Circular Dichroism in Core Photoelectron Emission from (1x1) Oxygen on W(110): Experiment and Theory

H. Daimon[1,4], R.X. Ynzunza[1,2], F.J. Palomares[1,2,3], E.D. Tober[1,2], Z. Wang[1,2], J. Morais[1],
R. Denecke[1,2], M. Rice[2], J.B. Kortright[2], Z. Hussain[2], M.A. Van Hove[1], and C.S. Fadley[1,2]
[1]Lawrence Berkeley National Laboratory, Berkeley, CA 94720
[2]Department of Physics, University of California-Davis, Davis, CA 95616
[3]ICMM-CSIC, Cantoblanco E-28049, Madrid, Spain
[4]Department of Materials Physics, Osaka University,Toyonake, Osake 560, Japan

INTRODUCTION

One of the several advantages of using synchrotron radiation is the possibility of varying it from linear polarization (LP) to left and right circular polarization (LCP and RCP), and we have used beamline 9.3.2 at the ALS [1(a)] to exploit this capability in high-resolution core-level photoelectron emission. This beamline is the only one at the ALS presently capable of varying polarization over a broad energy range from ~30 to 1500 eV. In connection with core photoelectron emission from surfaces, it then becomes possible to look for circular dichroism effects in which the intensity with LCP excitation (I_{LCP}) is not equal to the intensity with RCP excitation (I_{RCP}). Such effects are known to occur for both non-magnetic [2,3] and magnetic [4,5] systems. For the latter, they constitute a novel element-specific way of studying both atomic structure and local magnetic order [4,5], but the question then arises of clearly distinguishing non-magnetic from magnetic circular dichroism effects [2(b),3].

In order to better understand the interrelationship between non-magnetic circular dichroism [2,3] and magnetic circular dichroism [4,5], we have performed circular dichroism measurements for the non-magnetic system of a (1x1) oxygen overlayer on W(110). This incipient-oxide overlayer corresponds to a coverage of 1 ML of oxygen, leads to a (1x12) superstructure in its LEED pattern, and exhibits W 4f core spectra that are easily resolvable into "oxide" and bulk components separated by ~0.73 eV [6]. Such non-magnetic circular dichroism in core photoelectron angular distributions (CDAD) was first observed by Schönhense et al. from CO/Pd(111) [2(a)]. This experiment showed that, even in what are overall non-chiral atomic geometries, circular dichroism may be present in core photoelectron emission. Subsequent to this, Daimon et al. observed similar effects in core emission from Si(100) [3(a)], and we will relate our experimental findings for O/W to a theoretical model for these effects introduced by them, as well as to more accurate multiple scattering photoelectron diffraction calculations of such effects.

EXPERIMENT

The experiment was performed at beamline 9.3.2 of the ALS [1(a)], with angle-resolved and chemical-state-resolved photoelectron spectra being measured using its advanced photoelectron spectrometer/diffractometer [1(b)]. The (1x1)-(1x12) oxygen overlayer was prepared on a clean W(110) surface by a method described elsewhere [6]. The experimental geometry is shown in Fig. 1(a). The photons were incident normal to the sample surface and were chosen to be linearly polarized, left circularly polarized, or right circularly polarized. A degree of circular polarization of 85% can be achieved by means of a movable aperture at the entrance to the beamline [1(a)]. The first photon energy was 366 eV, leading to W 4f photoelectrons at 335-339 eV which were analyzed using a Scienta SES 200 spectrometer [1(b)]. A typical spectrum is shown in Fig. 1(b), and each member of the 5/2, 7/2 doublet consists of a bulk peak and an oxide peak that is shifted to higher binding energy (lower kinetic energy) by ~0.73 eV. Separate photoelectron diffraction patterns have been measured for these two types of photoelectron peaks. The sample was rotated in azimuthal angle (ϕ) and the analyzer was rotated in polar angle (θ) over a range of approximately 27.5°so as to preserve the normal incidence of the light. In this way, both intensities could be measured over a θ range (as measured with respect to the surface) of 16.5° to 44° and a solid angle corresponding to ~41% of the 2π steradians above the surface.

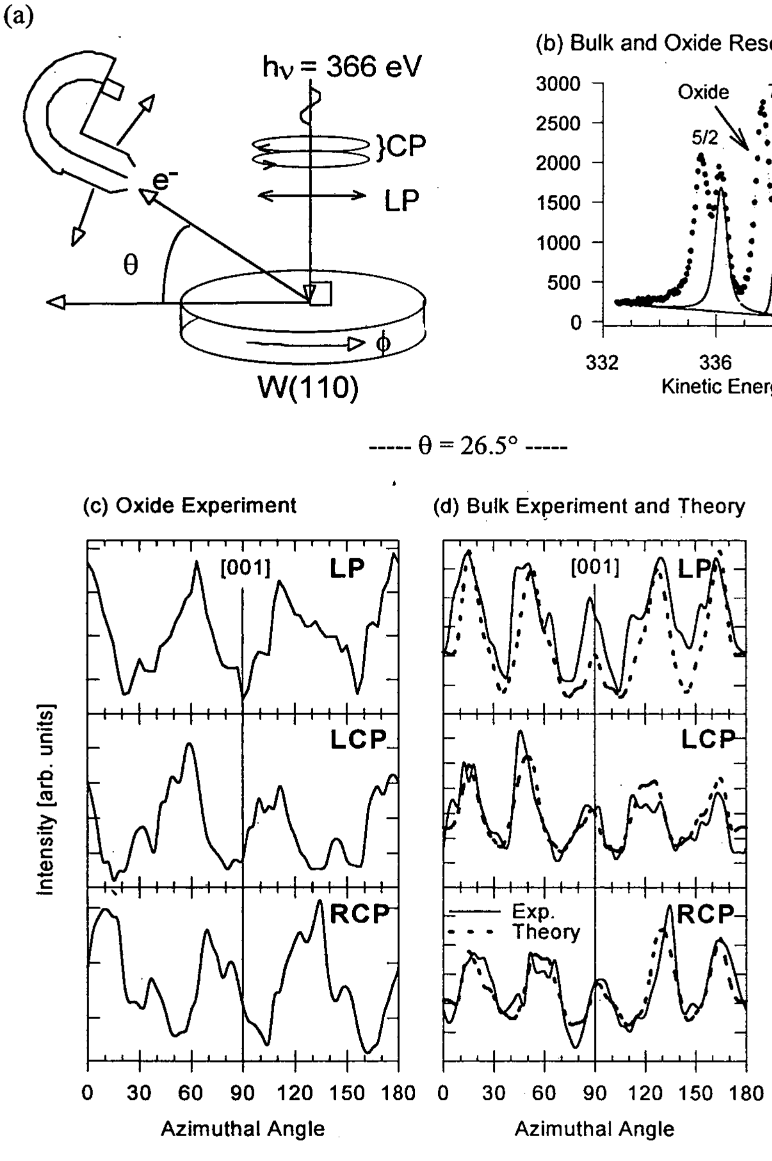

Figure 1. Circular dichroism in the angular distributions (CDAD) of photoelectrons from a (1x1) oxygen overlayer on W(110) with a (1x12) oxide superstructure: (a) The experimental geometry, with radiation incident normal to the surface and a rotating Scienta spectrometer being used to measure at various takeoff angles θ; (b) A typical W 4f spectrum with oxide and bulk peaks resolved in both the 5/2and 7/2 components; (c) Azimuthal scans at a takeoff angle of 26.5° for the oxide W4f component for linearly polarized light (LP), left circularly polarized light (LCP), and right circularly polarized light (RCP); (d) Comparison of the analogous experimental curve for bulk emission with theoretical photoelectron diffraction calculations.

Azimuthal photoelectron diffraction patterns at a 26.5° polar takeoff angle are shown in Figs. 1(c) and (d) for oxide and bulk emission in all three polarizations. Comparing the diffraction patterns for LCP and RCP excitation for either oxide or bulk, we see that some features appear to exhibit azimuthal peak "rotations" across the [001] mirror plane at ϕ = 90°, with the diffraction peaks for LCP being shifted to the left and those for RCP being shifted to the right. However, other differences between the LCP and RCP curves do not follow such a simple characterization. Fig. 2 shows a full data set for both oxide and bulk emission, with the photon energy here being 280 eV. Similar azimuthal peak rotations (especially visible in the oxide data) and other more complex changes between LCP and RCP can be seen here as well. The sum of I_{LCP} and I_{RCP} is also found to be very nearly equal to I_{LP}, a result which is not rigorously true for all cases, but can be shown to be a good approximation for W 4f in our geometry and for our kinetic energy range.

Such diffraction peak rotations with changing circular polarization were first observed and theoretically interpreted in terms of a physically intuitive model by Daimon et al. [3(a)]. This model relies on the dipole selection rules for circularly polarized light ($\Delta m = m_f - m_i = -1$ for LCP and $\Delta m = +1$ for RCP), combined with an estimate of the relative strengths of the various allowed transitions to different $|\ell_f, m_f\rangle = |\ell_i \pm 1, m_f\rangle$ final states. This leads to final-state wave functions that are for many cases dominated by $|\ell_f, m_f\rangle = |\ell_i + 1, \ell_i \pm 1\rangle$, with the two signs holding for the two different circular polarizations. The spherical harmonics associated with these wave functions in turn have an azimuthal dependence of $\exp(i m_f \phi)$, and they thus yield spiraling surfaces of constant phase in azimuth, rather than the simpler spherical surfaces of constant phase that are more often seen in the radial dependence of the wave functions. Since the photoelectron current will be carried perpendicular to these constant phase surfaces, the photoelectron diffraction features are predicted to be rotated in opposite directions by the two polarizations. Simple formulas for estimating these rotations have been presented elsewhere and compared to experimental data, where they are found to well reproduce Si(001) peak shifts [3].

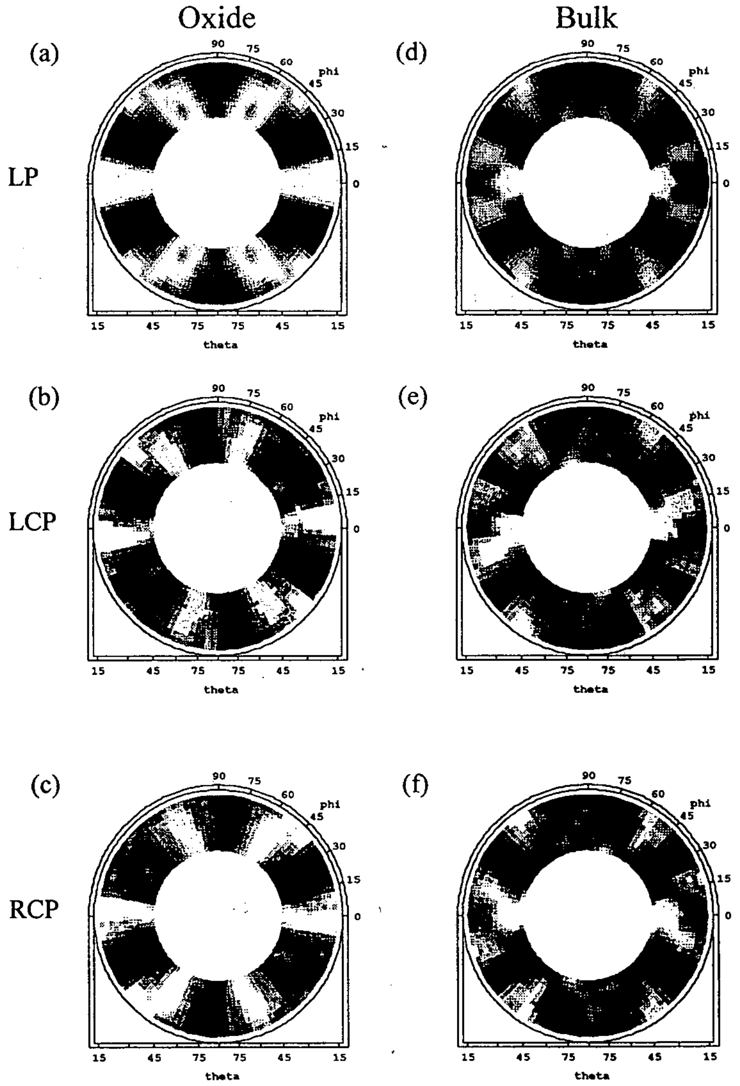

Figure 2. Large-solid-angle photoelectron diffraction patterns for oxide ((a),(b),(c)) and bulk ((d),(e),(f)) W 4f emission from a (1x1)-(1x12) oxygen overlayer on W(110). Panels (a) and (d) are for excitation with linearly polarized light, (b) and (e) are for left circularly polarized light, and (c) and (f) are for right circularly polarized light. Note the apparent rotations of certain major features in the patterns between left and right circular polatization.

A more accurate picture of these effects is to include all allowed transitions with their precise weightings, as well as single and multiple scattering of the outgoing photoelectron wave. Such calculations have been applied successfully to Si(001) by Kaduwela et al. [7], and we here apply them to our data for O/W. These calculations were performed using a program developed by Kaduwela et. al. [7] and based on the Rehr-Albers approximation for treating multiple scattering. The preliminary calculated curves in Fig. 1(d) were obtained for bulk emission. Even though the atomic cluster used did not include the O atoms (a reasonable first approximation due to their being much weaker scatterers than W), this theory correctly predicts not only the gross motion of certain features that one can describe as rotations, but also various other peak distortions beyond this simple description. It is thus clear that, although the model of Daimon et al. [3(a)] correctly describes the basic physics of the peak rotation phenomenon, a fully quantitative description of such non-magnetic CDAD effects will require a complete treatment of the excitation matrix elements, including photoelectron scattering and diffraction.

CONCLUSIONS

Circular dichroism in core photoelectron angular distributions for non-magnetic systems can result in large differences in I_{LCP} and I_{RCP} of up to ±50%, and such effects are expected to be very generally observable. Our results for O/W show that these effects can arise for different chemical states in a single sample and that they can be predicted quantitatively by photoelectron diffraction calculations. Such non-magnetic circular dichroism effects due to photoelectron diffraction must also be included in any interpretation of analogous MCD experiments with magnetic materials. For example, in the 2p levels of the 3d ferromagnetic metals, MCD is only ± a few % in magnitude [4], and thus potentially much smaller than the non-magnetic contributions [2(b)]. For the high-spin 4f ferromagnet Gd, MCD has been found to be about ±35%, and thus about 7 times larger than the non-magnetic diffraction contributions [5]; nonetheless, even for this case the non-magnetic diffraction effects cannot be fully neglected.

REFERENCES

[1](a) Z. Hussain, W. R. A. Huff, S. A. Keller, E. J. Moler, P. A. Heimann, W. McKinney, H. A. Padmore, C. S. Fadley, and D. A. Shirley, J. Elec. Spec. and Rel. Phen. **80**, 401 (1996) and abstract by E.J.Moler et al. elsewhere in this volume. (b) C.S. Fadley, M.A. Van Hove, Z. Hussain, and A.P. Kaduwela, J. Elec. Spec. and Rel. Phen. **75**, 273 (1995) and abstract by R.X. Ynzunza et al. elsewhere in this volume.

[2] (a) G. Schönhense, Phys. Scr. **T31**, 255 (1990); J. Bansmann et al., Phys. Rev. B**46**, 13496 (1992). (b) C. Westphal, A.P. Kaduwela, C.S. Fadley, and M.A. Van Hove, Phys. Rev. B **50**, 6203 (1994).

[3] (a) H. Daimon, T. Nakatani, S. Imada, S. Suga, Y. Kagoshima, and T. Miyahara, Jpn. J. Appl. Phys. **32**, L1480 (1993); H. Daimon, T. Nakatani, S. Imada, and S. Suga, J. Elec. Spec. Rel. Phen. **76**, 55 (1995); (b) .A.P. Kaduwela, H. Xiao, S. Thevuthasan, C.S. Fadley, and M.A. Van Hove, Phys. Rev. B **52**, 14927 (1995).

[4] L. Baumgarten, C.M. Schneider, H. Peterson, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492, (1990).

[5] R. Denecke, J. Morais et al., abstract elsewhere in this volume.

[6] K.E. Johnson, R.J. Wilson, and S. Chiang, Phys. Rev. Lett. **71**, 1055 (1993); R. Ynzunza et al., abstract elsewhere in this volume.

[7] A.P. Kaduwela, D.J. Friedman, and C.S. Fadley, J. Elec. Spectrosc. and Relat. Phenom. **57**, 223 (1991).

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098; and by ONR (Contract N00014-94-0162).

Principal investigator: R.X. Ynzunza, Materials Sciences Division, Lawrence Berkeley National Laboratory. Email: ramon@photon.lbl.gov. Telephone: 510-486-4581.