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Coster-Kronig contributions to magnetic circular dichroism in the $L_{2,3}$ x-ray fluorescence of iron

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High-resolution x-ray fluorescence spectroscopy has been performed on magnetically oriented polycrystalline iron samples. Circularly polarized synchrotron radiation was used to excite the Fe $L_{2,3}$ x-ray emission, either directly from a bending magnet (white radiation), or from an asymmetric wiggler followed by a monochromator tuned to the L_2 edge. Large differences in the magnetic circular dichroism (MCD) were observed. Spin-polarized relativistic linear muffin-tin orbital calculations and a simple qualitative model demonstrate that the L_3 x-ray emission dichroism is partially canceled by the L_2-$L_3M_{4,5}$ Coster-Kronig process. The Coster-Kronig process is large enough to make MCD x-ray absorption experiments, performed in the fluorescence mode, unreliable.

Magnetic circular dichroism (MCD) in x-ray emission spectra was observed recently.[1] It confirmed theoretical predictions, based on fully relativistic spin-polarized Korringa-Kohn-Rostoker band structure calculations for iron,[2] that x-ray fluorescence spectroscopy, performed with circularly polarized photons, could measure the spin polarization of valence states (defined as the filled conduction band states). The calculation assumed that the energy of the primary photon beam would be chosen to excite an Fe $2p_{3/2}$ electron to the empty part of the exchange-split d band just above the L_3 threshold. The intention was to leave behind a highly polarized core-hole intermediate state destined to act as a "spin detector" of valence electrons via the $3d \rightarrow 2p_{3/2}$ transition responsible for the $L\alpha$ x-ray emission. [Similar arguments would apply to the L_2 excitation responsible for the $L\beta$ ($3d \rightarrow 2p_{1/2}$) x-ray emission.]

The experiments in fact used white bending-magnet radiation instead of monochromatic radiation. Thus photoionization was almost exclusively to continuum states rather than to near-edge states. The continuum states do not interact with the system, yet MCD fluorescence may still be observed as it depends on the spin-resolved local density of occupied states and on the $2p$ spin-orbit and exchange interaction-split $2p$ core multiplets of the intermediate state. The latter are closely related to the Fe $2p$ x-ray photoelectron spectrum.[3,4] The advantage of using white radiation is that total incident flux is greatly enhanced.

Here we compare the MCD of the Fe $L\alpha$ and $L\beta$ fluorescence spectra excited by a monochromatic beam of circularly polarized photons tuned to the L_2 threshold, to that obtained with white radiation. We have picked out these particular results, from a series of experiments performed over a range of energies, because the sign of the MCD is unexpectedly reversed. Also they bring to light the presence of a polarization dependent Coster-Kronig (CK) transition contributing to the fluorescence. Not only are these findings of importance to future investigations relating to dichroic fluorescence in complex systems, but they should also be of interest to those engaged in interpreting x-ray absorption spectra recorded in the fluorescence mode.[5] Such a technique, though at present less in use than the photoelectron yield method, is particularly useful when dealing with magnetic materials in strong fields.

As an aid to interpreting the results, we use the computationally efficient spin-polarized relativistic linear muffin-tin orbital (SPR-LMTO) method.[6] The x-ray fluorescence MCD was calculated in the way set out by Strange *et al.*[2] We need only mention that the underlying electronic band structure was calculated self-consistently with the SPR-LMTO method.[7] The conduction band and core states were treated fully relativistically by solving the spin-polarized Dirac equation[6,8] and fully relativistic transition matrix elements were used. The procedure is essentially that used for calculating x-ray absorption in Refs. 9 and 10. Our treatment of the x-ray emission process implicitly assumes that the intermediate core hole state has had time to relax before emission. This is a reasonable approximation for a metal. For a more extensive discussion we refer the reader to Ref. 11.

Measurements were performed at the Super-ACO storage ring. The source for photon energies tuned to the Fe L_2 edge was an asymmetric wiggler,[12] followed by a 1200 lines mm^{-1} plane-grating toroidal-mirror monochromator. Right-hand circularly polarized photons (σ^- helicity and photon spin antiparallel to the direction of propagation) were selected from a portion of the beam below the orbit plane. The degree of circular polarization P_c was estimated to be ≈ 0.7. The monochromator entrance and exit slits were ad-

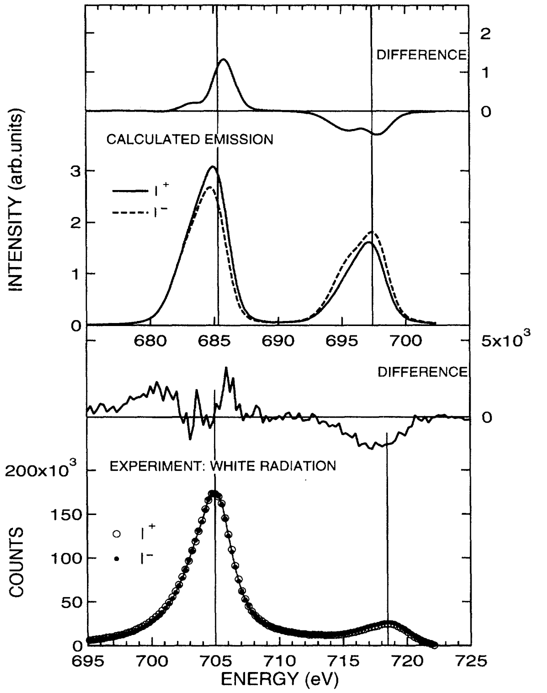

FIG. 1. Fe $L\alpha$ and $L\beta$ x-ray fluorescence spectra excited by bending-magnet right circularly-polarized white radiation and the calculated emission spectra. The latter are based on SPR-LMTO band structure calculations. MCD is the difference between spectra for the two magnetization directions. Apart from background subtraction raw experimental data are shown.

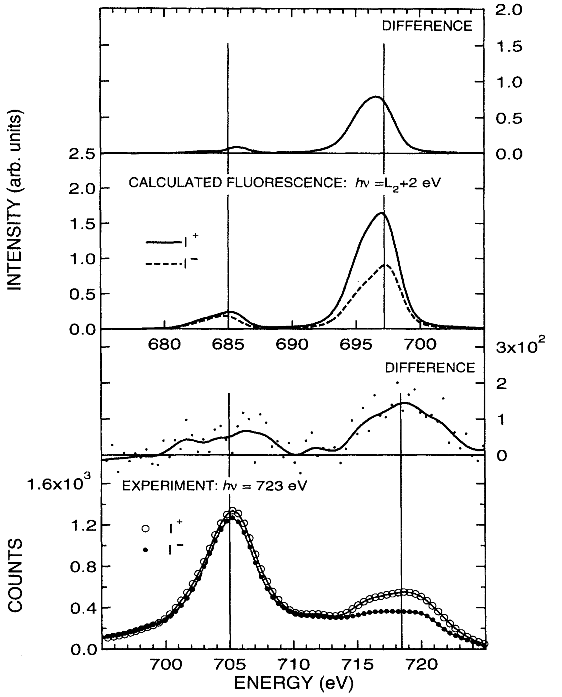

FIG. 2. Fe $L\alpha$ and $L\beta$ x-ray fluorescence spectra excited by monochromatic right circularly-polarized photons tuned to the L_2 x-ray absorption. As in Fig. 1 calculated spectra are based on band structure calculations. MCD is the difference in amplitude between the two magnetization directions. Smoothed experimental data are presented; dots in the difference curve are raw differences.

justed for maximum flux. Under these conditions the width of the Fe L_3 absorption edge was measured to be 1.9 eV.

The white radiation experiment was performed on a bending-magnet beamline fitted with an adjustable slit set above the orbit axis ($P_c \approx 0.6$). A highly oriented Fe sample was magnetized parallel to its surface along the [001] direction using Nd-Fe-B permanent magnets. The sample and the magnets could be rotated through 180° about a normal to the surface so as to bring the magnetic field antiparallel or parallel to the photon spin. The corresponding spectral intensities will be noted I^+ and I^-, respectively. The sample was placed 1 m behind the focal plane of the monochromator so as to be illuminated by a defocused beam approximately 3×20 mm^2. The photon beam impinged on the sample at a grazing angle of 15° so as to intercept the full height of the defocused beam. The defocused beam acted as an extended source to a bent crystal spectrometer fitted with a position sensitive detector and a rubidium acid phthalate crystal bent to a 0.627 m radius. The Fe $L\alpha$ and Fe $L\beta$ emission bands, separated by a spin-orbit splitting of 13.5 eV, were recorded together. The overall energy resolution of the fluorescence spectrum was estimated to be ≈ 0.7 eV.

Self-absorption effects were very much more severe with white radiation. This is identifiable as a reduction in the $L\alpha$ bandwidth (Figs. 1 and 2). It results from the penetration of high energy photons far into the target, so that the maximum path length of the emitted photons is large. On the other hand, for primary photons tuned to the L_2 edge, the incoming and outgoing photon path lengths are short because the photoabsorption cross section is high. Normalization of the spectra was performed by adjusting I^+ and I^- to the same average count rate summed across the whole spectrum (including background). This leads to a slight underestimate of the dichroic intensity but is a reasonable approximation because on the one hand dichroism is small compared with the total intensity in the white radiation experiment and on the other the $L\alpha$ peak amplitude-to-background intensity was only $\approx$2:1 for the data presented in Fig. 2.

In Fig. 1 we show the Fe $L\alpha$ and $L\beta$ fluorescence spectra obtained with white radiation along with the calculated x-ray emission spectra. Raw data, except for a small background correction, are presented. Figure 2 shows the equivalent spectra for a primary photon energy tuned to ≈ 2 eV above the L_2 absorption threshold. Here the count rate over the whole spectrum was low (≈ 30 counts s^{-1}) so data have been smoothed. The calculated Fe $2p$ fluorescence spectrum assumed excitation into the calculated L_2 x-ray absorption peak for $L\beta$ fluorescence, and therefore to ≈ 15 eV above the Fermi energy (E_F) for $L\alpha$ fluorescence. Both absorption and emission matrix elements are included. The experimental and calculated differences ($I^+ - I^-$) are also shown in the figures. Figure 1 shows positive dichroism in the region of $L\alpha$ and negative dichroism for $L\beta$. This is opposite in sign to the dichroism observed in the Fe $L_{2,3}$ absorption spectrum measured in the electron yield mode using the same convention for I^+ and I^-.[13] However, this is expected in application

TABLE I. Experimental and calculated magnetic circular dichroism of iron in terms of $L\alpha$ and $L\beta$ intensity anisotropy [$A(2p_{3/2})$ and $A(2p_{1/2})$, respectively]. Values are given for white radiation and monochromatic photon excitation to the L_2 x-ray absorption maximum. Values for the $L\beta/(L\alpha+L\beta)$ branching ratio for white radiation excitation are also given.

	Photon energy	Experiment [a]	Theory [b]	Model	Model+CK
$A(2p_{3/2})$	white	0.03	0.14	0.08	0.03
	$h\nu=L_2$	0.07	0.3	0.08	0.2
$A(2p_{1/2})$	white	–0.07	–0.20	–0.16	–0.16
	$h\nu=L_2$	+0.33	+0.58	+0.3	+0.3
$L\beta/(L\alpha+L\beta)$	white	0.13	0.35	0.33	0.167

[a] Experimental values are corrected for full circular polarization.

[b] SPR-LMTO.

of a sum rule formulated by Bennett and Stern[14] which stipulates that the total dichroism summed over all conduction states (occupied and unoccupied states inclusively) must be zero. It follows that a reversal in the sign of the $L\beta$ dichroism when the excitation frequency is close to the L_2 threshold (Fig. 2) is unexpected and remains to be explained.

The calculated Fe $2p$ emission spectra for bcc Fe should be equivalent to fluorescence spectra produced by an intermediate state in which the core electron has been excited to a nonpolarized continuum state. The anisotropy, defined as $A(2p)=(I^+-I^-)/[\frac{1}{2}(I^++I^-)]$, will therefore be independent of the excitation cross section. We have plotted differences and not anisotropies, because the statistical noise introduced by dividing, point by point, by $\frac{1}{2}(I^++I^-)$ makes it impractical. In Table I, however, we give anisotropies calculated from integrated intensities. Calculations are in good agreement with experiment as far as the sign of the dichroism is concerned and the calculated spin-orbit splitting is ≈ 12.5 eV which also agrees quite well with the experimental value of 13.5 eV. The calculated transition energy is too low but only by some 3%. The calculated spectra assume a 0.7 eV Gaussian broadening to account for experimental effects and 0.24 and 0.4 eV Lorentzian broadenings to account for the $2p_{3/2}$ and $2p_{1/2}$ core level lifetimes, respectively.

From Fig. 1 we see that the main disparity lies with the size of the dichroism. It is useful, for the insight it provides, to estimate the size of the dichroism to expect with the help of a simple atomic model. Reference 15 provides just such an approach to deal with x-ray absorption. First let us take the case of a $2p$ electron excited to a continuum state by means of left circularly polarized photons (magnetization is set parallel to the minority spin). The relative probability that the $2p_{3/2}$ core hole left behind will have majority (minority) spin can be evaluated from the matrix elements; it is 37.5% (62.5%). Similarly the relative probability for a $2p_{1/2}$ hole to have majority (minority) spin is 75% (25%) for left circularly polarized photons. The probability coefficients are opposite if right circularly polarized photons are used. Note that in this simple approach, we neglect the mixing of the $2p_{1/2}$ and $2p_{3/2}$ character and shifts in the $2p$ sublevels which can only be evaluated within the framework of a fully relativistic spin-polarized calculation.[8] (They do indeed show up as small shifts in the calculated spectra.) The anisotropy of the $3d\rightarrow 2p$ fluorescence can be written in terms of the probability coefficients and the integrated density of majority spin and minority spin valence states [$\Sigma n_\uparrow(E)$ and $\Sigma n_\downarrow(E)$, respectively]:

$$A(2p_{3/2})=[\tfrac{1}{4}\,\Sigma n_\uparrow(E)-\tfrac{1}{4}\,\Sigma n_\downarrow(E)]/\Sigma n(E)$$

and

$$A(2p_{1/2})=[-\tfrac{1}{2}\,\Sigma n_\uparrow(E)+\tfrac{1}{2}\,\Sigma n_\downarrow(E)]/\Sigma n(E),$$

where $\Sigma n(E)=\Sigma n_\uparrow(E)+\Sigma n_\downarrow(E)$. Assuming that in bcc iron 2/3 of the valence states are occupied by majority electrons (according to Ref. 16, there are 4.6 majority electrons and 2.34 minority electrons), we obtain $A(2p_{3/2})=1/12$ and $A(2p_{1/2})=-1/6$. Even after correction for the polarization rate our experimental values for white radiation are three to four times smaller than those predicted by the SPR-LMTO calculation and less than half the values expected according to the model (see Table I). From the $2p$ occupation numbers we should observe an $L\beta/(L\alpha+L\beta)$ branching ratio of 0.33, but experimentally we obtain a value of approximately 0.13. The relative intensities of $L\alpha$ and $L\beta$ may be modified by self-absorption effects but first we must consider the modifications in the branching ratio introduced by CK transitions.

The CK processes to be considered are L_1-$L_2M_{4,5}$, L_1-$L_3M_{4,5}$, and L_2-$L_3M_{4,5}$. The transition rates, noted f_{ij}^L, have been calculated by a number of authors (see Ref. 17) but we will base our discussion on recent experimental values for nickel.[17]

f_{12}^L and f_{13}^L CK rates are similar (for nickel, Sorensen *et al.*[17] give values of 0.35 ± 0.2 and 0.5 ± 0.2, respectively). This means that their contributions to creating $2p_{1/2}$ and $2p_{3/2}$ holes are about equivalent. We will neglect their effect on the branching ratio and concentrate on the main contribution: the L_2-$L_3M_{4,5}$ process. For nickel f_{23}^L is 0.6 ± 0.2. For simplicity we will guess f_{23}^L to be 0.5 for iron (using the value for nickel would be an overestimate). This means that 50% of the $2p_{1/2}$ holes created by the polarized photon excitation will be shifted to the $2p_{3/2}$ level. The $L\beta/(L\alpha+L\beta)$ branching ratio becomes 0.167 if we make the approximation that the L_3 fluorescence yield is the same whether the $2p_{3/2}$ hole is created directly or via the CK process. The hole when it shifts from the $2p_{1/2}$ to the $2p_{3/2}$ level will keep the same spin. Therefore, the probability for a $2p_{3/2}$ core hole to have a majority (minority) spin changes:

what was a 37.5% (62.5%) probability now becomes a 45% (55%) probability. This considerably reduces the $L\alpha$ dichroism (Table I) but should not affect $A(2p_{1/2})$. In fact the fluorescence yield following the CK process increases because of the extra vacancy in the valence band.[18] Though no quantitative estimates are available, this should appreciably increase the CK-induced dichroic contribution to $L\alpha$.

Self-absorption at the L_3 edge may largely be the cause of the spectacular difference in dichroism to the high energy side of $L\alpha$ compared to theory. However, it should also be born in mind that the CK contribution to $L\alpha$ (not accounted for in SPR-LMTO theory) does not have the same final state as $L\alpha$ because of the extra hole in the valence band. It will therefore be shifted in energy. $L\beta$ is also attenuated by the tail of the L_3 absorption jump.

Excitation by photons tuned to the L_2 edge should favor the $L\beta$ emission as is clearly depicted by the calculated spectrum (Fig. 2). This is trivial because the photoionization cross section for a $2p_{3/2}$ core electron excited to states ≈ 15 eV above E_F is low (roughly 10% that of the $2p_{1/2}$ level photoionized with the same energy). Yet this is not what is observed experimentally. The L_1-$L_2M_{4,5}$ and L_1-$L_3M_{4,5}$ CK processes are definitely not involved as the photon energy is insufficient to excite the $2s$ level. Again the L_2-$L_3M_{4,5}$ process contributes to the $L\alpha$ intensity. But, before pursuing this, we must first understand the sign reversal in the $L\beta$ dichroism.

Excitation to the L_2 edge means that the probability for creating a $2p_{1/2}$ core hole with majority (minority) spin will be modified by the density of unoccupied majority (minority) spin states. Thus our $2p_{1/2}$ level "spin detector" becomes far more sensitive to minority spin electrons because roughly 2.6 of the approximately three unoccupied states have minority spin character. Consequently $A(2p_{1/2})$ changes sign (Table I).

Considering now the $L\alpha$ intensity, we can break it up into its two components: one results from the direct photoionization of the $2p_{3/2}$ level, the other comes from the CK contribution. Assuming again that f_{23}^L is 0.5, half the $2p_{1/2}$ holes produced by initial $2p_{1/2}$ photoionization will shift to the $2p_{3/2}$ level. The CK contribution to the $L\alpha$ intensity, depending on the fluorescence yield after the CK process, is at least equivalent to the intensity observed for $L\beta$. The anisotropy it contributes to the spectrum is the same, i.e., $A(2p_{3/2})_{\mathrm{CK}} = +0.3$. The $L\beta/(L\alpha+L\beta)$ intensity we observe experimentally is in the ratio of 1/3 so half the $L\alpha$ anisotropy comes from the CK term and half from photoionization to continuum states. The expected anisotropy will therefore be ≈ 0.2. There are therefore important implications for MCD in x-ray absorption experiments measured in the fluorescence mode. From the integrated $L_{2,3}$ fluorescence signals for photons tuned to L_2 we estimate that the MCD at the L_2 absorption edge will be underestimated by $\approx 20\%$ in such an absorption experiment.

Experimental artifacts due to self-absorption, plus a limited span of the spectral window affecting the high energy side of $L\beta$, certainly contribute to making it difficult to draw quantitative conclusions at this point but these preliminary experiments show promising agreement between experiment and SPR-LMTO theory. The simplified model approach brings out the existence of strong CK transition effects which were not anticipated in the theory of dichroic x-ray fluorescence. Spin polarization can be estimated reliably from the $L\beta$ emission only unless CK transitions are eliminated by tuning photons to the L_3 edge.

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