Polarization dependence of the 2p-core-level photoemission spectra of Fe

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The energy distribution curves for 2p-core-level photoemission of Fe have been calculated based on a completely relativistic treatment of the core as well as the final states. In accordance with recent experiments, a pronounced dependence on the helicity of the exciting radiation has been found. All features of the experimental spectra could be explained in terms of ground-state properties calculated within the framework of local-spin-density-functional theory. From the results it is concluded that exchange interaction will in general contribute to an appreciable extent to the linewidth of core lines of magnetic systems.

I. INTRODUCTION

It was already realized in the 1930's that the symmetry-breaking properties of spin-orbit coupling gives rise to magneto-optical effects for spin-polarized systems.[1] In the visible regime of light, these effects have been extensively studied for a great variety of materials because of the possible application of the magneto-optical Kerr effect in storage technology.[2] Due to the availability of synchrotron radiation of well-defined polarization, a number of related magneto-optical phenomena in the x-ray regime could be found during recent years. For example, the existence of magnetic x-ray dichroism (MXD) in absorption of circularly and even linearly polarized radiation could convincingly be demonstrated by Schütz and co-workers[3] and by van der Laan *et al.*[4] The Faraday effect, which is intimately connected to the MXD, could later be observed at the K edge of Co by Siddons *et al.*[5]

Apparently somewhat different in nature from these phenomena, Baumgarten *et al.*[6] could show that the 2p-core-level photoemission spectra of Fe depend on the helicity of the used radiation. In the following it is demonstrated that the theoretical approach developed by Ebert *et al.*[7] to deal with the above-mentioned x-ray magneto-optical phenomena and applied successfully to various transition-metal systems[7–9] also allows for a straightforward, parameter-free-interpretation of this kind of experiment.

II. CORE-LEVEL PHOTOEMISSION SPECTROSCOPY USING CIRCULARLY POLARIZED LIGHT

Core-level photoemission spectroscopy [x-ray photoemission spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA)] is nowadays a standard tool for chemical analysis, investigations of chemical bonding, and study of surfaces.[10] In these types of experiments core electrons are excited by electron bombardment or unpolarized x-ray radiation. As one would expect from the various x-ray magneto-optical phenomena, the use of circularly polarized instead of unpolarized radiation should give additional information on the electronic structure especially in the case of magnetic materials. This was indeed demonstrated recently by Baumgarten *et al.*[6] These authors used circularly polarized x rays supplied by a storage ring in combination with a grazing incidence monochromator to study the photoemission from the Fe 2p core levels. The recorded spectra showed a pronounced dependence on the relative orientation of the photon polarization vector and the magnetization. For a fixed magnetization, the $2p_{1/2}$ and $2p_{3/2}$ peaks changed their heights slightly and got shifted in position (in opposite direction) by some tenth of an eV upon reversal of the helicity of the radiation. These findings could qualitatively by explained by taking into account the spin-orbit splitting of the 2p level in combination with an exchange splitting of the sublevels.

Within the one-particle picture, a very rigorous and quantitative description of this experiment could, in principle, be obtained by a straightforward extension of modern photoemission theory for bandlike states,[11] which here, of course, has to treat spin-orbit coupling and spin polarization at the same time. Within this approach, the final state is then described by a time-reversed low-energy electron-diffraction (LEED) state which allows one to calculate the helicity-dependent photoelectron current in a straightforward manner.[11] In contrast to this one-step model of photoemission, we adopt here the simpler point of view that the helicity dependence of the photoelectron current should essentially be determined by the corresponding absorption probability $W_i^{\mathbf{q}\lambda}$ for photons of wave vector $\mathbf{q}$ and helicity λ, exciting electrons from core states i. If the final state is treated as a bulklike state, just as in the three-step model of photoemission, the formalism developed earlier by Ebert *et al.*[7] to study the MXD in core-level absorption spectroscopy can be applied without modifications.

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Within this approach, $W_i^{q\lambda}$ is given by

$$W_i^{q\lambda}(\hbar\omega) = -\frac{1}{\Gamma}\int\int d^3r\, d^3r' \Phi_i^\dagger(\mathbf{r}) X_{q\lambda}(\mathbf{r}) \times \mathrm{Im}G(\mathbf{r},\mathbf{r}',E_i+\hbar\omega) \times X_{q\lambda}^\dagger(\mathbf{r}') \times \Theta(E_i+\hbar\omega-E_F) \,. \quad (1)$$

Here the Dirac bispinor $\Phi_i(\mathbf{r})$ stands for the initial state i, having the energy eigenvalue E_i. The manifold of bandlike final states at energy $E=E_i+\hbar\omega$ is represented by the Green's function $G(\mathbf{r},\mathbf{r}',E)$. The interaction of the electronic system and the photon field is described by the operator

$$X_{q\lambda}(\mathbf{r}) = -e\boldsymbol{\alpha}\cdot\mathbf{A}_{q\lambda}(\mathbf{r}) = -e\boldsymbol{\alpha}\cdot\mathbf{a}_\lambda e^{i(\mathbf{q}\cdot\mathbf{r}+\omega t)} \,, \quad (2)$$

where $\boldsymbol{\alpha}$ is the Dirac matrix vector and $\mathbf{A}$ is the vector potential due to the photon field. The polarization vector $\mathbf{a}_\lambda$ is chosen perpendicular to $\mathbf{q}$ (for further details see Refs. 7–9).

In the following we will restrict ourselves to a polar geometry, i.e., $\mathbf{q}$ is parallel to the sample magnetization. It is, however, straightforward to apply the above formalism to nonplanar geometry using the well-known transformation properties of tensor operators under rotation.[12,13]

To compare with experiment, the corresponding theoretical energy distribution curve (EDC) is obtained by representing the various possible transitions from core states i by a Lorentzian line of a width corresponding to the lifetime of the hole and a height determined by the absorption probability $W_i^{q\lambda}$. The relative position of these Lorentzians is, neglecting all further self-energy corrections, then determined by the corresponding energy eigenvalues E_i of the core states i. This simplification is surely not allowed in all cases but turned out to be well justified in the case of the Fe K-edge absorption spectra.[7] Apparative broadening, finally, is taken into account by folding the superposed Lorentzians with a Gaussian of appropriate width.

III. RESULTS AND DISCUSSION

Adopting the approach outlined above, the EDC's for the various $2p$ core levels of Fe have been calculated. The results for left circularly polarized radiation are shown in Fig. 1. The core-level eigenvalues E_i, which fix the relative position of the various Lorentzian lines, have been obtained by solving the Dirac equation for a spin-polarized potential,[14] as described in Ref. 15; this way spin-orbit coupling and spin polarization are treated on the same level as it is done in the evaluation of the wave functions for the final state.[16] For the calculation of the wave function and scattering path operator used to set up the electronic Green's function $G(\mathbf{r},\mathbf{r}',E)$ (Ref. 16) in Eq. (1), an angular-momentum expansion with $l_{max}=4$ has been applied.

As is obvious from Fig. 1, the spread of the E_i's over an appreciable range of binding energy (see below) will

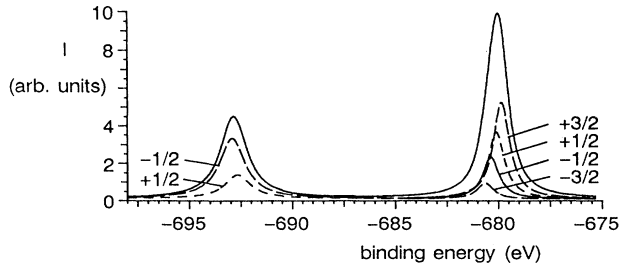

FIG. 1. Theoretical energy distribution curves for excitation from the $2p$ core levels of Fe by absorption of left circularly polarized radiation of energy $\hbar\omega=800$ eV. The contributions from the various μ sublevels are labeled by the corresponding μ value. The abscissa gives the binding energy relative to the muffin-tin zero of the spin-averaged potential (Ref. 14). The width of the Lorentzians has been chosen to be 0.63 eV for the $2p_{1/2}$ levels and 0.4 eV for the $2p_{3/2}$ levels (Ref. 17). No apparative broadening has been included.

contribute to the width of the core lines because, in general, one will not be able to resolve the contributions from the μ sublevels. This is already assumed to have occurred by Fuggle and Alvarado[17] in the extensive study of the core-level width in photoemission. Nevertheless, we have used in Fig. 1 the widths given by these authors: 0.63 eV for the $2p_{1/2}$ and 0.4 eV for the $2p_{3/2}$ states (the larger width of the $2p_{1/2}$ level is caused by rapid $L_2L_2M_{45}$ Coster-Kronig processes[18]). Due to the presence of the spin polarization or, equivalently, an exchange splitting, the $2p$ sublevels of Fe possess no unique total angular-momentum character, i.e., j is no longer a good quantum number. Nevertheless, because the effect of the exchange splitting is small compared to that of spin-orbit splitting, the $2p$ subshells can still be unambigously labeled as $2p_{1/2}$ and $2p_{3/2}$. In contrast to j, the magnetic quantum number μ is still left as a good quantum number and the $2p$ sublevels are characterized accordingly in Fig. 1.

As can be seen from Fig. 1 of Ref. 15, a perturbational treatment of the exchange splitting accounts fairly well for the energetic splitting of the $2p$ sublevels of a hypothetical paramagnetic reference state of Fe. Within this approach, the μ-level splitting is (to first order) proportional to the expectation value of the spin operator σ_z, which is $+\frac{1}{3}$ and $-\frac{1}{3}$ for the $2p_{1/2}$ ($\mu=-\frac{1}{2}, +\frac{1}{2}$) and -1, $-\frac{1}{3}$, $+\frac{1}{3}$, and $+1$ for the $2p_{3/2}$ sublevels ($\mu=-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$). These values of $\langle\sigma_z\rangle$ easily explain the reversed order of the various μ levels of the $2p_{1/2}$ and $2p_{3/2}$ subshells in Fig. 1. Quite similar, the relative peak heights can be explained from the properties of the unperturbed $2p$ sublevels of the hypothetical paramagnetic reference state. For an excitation energy of around 1 keV, the matrix elements from these initial states are completely determined by their dipole-allowed contributions. These permit transitions to final states of $s_{1/2}$, $d_{3/2}$, and $d_{5/2}$ character, with the $2p\rightarrow d$ absorption channel dominating. Inspection of the angular part of the matrix elements easily shows that $W_i^{q\lambda}$ increases

with μ for left circularly polarized radiation, while it decreases for a right circularly polarized one. For the paramagnetic reference state, the μ substates of the $2p_{1/2}$ and the $2p_{3/2}$ shell are, of course, energetically degenerate and the variation of $W_i^{q\lambda}$ with μ for fixed helicity is exactly compensated by the different behavior for reversed helicity. From this it is clear that the resulting photocurrent will not depend on the polarization of the radiation. However, if the system gets spin polarized, the μ sublevels will be shifted in energy as it is visible in Fig. 1, leading to a mismatch of the EDC's for left and right circularly polarized radiation. In addition to this, the core wave functions will get disturbed leading to a μ dependence and an admixture of $2p_{1/2}$ character to the $2p_{3/2}$ states and vice versa. This distortion, which is also present in the final states, affects, of course, the corresponding transition probability $W_i^{q\lambda}$. Accordingly, one can expect that the EDC's for left and right circularly polarized radiation are not only shifted energetically with respect to one another, but are also slightly different in their peak heights. This behavior has been found exactly by Baumgarten *et al.*[6], whose results are reproduced in Fig. 2, in their investigation of the $2p$ photoemission spectra of Fe. Because, in performing these measurements, emphasis has been laid on the spin-dependent effects, the good apparative resolution that is now standard in core-level x-ray spectroscopy[17,18] could not (yet) be achieved due to the low intensity. Comparing our theoretical curves, which have been obtained by a superposition of the various contributions from the μ sublevels (see Fig. 1), we have broadened them accordingly to mimic this effect. As can be seen from Fig. 2, the theoretical polarization-resolved curves show the effects of exchange

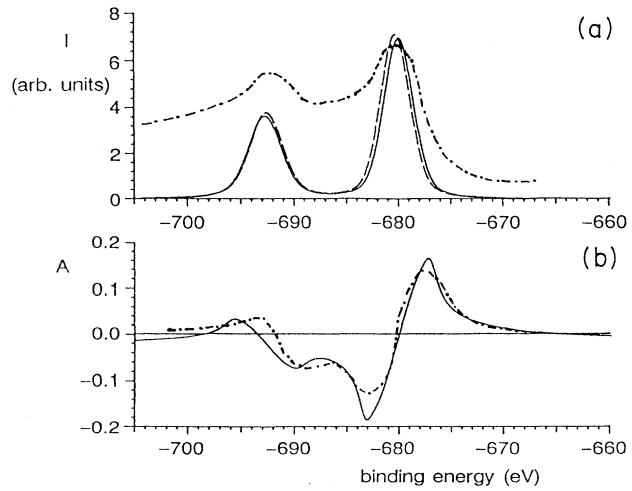

FIG. 2: (a) Energy distribution curves for the $2p$-core-level photoemission of Fe ($\hbar\omega = 800$ eV). The dash-dotted line gives the experimental, polarization-averaged spectrum, while the solid and dashed lines represent the theoretical curves for left and right circularly polarized radiation. (b) Relative difference of the EDC's for left and right circularly polarized radiation (assymetry A). Dash-dotted line: experiment (multiplied by a factor of 6, see text); solid line: theory.

splitting as described above and also found experimentally by Baumgarten *et al.* (see inset if Fig. 1a of Ref. 6). The energetic splitting of these curves can especially be seen. Experimentally it was found to be 0.5 ± 0.2 eV and to be more pronounced for the $2p_{3/2}$ than for the $2p_{1/2}$ peak. This finding is in full accordance with the eigenvalues E_i that are spread over a range of 0.36 eV for the $2p_{1/2}$ and 1.11 eV for the $2p_{3/2}$ shell.[15] From Fig. 1 and the discussion above, it is obvious that the splitting of the EDC's is caused by the exchange interaction. Because all μ sublevels are shifted to a different extent with respect to the paramagnetic reference value, the term exchange splitting for this should, however, not be taken too literally.

The MXD in photoemission, that is expressed by the results of Fig. 2(a), can be seen more clearly in Fig. 2(b), where the relative difference of the EDC's for left and right circularly polarized radiation, i.e., the asymmetry A, is shown. Because of limited apparative resolution and the appreciable widths of the core lines compared to the spin-orbit splitting, the contributions of the $2p_{1/2}$ and $2p_{3/2}$ levels are obviously merged together. Nevertheless, one can still identify both of these contributions in the curves of Fig. 2(b). For the comparison of the theoretical and experimental curves in Fig. 2(b), the experimental asymmetry has been multiplied by a factor of around 6. This, however, does not imply a corresponding discrepancy between theory and experiment. One reason for this is the uncertainty for the degree of polarization of the photonbeam, which was estimated to be 60–80 %. Furthermore, no background subtraction has been applied to the experimental curves of Fig. 2(a). Doing this would lead to a much stronger asymmetry increasing with increasing binding energy. On the other hand, the theoretical asymmetry depends on the broadening that is applied for a comparison with experiment. Keeping these points in mind, the quantitative agreement of both the curves in Fig. 2(b) is completely satisfying, leaving no doubt on the interpretation given above.

Baumgarten *et al.* studied the importance of final-state effects by varying the photon energy between 750 and 850 eV, corresponding to a kinetic energy between around 80 and 180 eV. No significant changes in the asymmetry could be found apart from that caused by increasing secondary electron background. This will surely not hold in all cases because the matrix elements for the various absorption channels may have a different energy dependency — a situation that occurs, for example, in the vicinity of a Cooper minimum.[19] In Fig. 3 we show theoretical asymmetry curves corresponding to a photon energy of 750 and 800 eV. As one can see, some variation of the curves with photon energy is present for large binding energies. Unfortunately, this is the range of energy where secondary electron effects are most pronounced. This means that final-state effects will be obscured in most cases — at least partly — by this mechanism.

Our discussion given above makes clear that the experimentally observed phenomenon of an asymmetry in the polarization of the core- electron photon current using circularly polarized light is caused by the simultaneous presence of spin-orbit coupling and spin polarization.

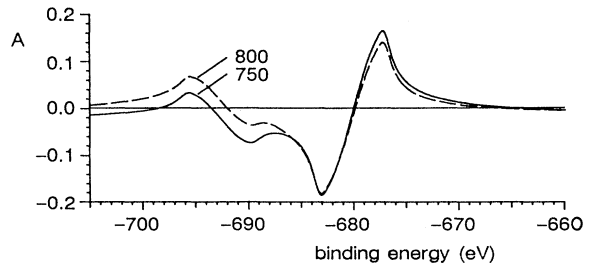

FIG. 3. Relative difference of the EDC's for left and right circularly polarized radiation (asymmetry A) for photon energies (in eV) as indicated.

For this reason it is obviously very closely related to the now quite familiar magnetic x-ray dichroism. Like this effect, the core photoelectron emission provides a very localized probe and for this reason, in addition to its surface sensitivity, will be an interesting tool to study alloying effects. Obviously, an important source for the observed asymmetry is the exchange splitting of the various initial core states. This point of view is, however, in contrast to that taken by Mizuta and Kotani[20] in discussing Auger emission spectra of Fe involving $2p$ states assuming no exchange splitting in the initial core states to be present. However, as it has already been pointed out by Baumgarten *et al.*[6], the existence of large contributions by the core states to the hyperfine fields in ferromagnets completely rules out the correctness of this assumption. Although it is well known that local density-functional theory has problems to account in a fully quantitative way for the core-polarization contribution to the hyperfine field (e.g., the theoretical fields for Fe are approximately 23% too approximately small[21]), there is no doubt that this contribution to the hyperfine field exists.[22]

In summary, our results demonstrate that all features of the experimental $2p$ photoemission spectra of Fe, obtained by using circularly polarized radiation, can be understood on the basis of a fully relativistic calculation of the electronic structure for the ground state within the framework of local-spin- density theory. Finally, one should mention that the situation for the $2p$ photoemission spectra of Fe treated here is fairly clearcut because the effect of the exchange interaction is still small compared to spin-orbit coupling. For the $3p$ levels, the interpretation of the spectra would be much more complicated because the effects of spin-orbit coupling and spin polarization are of the same order of magnitude.[15]

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