-minus feature at $p_{3/2}$ and a minus-plus feature at $p_{1/2}$—as observed in the experiment. For reasons of simplicity we reversed the helicity in the argument, but the same result is obtained if the magnetization is reversed instead. In our modeling we included a lifetime broadening of the $p_{1/2}$ level 50% larger than that of the $p_{3/2}$ level, guided by the x-ray photoemission spectroscopy (XPS) line-shape analysis by Fuggle and Alvarado,[13] and a small satellite of opposite spin direction in the $2p_{3/2}$ level, which is not resolved in the experiment, to reproduce the net spin polarization of -50% in the atomic picture. The broadening is seen to reduce the amplitude of the asymmetry, which partly explains why in the experiment the asymmetry features at the $p_{1/2}$ level appear smaller. Another, and perhaps more important, reason is that this peak is of low intensity and rides on a larger background than the $p_{3/2}$ peak. The large background reduces the asymmetry substantially, but since we do not yet have a good knowledge of the background, we refrain from calculating anything like an "effective asymmetry." However, considering the peak-to-background ratio, the incomplete light polarization, and instrumental broadenings, we expect the net asymmetry effects to be roughly a factor of 5 larger than measured here.

In conclusion, the effect of magnetic x-ray dichroism in core-level photoemission may be explained qualitatively by the combined action of preferential excitation from a particular spin state by circularly polarized light (mediated by spin-orbit interaction in the core states) and the energetic splitting of a particular core level due to exchange interaction with the valence-band d electrons. Unlike in x-ray absorption, the density of empty states plays no essential role since the excited electrons are far above the Fermi level. For a quantitative interpretation, though, our reasoning is certainly too simplistic. This concerns, in particular, the origin and magnitude of the exchange splitting of the core levels, which we introduce *ad hoc*.

We cannot decide experimentally whether this exchange splitting should be a ground-state property or whether it is due to exchange interaction of the photohole with the polarized conduction d bands in the excited state, since we observe the excited state only.[14] However, there is evidence for substantial exchange interaction from the existence of spin-polarized Auger electrons from Fe of the type LMM, where only core levels are involved.[15] Other evidence comes from a recent spin-polarization analysis of photoelectrons from Fe $3p$ core levels[16] (spin-orbit splitting not resolved; excitation by linearly polarized light). In these latter experiments an exchange splitting of 0.45 eV was found, with the minority electrons shifted to smaller binding energy. Analyzing the Auger-emission results of Landolt and co-workers,[15] Mizuta and Kotani[17] assumed the core levels not to be exchange split in the ground state, but the core hole to interact with the valence d electrons. They estimated a revised $(2p\text{-}3d)$ exchange parameter $J_2=0.35$ eV, assuming a magnetic moment of $2\mu_B$ for the d electrons, and found good agreement with the experiment. On the other hand, magnetic hyperfine fields are known to exist at the nucleus, which have their origin in

an inhomogeneous spin density of the core electrons. Thus, a ground-state exchange splitting should be expected as well. Ebert[18] recently treated core states of ferromagnets in a fully relativistic theory and calculated core-state eigenvalues. For iron $2p_{1/2}$ he found two levels split by ~ 0.3 eV, while for $p_{3/2}$ he found four levels distributed over a width of ~ 0.8 eV. The lowest and highest level are pure spin states ($|m_j| = \frac{3}{2}$), while the two intermediate states ($|m_j| = \frac{1}{2}$) are mixed spin states. Thus, from a point of view completely opposite to that of Mizuta and Kotani (i.e., exchange splitting determined by ground state; no exchange interaction with the core hole) one would arrive at about the same values for the exchange splitting in the photoelectron lines as the experiment. Obviously, neither of the two limiting cases can be completely correct, but both lead to the same conclusion of substantial exchange splitting in the core levels—which is what we had to invoke to explain our experimental findings.

Our results also resolve the issue of abnormal broadening of core lines in the $3d$ transition series, at least for Fe. A decade ago, Fuggle and Alvarado[13] conjectured that the unusually broad L_2 and L_3 lines were due to unresolved exchange-split lines rather than to very short core-hole lifetimes. We can now confirm this view by stating that the $2p_{1/2}$ and $2p_{3/2}$ lines of Fe both contain (normally unresolved) exchange-split doublet ($p_{1/2}$) or multiplet ($p_{3/2}$) lines, which looks like an "anomalous" broadening.

We wish to add a few words on the potential applications of magnetic x-ray dichroism in photoemission. First, the method is surface sensitive, with tunable depth of information via change of the photon energy. It is therefore ideally suited for studies of magnetism at surfaces, at interfaces, and in thin films. The method is element specific and probes the local magnetic properties on an atomic scale. Ferromagnetic and ferrimagnetic samples can obviously be studied by switching the magnetization, as we did here. Even binary antiferromagnets with the two components carrying opposite magnetic moments may be investigated by switching the light helicity. The only condition is that the area illuminated by the photon beam must be in a single-domain state aligned with the photon momentum. This can, e.g., be accomplished by cooling the sample down to below the Néel temperature in the presence of a magnetic field, which then is removed.

In many instances an explicit analysis of the electron-spin polarization is desirable (such as for $2s$ and $3s$ states, for example), but in many other cases the present technique of magnetic x-ray dichroism in photoemission is likely to replace it for many reasons. Relative to an ordinary intensity measurement, spin-polarization analysis costs typically 3 orders of magnitude in count rate. Using the off-plane circular polarization from a bending magnet costs about 1 order of magnitude in light intensity. The net gain in intensity over a spin-polarization measurement is therefore 2 orders of magnitude, which may even be increased to 3 orders by using a spectrometer with multichannel detection. Magnetic information may therefore be gathered with about the same ease as present-day standard XPS data.

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