CONF-941144--162-Rev. 1

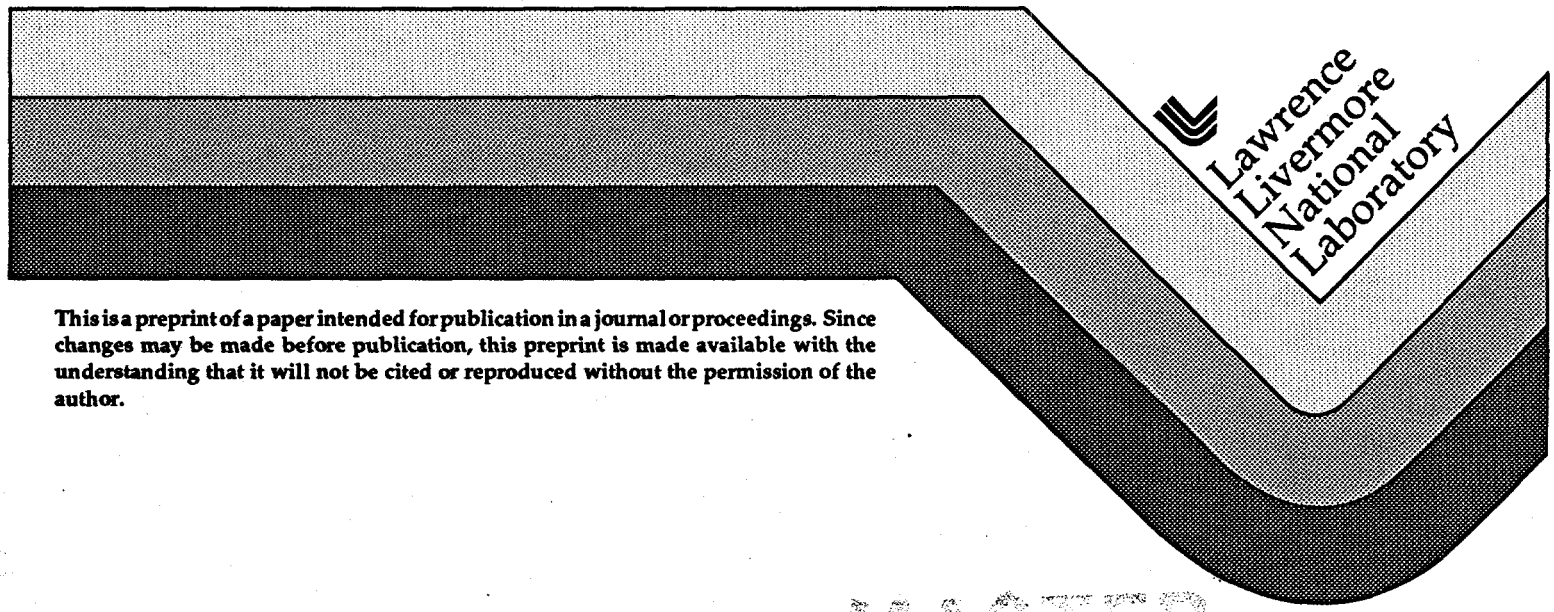
UCRL-JC-116442 Rev 1
PREPRINT

Linear and Circular Dichroism in Angle Resolved Fe 3*p* Photoemission

E. Tamura
G. D. Waddill
J. G. Tobin
P. A. Sterne

This paper was prepared for submittal to the
Fall Meeting of the Materials Research Society
Boston, Massachusetts
November 28–December 2, 1994

December 7, 1994



GH

Linear and Circular Dichroism in Angle Resolved Fe 3p Photoemission

E. Tamura[1], G. D. Waddill[1], J. G. Tobin[1], and P. A. Sterne[2,1]
[1]*Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550*
[2]*Department of Physics, University of California, Davis, CA 95616*

ABSTRACT

Using a recently developed spin-polarized, fully relativistic, multiple scattering approach based on the layer KKR Green function method, we have reproduced the Fe 3p angle-resolved soft x-ray photoemission spectra and analyzed the associated large magnetic dichroism effects for excitation with both linearly and circularly polarized light. Comparison between theory and experiment yields a spin-orbit splitting of 1.0 – 1.2 eV and an exchange splitting of 0.9 – 1.0 eV for Fe 3p. These values are 50 – 100 % larger than those hitherto obtained experimentally.

INTRODUCTION

Magnetic linear and circular dichroism (MLD,MCD) in core-level photoemission from ferromagnetic materials have been recognized as potentially valuable probes of the magnetic properties of both bulk and surface atoms [1]. Surface sensitivity can be enhanced by grazing-angle emission configurations or by the use of lower photoelectron kinetic energies (below 100 eV), in which case it is well known from low-energy electron diffraction (LEED) that multiple scattering of photoelectrons by crystal atoms plays an essential role. Previous theories of magnetic effects in core-level photoemission either treat isolated atoms with no multiple scattering effects [2], or include multiple scattering, but neglect the surface completely [3]. So far no theory has been reported in which these multiple scattering effects are taken into account in the propagation of photoelectrons through the surface including both spin-orbit and exchange interactions on an equal footing. These two interactions and their interference effects are essential for a complete description of magnetic dichroism. Hence, a full interpretation of magnetic dichroism photoemission requires a fully relativistic and spin-specific multiple scattering approach.

Recently, a large MLD effect was reported in angle-resolved soft x-ray photoemission from the 3p state of the Fe(001) surface [1], in which a striking dependence of photoemission line shape upon the directions of magnetization, light polarization, and electron emission was found. The multiplet structure of the magnetic Fe 3p state, which is not well understood [4], is very challenging theoretically in that neither spin-orbit nor exchange interaction can be treated as a perturbation [5].

In this work, we demonstrate the importance of appropriate theoretical modeling in the interpretation of magnetic dichroism measurements using angle-resolved soft x-ray core-level photoemission as a probe of the surface and bulk electronic structures of magnetic materials. Using a recently developed spin-polarized photoemission theory, we show for the first time that these spectra can be quantitatively explained within a simple single-particle picture taking account of bulk and surface multiple scattering effects in final photoelectron states.

We also present a theoretical analysis of experimental data for Fe/Cu(001) [6], revealing a strong emission angle dependence in MCD spectra.

RELATIVISTIC PHOTOEMISSION THEORY

Neglecting scattering between photoelectrons and their holes in the photoexcitation process [7], the spin density matrix of the photoelectrons can be written in the form

$$\rho_{\sigma\sigma'} = -\frac{1}{\pi} v_e < \psi^{\sigma} | \Delta \mathrm{Im} G \Delta^{\dagger} | \psi^{\sigma'} > \qquad (1)$$

where $|\psi^{\sigma}>$ is the time-reversed LEED state for spin σ, G the single hole Green function, and v_e the velocity of the photoelectrons. The electron-photon interaction Δ is well approximated here by the dipole form and the intensity and spin polarization of photoelectrons are obtained from the spin density matrix [8]. Although the photocurrent can be fully described by the single-hole Green function, it is difficult to renormalize the Green function to account for the many-body interaction between the hole and the other crystal electrons [9]. For materials that are well described by a localized picture, it might be easier to treat the many-body effects by explicitly assuming several atomic configurations with a core-hole Thole,Laan. This approach has been used to interpret Ni $3p$ core-level photoemission in terms of multiplet and satellite structures [11]. For delocalized systems like metallic Fe, the problem is more complicated and has been studied only for the free electron system, in which the line spectra are modified with a Doniach-Sunjic (DS) line shape characterized by a singularity parameter [12]. Since a DS line-shape modification does not affect the positions of lines in the multiplet structures, we have not included this type of many body effect in our calculations.

Many-body effects are included in our calculation in two different ways. First, finite hole lifetime effects are included through an imaginary part of the optical potential in the hole Green function, broadening the discrete energy eigenstates into a continuous spectrum. Second, the effective potentials (i.e. self-energy correction) for the $3p$ holes are expected to be strongly energy- (state-) dependent and act differently on the majority and minority spin so that the effective spin-orbit and exchange splittings can be modified from the ground-state values in the photoexcitation process. Instead of estimating the effective potentials in a many-electron theory [9], we treat these splittings and a center binding energy of the $3p$ holes as adjustable parameters and determine them by comparing to the experimental spectra. The magnetic Dirac equation based on density functional theory is accordingly modified in the core-state calculations [13]. The exchange splitting is reduced by renormalizing the difference between the majority and minority spin ground-state potentials. For the spin-orbit interaction, we construct a quasi-relativistic Dirac equation in which the strength of the spin-orbit coupling can be continuously tuned from the fully relativistic to the scalar relativistic Dirac equation[13],Takeda.

These approximations to the many-body effects allow us take full advantage of the realistic final state wavefunction calculated by our fully relativistic multiple scattering computer code based on the layer KKR Green function method [8]. An accurate representation of the final LEED state is very important, since it is known to be very energy-sensitive in the low energy region, and its character can change across the entire Fe $3p$ linewidth, thereby altering the photoemission spectra.

NUMERICAL RESULTS

Underlying our spectral analysis is a calculation of the angular-momentum specific density of states (DOS) of the Fe $3p$ core level. In Fig.1, we show the $3p$ DOS, the imaginary part of

the Green function, with both spin-orbit and exchange splittings chosen to be 1 eV, compared to the original values of 1.6 and 2.4 eV from bandstructure calculations. While an exchange-splitting reduction is commonly observed in photoemission spectra and has been explained theoretically [9], the spin-orbit splitting reduction might be understood as a consequence of the screened interaction between the nucleus and the hole by the other electrons, since the $3d$ orbitals are more localized than the $3p$ orbitals in an atomic picture.

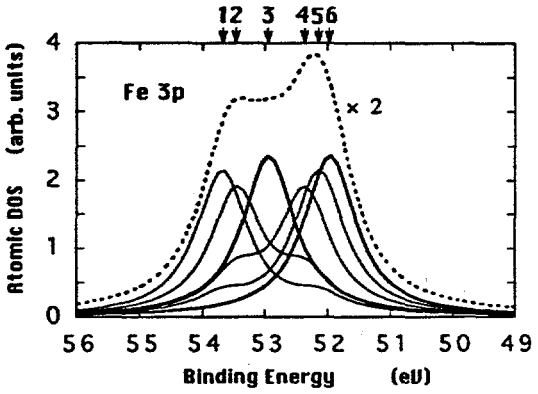


FIG.1 Angular momentum projected density of states (DOS) of the Fe $3p$ state of the bulk atom. To facilitate comparison with experiment, the DOS has been shifted 1 eV to higher binding energy. The thick solid lines correspond to (j, μ) of $(3/2, 3/2)$ and $(3/2, -3/2)$, the thin lines to $(1/2, -1/2)$, $(1/2, 1/2)$, $(3/2, 1/2)$, and $(3/2, -1/2)$, in the order of peak location in decreasing binding energy. The dotted line is to the total DOS. The quantization axis is parallel to the majority-spin direction. The arrows indicate the energies of the eigenstates without lifetime broadening.

The hole lifetime is assumed to be $(0.5\ \text{eV})^{-1}$ and energy-independent. In general, the lifetime is shorter for higher binding-energy states. The exchange splitting can be deduced from the energy difference between the states $\mu = 3/2$ and $-3/2$ of $j = 3/2$ (indicated by the arrows 3 and 6) since these are pure spin states and their relative energy positions are independent of the spin-orbit interaction. The spin-orbit splitting can be identified by calculating an energy center of the j-states, or by setting the exchange splitting to be zero in the hole Green function calculation. Since the total angular momentum j is not a good quantum number for the other four states, they are strongly hybridized between $j = 1/2$ and $j = 3/2$ within the same gyromagnetic quantum number μ.

MLD from Fe(001)

Using this $3p$ DOS as a basis, we can analyze the experimental $3p$ MLD results. The photoemission spectra corresponding to our Fe $3p$ DOS, excited normally by linear polarized light, are compared in Fig. 2 with the experimental data of Ref. [1]. Use of the original bandstructure values for the spin-orbit and exchange splittings does not qualitatively alter the $3p$ DOS, but the calculated spectra are dramatically affected, and this strong dependence was used to determine the best values for these parameters. Calculation of the final LEED states uses the same bulk muffin-tin potential as the $3p$ state calculation, but with spin-orbit and exchange splittings taken without modification from the original bandstructure calculation. We assume a truncated bulk geometry for the Fe(001) surface atomic arrangement. Allowing for the background which has not been subtracted from the experimental data, the agreement is excellent for all the spectra with respect to the peak positions, crossover points for the different magnetization directions $\mathbf{M}$, and intensity ratios between s- and p-polarized light. The main differences are due to omission of Doniach-Sunjic lineshapes and state-dependent lifetime broadenings in the theoretical spectra. Best agreement is obtained with calculations using a spin-orbit splitting of 1.0–1.2 eV and an exchange splitting of 0.9–1.0 eV for the Fe

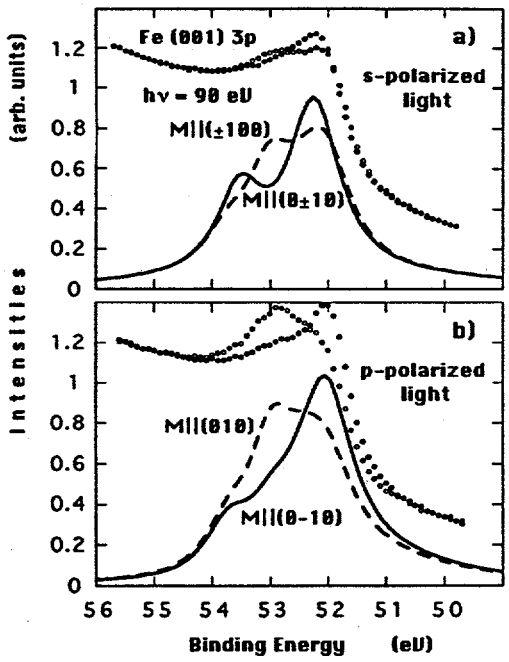


FIG.2 Experimental and theoretical photoemission spectra emitted normally from the $3p$ state of the Fe(001) surface by linearly polarized light of 90 eV incident at polar angle $\theta = 74°$ parallel to [100]. Magnetic moment vectors lie in the surface-parallel plane: (a) parallel/antiparallel to [100] (solid circles and solid line) and to [010] (the open circles and dashed line) for s-polarized light (electric field vector **E** parallel to [010]), and (b) parallel (solid circles and solid line) and antiparallel (open circles and dashed line) to [010] for p-polarized light (**E** in the plane perpendicular to [010]).

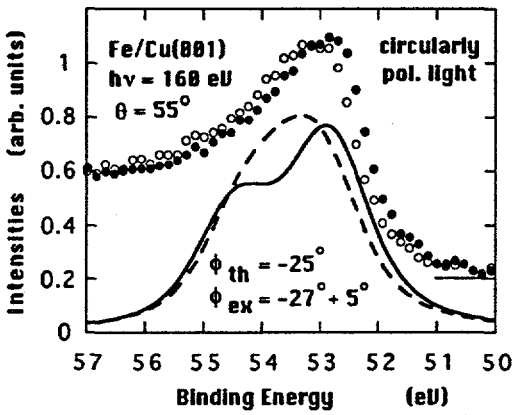
$3p$ state. A spin-orbit splitting of The peak around 53 eV in both panels is clearly attributed to the transition from the state $\mu = -3/2$ $j = 3/2$ (c.f. Fig. 1). From initial-state-projected calculations in which all transitions are identified, we found that the transitions from the states $\mu = \pm 3/2$ $j = 3/2$ do not contribute to the spectra when **M** is parallel to the electric field vector **E** of s-polarized light (solid line in (a)). The spatial part of these initial states is symmetric with respect to the (010)-mirror plane (perpendicular to **M**), and the final LEED states are also well approximated by a product of a symmetric spatial function and spin functions for normal emission. The matrix element vanishes for $\mathbf{E} \parallel \mathbf{M}$ which acts as an antisymmetric function in the dipole matrix element calculation. Thus these transitions dominate changes in the spectral line-shape with changes in magnetization direction. This was found to be moderately true also for the case of p-polarized light.

MCD from Fe/Cu(001)

As a further test of the theory, we have studied the system composed of two monolayers of fcc Fe on Cu(001), both experimentally and theoretically, using magnetic circular dichroism photoemission. The Fe layers were remanently magnetized along the surface normal and circularly polarized light incident normally. The photoelectrons were collected at a polar emission angle 55° and an azimuthal angle $-27° \pm 5°$. Both the helicity and magnetization were independently varied, to consider all four possible configurations.

In our calculations, the geometrical arrangement of the Fe atoms is assumed to be a perfect continuation of the bulk fcc Cu crystal. The potentials are obtained from a scalar relativistic LMTO calculation within the atomic-sphere approximation for the 12-layer super lattice with five Cu, four Fe, and three empty layers. From our LEED analysis where a strong diffuse pattern was observed, we concluded that the Fe layers do not grow ideally and a possible clustering takes a place under our experimental condition. To allow for this, we neglect the intralayer-multiple scattering for the Fe layers. The self-energy correction for the

Fe $3p$ core-hole state is treated in the same way as in the Fe(001) surface calculations. The results are presented in Fig. 4 where the theoretical spectra are Gaussian-convoluted by the experimental resolution of 0.75 eV. The agreement is quite satisfactory, given the simplicity of the model used to describe the quasi-ordered surface. The main dichroism feature in the energy region 52–53 eV, the splitting of 0.25 eV, is well reproduced theoretically and can be attributed to the transition from the state $\mu = -3/2$ $j = 3/2$ as in the case of linearly polarized light.



Experimental and theoretical photoemission spectra emitted from the Fe $3p$ state of the Fe/Cu(001) surface by left-handed circularly polarized (positive helicity) light of 160 eV incident normally. Polar emission angle $\theta = 55°$ and azimuthal angle $\phi = 27°$ (25°) for experiment (theory) referred to the [001] direction. The magnetic moment vector is parallel (solid circles and solid line) or antiparallel (open circles and dashed line) to the light helicity.

Further calculations were done using different azimuthal angles to find the emission-angle dependence of the splitting; it was found that the splitting varies slowly from 0.0 to 0.4 eV for rotation through 45°. In the past this splitting has often been interpreted as the exchange splitting of Fe $3p$. Unfortunately this is incorrect, although it is certainly introduced by exchange interaction. The splitting simply depends on how strongly the dipole-allowed components are excited in the final states. The specific components are $\mu = -1/2$ $j = 1/2$ and $5/2$ (s- and d-waves) for the transition by the positive helicity light and $\mu = -5/2$ $j = 5/2$ (d-wave) by the negative helicity light from the state $\mu = -3/2$ $j = 3/2$. The relative strength can be predicted numerically for the off-normal emission into nonsymmetric directions. Based upon our theoretical analysis, in general the MCD effect is as large as the MLD in some emission angle extent.

CONCLUDING REMARKS

We have demonstrated that magnetic dichroism in angle-resolved soft x-ray core-level photoemission is a powerful tool for studying the electronic structure of magnetic materials. Interpretation of experimental results is not straightforward, but requires appropriate theoretical modeling to extract unique information. Using our newly developed computer code based on the spin-polarized fully relativistic multiple scattering theory to model linear and circular dichroism spectra we have determined the spin-orbit and exchange splittings of the Fe $3p$ core level. Our calculations demonstrate that appropriate experimental conditions can further elucidate the role of spin-orbit and exchange interactions in the photoemission process.

* * *

The authors gratefully acknowledge A. Gonis for his encouragement. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

REFERENCES

[1] Ch. Roth *et al.*, Phys. Rev. Lett. **70**, 3479 (1993), Solid State Commun. **86**, 647 (1993)
[2] B. T. Thole and G. van der Laan, Phys. Rev. B **49**, 9613 (1994)
[3] H. Ebert *et al.*, Phys. Rev. B**44** 4406 (1991)
[4] F. Sorotti *et al.*, Phys. Rev. B**48** 8299 (1993)
[5] H. Ebert, J.Phys. Matter **1**, 9111 (1989)
[6] D.P. Pappas *et al.*, J. Appl.Phys. **73**, 5926 (1993)
[7] H. Gollisch *et al.*, Solid State Commun. **82** 197 (1992)
[8] E. Tamura, *Mat. Rec. Soc. Symp. Proc.* **253**, 347 (1992)
[9] A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1979), Phys. Rev. B**23** 5203 (1981)
[10] B. T. Thole and G. van der Laan, Phys. Rev. Lett. **67**, 3306 (1991), Phys. Rev. B**44**, 12424 (1991)
[11] G. van der Laan *et al.*, Phys. Rev. Lett. **69**, 3827 (1992)
[12] S. Doniach and M. Sunjic, J. Phys. C**3**, 285 (1970)
[13] E. Tamura, in preparation. In contrast to the usual core-state calculation (e.g. Ref.[5]) we solve the Dirac equation in a Green function formalism on the complex-energy plane.
[14] T. Takeda, Z. Physik B**32**, 43 (1978)
[15] E. Tamura and R. Feder, Europhys. Letters **16**, 695 (1991)