Original Paper

Relativistic Spin-Polarized X-ray Photoelectron Diffraction Theory from Heavy Elements

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Spin-Polarized X-ray Photoelectron Diffraction (SPXPD) is a useful tool in studying magnetic structure of solid surfaces. In this work SPXPD is studied on the basis of multiple scattering theory in the relativistic framework. This approach is inevitable in studying the XPD and SPXPD patterns from heavy elements (Z>50), where relativistic effects play important roles.

1. Introduction

Magnetic ordering at the outermost surface layers can be different from that in the bulk [1]. Among several tools for the study of surface magnetic structures, spin-polarized x-ray photoelectron diffraction (SPXPD) is one of the promising methods because its patterns directly provides the information about important local surface magnetic structures. Here SPXPD is studied on the basis of multiple scattering theory in the relativistic framework. This approach is inevitable in studying the XPD patterns from heavy elements [2]. XPD patterns give the information on structures at surface, while SPXPD patterns give the information on magnetic structures at surface.

The mechanism which induces the spin polarization is classified into two modes. One mode is to utilize the spin polarization caused by multiplet splitting as observed in magnetic materials like Gd metals. This splitting (^7S and ^9S peak) is caused by the difference in the exchange interaction between the two core-hole states. If we look at the multiplet splitting in Gd 4s, 5s photoemission [3], we can detect spin-polarized photoelectrons excited even by conventional X-ray sources without use of circularly polarized synchrotron radiation. We thus expect that SPXPD patterns from solid surface could provide some useful information about magnetic order in experimentally feasible ways.

The second mode is to use circularly polarized X-rays to induce the spin polarization of photoelectron due to the spin-orbit (s-o) coupling [4]. These spin-polarized photoelectrons must be detected at the specific directions even when the absorbing atoms and scattering atoms have no magnetic moment [5]. In this case spin polarization due to the multiplet splittings in the sense of the first mode does not occur, but in the case of magnetic materials, spin polarization by both the first and the second mode occur if we use circularly polarized light. In this work we study the relativistic effects in SPXPD patterns from light and heavy elements by circularly polarized light, and discuss necessity of the relativistic SPXPD calculations.

2. Theory

A general one-electron relativistic SPXPD theory has been developed by the present authors on the basis of multiple scattering theory [2]. This theory can describe the second mode of SPXPD, whereas the first mode is out of the scope because the multiplet splittings are a many-body effect in the core-hole states. We thus have developed a many-body SPXPD theory based on a relativistic quantum electrodynamic (QED) theory [6, 7]. This theoretical framework provides a unified view of these two SPXPD modes. With this framework we can calculate SPXPD patterns by circularly polarized light from magnetic materials which give rise to multiplet

splittings. A useful formula of the photoelectron current with momentum $\mathbf{p}$, spin σ and kinetic energy $\varepsilon_p(=p^2/2)$ excited by ($\mathbf{k}s$) X-ray photons is given by [7]

$$\begin{aligned}
&\mathbf{j}_{\mathbf{p}\sigma} \propto \mathbf{p}\sum_n |S_n|^2 \left|M_1+M_2+M_3+\cdots\right|^2, \\
&M_1(\mathbf{p},\sigma)_{\mathbf{c}} =< f^-_{\mathbf{p}\sigma}|\triangle|\varphi_{\mathbf{c}}>, \\
&M_2(\mathbf{p},\sigma)_{\mathbf{c}} =< f^-_{\mathbf{p}\sigma}\left|\delta T^{\mathbf{r}} g^{\mathbf{r}}_{\mathbf{11}}\triangle\right|\varphi_{\mathbf{c}}>, \\
&M_3(\mathbf{p},\sigma)_{\mathbf{c}} =< f^-_{\mathbf{p}\sigma}\left|Q\triangle\right|\chi_{\mathbf{c}}>,
\end{aligned} \tag{1}$$

where $|\varphi_c\rangle$ and $|\chi_c\rangle$ are the large and the small components of the core function, $< f^-_{\mathbf{p}\sigma}|$ is the photoelectron function, $\triangle$ is the electron-photon interaction operator, $\mathbf{k}$ and s denote the X-ray wave vector and its polarization, δT^r include s-o interaction which acts on the photoelectron and describe the longitudinal relativistic effects on the photoelectron propagation in the target, $S_n =< n, N-1\,|b|\,0, N>$ is the nonrelativistic intrinsic amplitude, where b is the core electron annihilation operator, and $Q=(\sigma\cdot\mathbf{p})/(2c)$. The different states $|n, N-1>$ are responsible for the multiplet splittings. M_1, M_2 and M_3 are direct, single scattering and double scattering term respectively. This formula is the basis for the SPXPD analyses used in the present study. For $f^-_{\mathbf{p}\sigma}$ we can apply site T matrix expansion, which yields multiple scattering series [2].

3. SPXPD by circularly polarized X-rays

In this section we discuss SPXPD by circularly polarized X-ray. For this purpose eq.(1) plays a central role. The SPXPD by circularly polarized X-ray from 1s-core is quite different from 2p-core, since the s-o coupling only works for photoelectrons in the former whereas it dominantly contributes to the splitting of 2p level to $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ levels in the latter. When the many-body effects in δT^r are neglected, it is simply written as

$$\begin{aligned}
&\delta T^r \sim Q(V_H-\varepsilon_p)Q \\
&=-\frac{1}{(2c)^2}[\nabla V_H\cdot\nabla+(V_H-\varepsilon)\nabla^2] \\
&\quad+\zeta(r)\sigma\cdot\mathbf{L}
\end{aligned} \tag{2}$$

where $\zeta(r)$ is related to the spherically symmetric potential v_A at the X-ray absorbing site A ($V_H+\Sigma^a(\varepsilon_p)=v_A+\sum_\alpha v_\alpha$),

$$\zeta(r) = \frac{1}{(2c)^2 r}\frac{dv_A(r)}{dr}. \tag{3}$$

The operator δT^r acts on photoelectron wave functions, but the influence is quite small because of the factor $(2c)^{-2}$. The first two operators in eq. (2) only change the radial integrals $\rho_c(j_c l_c; l)$, whereas the third term, i.e. the spin-orbit interaction term

$$\delta V = \zeta(r)\sigma\cdot\mathbf{L} \tag{4}$$

can contribute to anisotropy in angular distribution and the spin polarization, therefore it is important in calculating SPXPD patterns from 1s-core. We explicitly take that term into account, which yields the approximation for the amplitude M_2 in eq.(1)

$$\begin{aligned}
M_2 &= < f^-_{\mathbf{p}\sigma}\,|\delta T^r g^r_{11}\triangle|\,\varphi_c> \\
&\sim < \varphi^0_{\mathbf{p}\sigma}\,|(1+V^\sigma G^\sigma)\delta V G(\varepsilon_{\mathbf{p}})\triangle|\,\varphi_c>
\end{aligned} \tag{5}$$

where $G(\varepsilon)=(\varepsilon-T_e-V+i\eta)^{-1}$, V is the 2×2 potential which contains the potential acting on up spins V^+ and the potential acting on down spins V^-.

In similar approximation, the amplitude M_3 in eq.(1) is given

$$\begin{aligned}
M_3 &= < f^-_{\mathbf{p}\sigma}\,|Q\triangle|\,\chi_c> \\
&\sim < \varphi^0_{\mathbf{p}\sigma}\,|(1+V^\sigma G^\sigma)\delta U G(\varepsilon_{\mathbf{p}})\triangle|\,f_c y^{l_c}_{j_c\mu_c}>
\end{aligned} \tag{6}$$

where $f_c(r)$ is the radial function of the small component, $y^{l_c}_{j_c\mu_c}$ is Pauli spinor, and δU is

$$\delta U = \frac{1}{2cr}\sigma\cdot\mathbf{L}\ . \tag{7}$$

We can apply the site T-matrix expansion to eq.(5) and eq.(6), then we get multiple scattering series for the second and third terms in eq. (1).

3-1. SPXPD from spherical core levels

In this case (SPXPD from spherical core levels ($l_c=0$)) the spin-orbit coupling only acts on photoelectrons. There is ^5S, ^7S final state multiplet splitting in the photoemission from Mn d^5 (^6S) ground state (high spin state) [8] and ^7S, ^9S final state multiplet split-

ting in the photoemission from Gd f^7 (^8S) ground state (high spin state) [3]. Figure.1 shows the model used for the present calculations and Mn $3s$ θ scan SPXPD patterns for the ^5S and ^7S final states. Figure.2 shows Gd $4s$ θ scan SPXPD patterns for the ^7S and ^9S final states. The higher binding energy peak (Mn ^5S, Gd: ^7S) has only spin-up photoelectrons and the lower binding energy peak (Mn: ^7S, Gd: ^9S) mainly has spin-down photoelectrons, but it has also spin-up photoelectron by the spin flip effect [2, 5]. There can be difference between angular distribution of the higher binding energy peak and the lower binding energy peak due to not only the exchange interaction between the photoelectron and the magnetic atom but also the relativistic effects on the photoelectron. We can see that the relativistic effects are very small in this Mn $3s$ SPXPD pattern (Fig.1) : I_u is very small for the ^7S final state. In contrast we observe a large relativistic effect in Gd $4s$ SPXPD pattern (Fig.2). As clearly seen, the relativistic effects are important in calculating the branching ratio ($^7S/^9S$) in SPXPD by circularly polarized light in heavy elements like Gd.

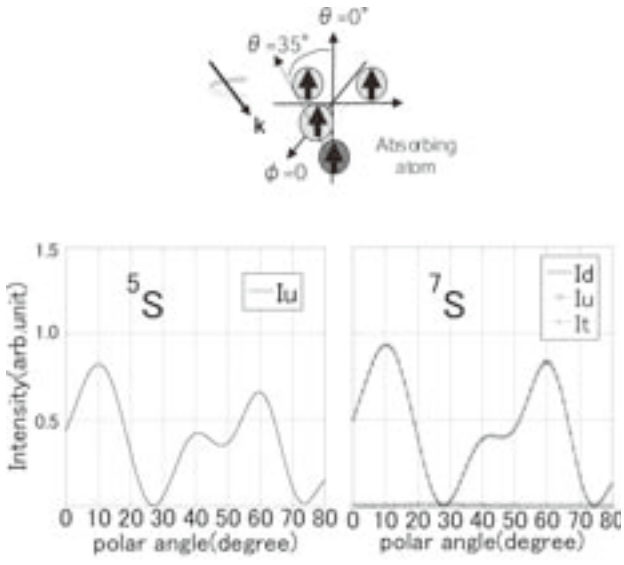

Figure 1: Model cluster and calculated Mn $3s$ SPXPD patterns (^5S and ^7S). In the upper panel three atoms are in the x-y plane and the absorbing atom is on the z-axis in the second layer. The incident + circularly polarized light propagates in the ($\theta = 145°, \phi = 180°$) direction. In the lower panel we show θ scan (fixed at $\phi = 0°$) SPXPD patterns. Photoelectron kinetic energy is 100 eV (^5S:left) and 104 eV (^7S :right). The photoelectron inelastic mean free path (MFP) is set to be 3.5 Å. I_d and I_u show the intensities measuring down and up spin photoelectrons. I_t is the sum ($I_u + I_d$).

In case of linearly polarized light or unpolarized light, the relativistic effects are not very important in SPXPD calculation even for heavy elements, because there are no relativistic spin conserved terms, so that there is no interference between the relativistic and non-relativistic spin conserved amplitudes [2]. However, when we observe the XPD pattern in the direction which the pattern is very weak, it might be important to consider these effects.

3-2. SPXPD from nonspherical core levels

In this subsection we show the SPXPD patterns for the excitation from nonspherical core ($l_c \neq 0$) by circularly polarized light. In these cases the core functions are split into two subshells with $j_c = l_c \pm 1/2$ because of the relativistic effects, and they are written as superposition of up-spin and down-spin. Furthermore there can be multiplet splittings if absorbing atoms have open shells. It is a little complicated problem to consider both the spin-orbital interaction and the multiplet splitting simultaneously, so we simply consider the SPXPD patterns for systems which have nonmagnetic absorbing atom. In the case of $2p$ excitation, for example, the first term in eq. (1) dominantly contributes to the spin polarization by circularly polarized X-ray. There is large spin polarization even in photoemission from core orbitals on light elements like Cu $2p$ (Fig3). In this case we cannot separately measure up-spin and down-spin photoelectron intensities without spin-detectors, and there is no MCDAD (Magnetic Circular Dichroism in Angular Distribution) in θ scan (Fig3). At $\theta = 35°$ I_u happens to be equal to I_d, which could be related to the Daimon

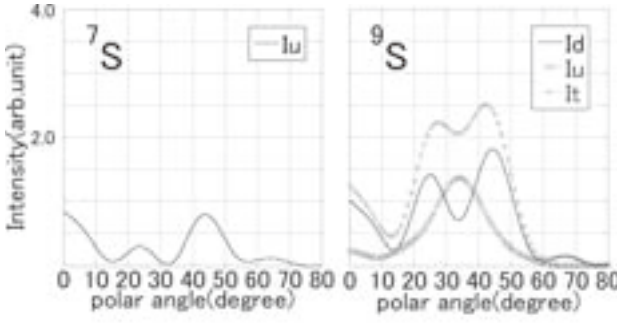

Figure 2: Gd $4s$ θ scan SPXPD patterns (^7S and ^9S) calculated for the same model used in Fig. 1. Photoelectron kinetic energy is 100 eV (^7S : left) and 104 eV (^9S : right). MFP is 2.5 Å. I_d and I_u show the intensities measuring down and up spin photoelectrons. I_t is the sum total ($I_u + I_d$).

effect [9]. This is, however, not true because that effect is observed for ϕ scan XPD. When the scatterer is placed at $\theta = 45°$, we observe that $I_u \neq I_d$ there. When surrounding atoms have magnetic moment, MCDAD is an effective way in studying surrounding local magnetic structure. For example, we can study the local magnetic structure around dilute nonmagnetic atoms in a magnetic material. When absorbing atoms have magnetic moments, we can expect the larger spin polarization and MCDAD pattern than the above cases. In general the contributions from the second and the third term in eq.(1) to SPXPD and MCDAD patterns are smaller than the first term, when the core s-o splitting is large enough. These two terms are crucial for the spin polarization of photoelectrons excited from spherical cores by circularly polarized X-ray.

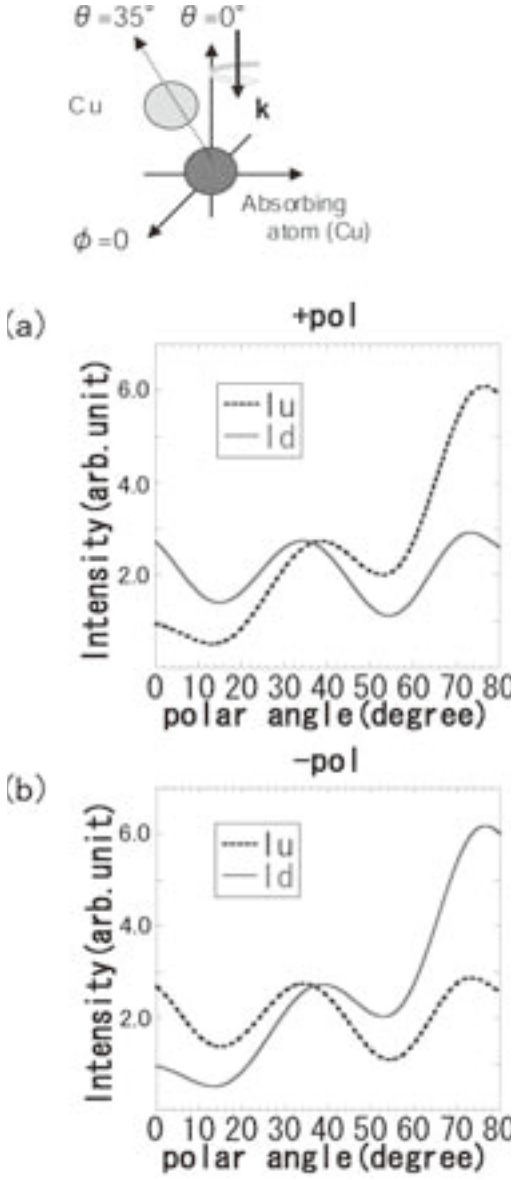

Figure 3: Calculated Cu $2p_{\frac{3}{2}}$ SPXPD patterns for the model shown in the upper panel (Cu 2 atom model). Incident light has + circular polarization (a) and – circular polarization (b). θ scan SPXPD (fixed at $\phi = 0°$) are shown. The photoelectron kinetic energy is 100eV, and photoelectron wave damping is neglected. I_d, I_u shows the intensities measuring down and up spin photoelectrons.

4. Conclusion

In describing SPXPD from spherical core levels by circularly polarized light, the relativistic effects are important only in the case of photoemission from heavy elements. In this case we should take both the exchange interaction and the relativistic effects into account. In the SPXPD from nonspherical core levels large spin polarization is caused by circularly polarized X-rays, because the $2p$ core level is split into two subshells. Thus considerably large spin polarization can be expected even for the photoemission from light elements. The present study demonstrates the potential usefulness of SPXPD and MCDAD for the magnetic structures in surface regions and magnetic-nonmagnetic systems.

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