Circular dichroism from non-chiral and non-magnetic materials observed with display-type spherical mirror analyzer

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Strong circular dichroism in 2-dimensional photoelectron diffraction patterns was observed for the photoelectron from the Si 2p core on the Si(001) surface using a display-type spherical mirror analyzer, although this Si(001) surface has no chirality and magnetism. The forward focusing peaks in the pattern rotate in the same direction as the incident light, i.e., clockwise or counterclockwise when the helicity of the incident circularly polarized light is reversed. These rotations of the pattern are explained by the phenomenon that the wave-front of the photoelectron wavefunction rotates as it propagates outward. This is the first direct observation of the rotation of the wavefront of the electronic wavefunction and clarifies the correspondence between the classical and the quantum mechanical ideas of angular momentum. This phenomenon offers a new possibility to measure the three dimensional surface structure.

1. INTRODUCTION

Recently, there have been reported many photoelectron spectroscopic studies using circularly polarized light, such as circular dichroism in angular distribution (CDAD)[1,2] or magnetic circular dichroism (MCD) by means of photoemission spectroscopy[3,4]. This study[5,6] is on a new type of circular dichroism in the angular distribution (CDAD) of photoemission for non-chiral and non-magnetic materials. To date, the CDAD study has been performed for originally nonchiral systems (surface or molecule) in a chiral configuration, in which the directions of the incident light, system orientation, and the wave vector of photoelectrons are not in a plane. Although the direction of the photon coincides with the surface orientation (surface normal) in contrast to the above condition, strong CDAD is observed in the present case.

The orbital angular momentum of an electron is the most essential idea of quantum mechanics. The correspondence between the classical idea of the rotational motion of electrons and the quantum mechanical idea of the orbital angular momentum, however, is not very clear and has not yet been directly observed. This study clarifies the correspondence between the classical and the quantum mechanical ideas of angular momentum.

The two-dimensional patterns of the Si 2p photoelectron were measured using a display-type spherical mirror analyzer[7-10] developed by ourselves. This analyzer can measure the angular distribution pattern of the energy-selected photoelectrons on the screen without distortion. For the study of photoelectron diffraction or photoelectron holography, the pass energy is fixed to the kinetic energy of the inner-shell photoelectrons and the intensity distributions on the screen are measured directly by a charge-coupled-device (CCD) camera and stored in the computer memory. Almost all kinds of photoelectron measure-
2. EXPERIMENT

The experiment was performed at the NE1-B beamline[11] of the 6.5-GeV accumulation ring (AR) of the National Laboratory for High Energy Physics in Tsukuba. Circularly polarized synchrotron radiation from an insertion device[12] operated in the helical undulator mode was monochromatized by a vertical-dispersion grazing incidence monochromator, and was incident perpendicularly to the Si(001) surface. Obviously, this surface is not chiral in the ground state. The spot size of the light on the sample was about 1 mm. The gap of the undulator was optimized so as to maximize the intensity and the polarization at each photon energy employed in the experiment.

![Diagram of the display-type spherical mirror analyzer](image)

Fig. 1. Schematic cross-sectional view of the display-type spherical mirror analyzer.

Figure 1 shows a schematic cross section of the display-type spherical mirror analyzer[7-10] developed by ourselves. The emitted direction of the energy-selected photoelectrons can be directly observed on the screen of the detector. It consists mainly of a hemispherical grid G, an outer-sphere electrode D, obstacle rings J, and guard rings U. The electrostatic field inside the electrodes G,D,J, and U is spherically symmetric. The lower surfaces of J are parts of spheres, and their potentials are set to realize a spherically symmetric field. The guard rings are used to correct fringe field. The emitted electrons from the sample are reflected by this field obeying the Kepler's law and converge strictly to the exit aperture A. The electrons passed through the retarding grid are amplified by a pair of microchannel plates MCP and converted by the phosphor screen P to light pulses which are detected by CCD camera. The angular distribution on P reflects the original distribution without distortion because the incident angle at A is equal to the emission angle from the sample surface.

A highly brilliant excitation source, such as synchrotron radiation SR, is preferable to realize a good energy and angular distribution. In the present experiment, SR is introduced through the hole N in J. The acceptance cone of the analyzer can be as large as ±90°. The analyzer shown in Fig. 1 can cover the angular spread as large as ±50°, but the region covered by a CCD camera by use of two plane mirrors is limited to about ±43° in this study. The obstacle rings J cut the electrons which has more than 0.5% higher kinetic energies than the pass-energy, and the retarding grids R cut the electrons having a bit lower kinetic energies. The energy resolution (ΔE/E) is thus set to 1% of the pass energy. When the kinetic energy (Ek) of the photoelectrons is 250 eV, the energy resolution ΔE is 2.5 eV in this study. The spin-orbit splitting of the Si 2p state is not resolved in this measurement. The angular resolution is about ±2°. It took about 40 to 60 minutes to obtain one pattern.

3. RESULTS AND DISCUSSIONS

Figures 2(a), (b), (c) and (d) show typical CD patterns obtained as a difference of the two patterns(such as those in Fig.
3 shown below) obtained for the left and right helicity lights at the photoelectron kinetic energy \( E_k \) of 150 eV (a), (b), and 450 eV (c), (d), respectively. In this experiment, the polarization of the left helicity light is defined so that the rotational direction of the electric field on the sample viewed from behind is counterclockwise (ccw), and that of the right helicity light is clockwise (cw). We showed both difference patterns (ccw-cw and cw-ccw) here because we cannot see the detail of the dark area in these density plots.

\[
\text{Asymmetry } A = \frac{I_{(ccw)} - I_{(cw)}}{I_{(ccw)} + I_{(cw)}}.
\]

The maximum values of \( A \) are 25\% in Fig. 2(a), (b), and 7\% in (c), (d), respectively.

![Figure 2](image)

**Fig. 2.** CD (circular dichroism) pattern of Si(2p) photoelectron diffraction patterns from the Si(001) surface. (a) \( E_k = 150 \) eV, obtained by subtracting the pattern for cw helicity light from that for ccw light, (b) \( E_k = 150 \) eV, ccw-cw, (c) \( E_k = 450 \) eV, ccw-cw, and (d) \( E_k = 450 \) eV, cw-ccw, respectively.

Figures 2 (a) and (c) are ccw-cw patterns, and (b) and (d) are cw-ccw patterns. The center of the pattern corresponds to the surface normal and the peripheral corresponds to the polar angle of 43°. Strong CD is found at all kinetic energies, although this Si(001) surface has no chirality and magnetism. The asymmetry \( A \) in intensity \( I \) is defined as \( A = \frac{I_{(ccw)} - I_{(cw)}}{I_{(ccw)} + I_{(cw)}} \). The maximum values of \( A \) are 25\% in Fig. 2(a), (b), and 7\% in (c), (d), respectively.

![Figure 3](image)

**Fig. 3.** The original Si(2p) photoelectron diffraction patterns from the Si(001) surface excited by cw or ccw helicity light. These patterns were obtained after the normalization by the transmittance efficiency of the detector. (a) \( E_k = 150 \) eV, and the rotating direction of the light is ccw, (b) \( E_k = 450 \) eV, cw, (c) \( E_k = 250 \) eV, ccw, and (d) \( E_k = 250 \) eV, cw. The small crosses indicate the calculated positions of the forward focusing peaks by the nearest-neighbour atoms in [115], [118], [112], and [101] directions.

One can recognize strong CD even in the original photoelectron diffraction patterns. Figure 3 shows the original patterns at \( E_k = 250 \) eV excited by left (c) and right (d) helicity light. These patterns are obtained by dividing the recorded pattern by the transmittance-efficiency pattern of the de-
The azimuthal rotation is seen in these patterns. The peaks rotate in the same direction as the rotational direction of the electric field of light, i.e., ccw direction when the light has left (ccw) helicity, and vice versa. This rotation of the peaks induces circular dichroism in photoemission intensity at a fixed angle as shown in Fig. 2. The rotation angle is not constant but larger for the peaks closer to the center of the screen. The amount of rotation increases when the kinetic energy decreases (a). The small full crosses in these figures show the positions theoretically predicted as discussed later.

This rotation of the peak is explained quantum mechanically by considering the rotation of the propagating vector of photoelectrons around the nuclei, whose angular momentum was selected by the circularly-polarized light.

We consider the wave function $\Psi$ of the emitted photoelectron at $(r, \theta, \phi)$ outside the emitting atom, which is the original direct wave in photoelectron diffraction. $\Psi$ is expressed as

$$\Psi \propto \frac{e^{ikr}}{r} \times Y_l^m(\theta, \phi) \propto \frac{e^{ikr}}{r} f_m(\theta) e^{im\phi}. \quad (1)$$

where $k$ is the wave vector of the photoelectron, $Y_l^m$ is the spherical harmonics, $l$ is the quantum number of the angular momentum, $m$ is the quantum number of the $z$-component. $f_m(\theta)$ is a function of $\theta$, e.g., $f_{11}(\theta)=1$ and $f_{22}(\theta)=\sin^2\theta$.

We take the $z$-axis as being along the propagation vector of the light. A circularly polarized light with the angular momentum of $+1 \ (-1)$ changes $m$ to $m + 1 \ (m - 1)$. In the case of the photoelectron from the Si 2p core, the final $l$ is either 2 or 0, and the probability of realizing $l = 2$ is much higher than that of realizing $l = 0$. From the Clebsch-Gordan coefficient, the probability of obtaining $m = 2$ for the final state from the 2p initial state is the highest when the angular momentum of the circularly polarized light is $+1$, and $m = -2$ is the most probable when the momentum of the light is $-1$.

When the spin-orbit interaction is considered, the good quantum numbers are the total angular momentum of the photoelectron $j$ and its $z$-component $j_z$. From the selection rule, the final state with $(j; j_z)$ can be reached from the initial state with $(j \pm 1, j_z - 1)$ when the angular momentum of the circularly polarized light is $+1$. The wave function of the final state with $j, j_z$ is written
\[ \Psi_{j}^{l} = C_{1}Y_{l}^{j}e^{-\frac{1}{2}i\alpha} + C_{2}Y_{l}^{j}e^{+\frac{1}{2}i\beta}, \]  
where \( C_{1} \) and \( C_{2} \) are constants depending on \((l, j, j_z)\) and \( \alpha \) and \( \beta \) are spin functions of up and down spins, respectively. The observed pattern is the simple sum of the each pattern from the first \((m = j_z - \frac{1}{2})\) and second \((m = j_z + \frac{1}{2})\) terms because the spin functions are orthogonal. Hence, we should consider only the independent scattering of \(m\)-wave (eq. (1)). Even in this spin-orbit included case, the probability of \(m = 2\) \((m = -2)\) is the highest when the angular momentum of the circularly polarized light is \(+1\) \((-1)\).

To obtain a propagating curve, which is a linkage of the velocity vector, first we calculate a velocity vector \((v_x, v_y, v_z)\) using a velocity operator \( \frac{\hbar}{\mu} \nabla \), where \( \mu \) represents the mass of electron instead of \( m \) which is used for the quantum number of \(z\)-component of the angular momentum in this paper. The \(x\)-component of the velocity \(v_x\) is expressed as

\[ v_x = \frac{Re(\Psi^* \frac{\hbar}{\mu} \frac{\partial}{\partial x} \Psi)}{\Psi^* \Psi}. \]

Then, the velocity components are obtained as

\[ \frac{dx}{dt} = v_x = \frac{\hbar}{\mu} \left( \frac{k_x}{r} - \frac{m - y}{x^2 + y^2} \right) \]

\[ \frac{dy}{dt} = v_y = \frac{\hbar}{\mu} \left( \frac{k_y}{r} + \frac{m - x}{x^2 + y^2} \right) \]

\[ \frac{dz}{dt} = v_z = \frac{\hbar}{\mu} \frac{k_z}{r}. \]

In these calculations, the terms including \(f(\theta)\) vanish because they are not imaginary.

Next, we calculate the propagating curve \((r, \theta, \phi)\). The expressions of the velocity in spherical coordinates are

\[ \frac{dr}{dt} = \frac{x dx}{r dt} + \frac{y dy}{r dt} + \frac{z dz}{r dt} = \frac{h k}{\mu} \]

\[ \frac{d\theta}{dt} = 0 \]

\[ \frac{d\phi}{dt} = \frac{m \hbar}{\mu r^2 \sin^2 \theta}. \]

Equation (8) implies that the propagating curve do not move in the \(\theta\) direction. Equation (9) corresponds to Kepler's second law or conservation of angular momentum. From eqs.(7) and (9), we obtain

\[ \frac{dr}{d\phi} = \frac{kr^2 \sin^2 \theta}{m}. \]

Solving this equation, we obtain the formula of the propagating curve as

\[ \phi = -\frac{m}{kr \sin^2 \theta} + C. \]

Four of these propagating curves passing through the upward four atoms such as A are shown by solid lines in Fig.5.

Fig. 5. The solid lines indicate some of the propagating curves of photoelectrons with some angular momentum.

For easier understanding of the deviation of \(\phi\), it is helpful to project the propagating curve into the plane perpendicular to the angular momentum axis because eq.(11) shows that the change of \(\phi\) is the same for the same \(k_\parallel = k \sin \theta\) and \(r_\parallel = r \sin \theta\).
We consider the scattering of this wave by surrounding atoms in the propagation process. Suppose that an atom A exists at \( r_\parallel = R_\parallel \) from the emitting atom O.

Assuming that the direction of OA is \( \phi = 0 \), the constant \( C \) is obtained from eq.(11) as \( C = \frac{m}{k||R||} \). Then the deviation of \( \phi \) at infinity, \( \Delta \), is obtained as

\[
\Delta = C = \frac{m}{k||R||} = \frac{m}{kR \sin^2 \theta}.
\]

This is the equation that shows the direction of the forward focusing peak for the photoelectron with an angular momentum \( m \).

The mechanism of the azimuthal shift is now explained as follows. When this wave scatters on the atom A at the distance \( R_\parallel \), the forward direction is not the direction OA but along this propagating curve. The angle between OA and the direction of this curve at infinity gives the azimuthal shift \( \Delta \), and this shift increases as \( R_\parallel \) decreases or angular moment increases.

The angle \( \alpha \) between the curve and the OA direction is calculated in first order by eq. (10) as

\[
\tan \alpha = \left( \frac{r_\parallel d\phi}{dr_\parallel} \right)_{R_\parallel} = \frac{m}{k||R||}.
\]

This first order formula for \( \alpha \) is the same as \( \Delta \) in eq.(12), which is correct when the curve is straight.

In short, when the scattering atom exists at \( (R, \theta, \phi) \) from the emitting atom, the forward focusing peak appears in the direction \( (\theta, \phi + \frac{m}{k||R|| \sin^2 \theta}) \).

It is helpful to note that the above result can be obtained more easily using the feature that the direction of the wave is perpendicular to the wave front. In order to simplify the formula, we neglect the \( \theta \) term in eq.(1) and consider the 2-dimensional plane \( (R, \phi) \). We then have

\[
\Psi \propto \frac{e^{ikR}}{R} e^{im\phi} = \frac{1}{R} e^{i(kR + m\phi)}
\]

instead of eq.(1). Then the equation of the constant-phase plane (wave front) is expressed as \( kR + m\phi = \text{constant} \), which is shown by the broken line in Fig. 6. The equation of the propagating curve which is perpendicular to this constant-phase plane is \( \frac{dR}{d\phi} = kR^2/m \), which is the same as eq.(10), and the results, eqs.(11)-(12), can be obtained in the same manner.

![Fig. 6. The solid line indicates a propagating curve of photoelectron wavefunction with some angular momentum and broken line indicates a constant phase plane.](image)

It is also useful to observe the difference between this result and that of a classical straight trajectory of the particle having an angular momentum \( mh \). The distance between the classical straight line and the origin O is \( b \), which is called impact parameter. The value of \( b \) is determined as \( b = m/k \) from the angular momentum \( \mu b = mh \) and \( \mu = \hbar k \). This straight line coincides with the propagating curve of eq.(11) and the solid line in Fig. 3 when \( R \) is large enough. In this case, \( \Delta \) can be obtained as

\[
\Delta = \sin^{-1} \left( \frac{b}{R} \right) = \sin^{-1} \left( \frac{m}{kR} \right).
\]

This formula gives the same results as eq.(12) when \( R \) is large. This classical straight trajectory of the particle having
an angular momentum $\hbar m$ is tangent to the limit of the propagating curves.

The small crosses in Fig. 3 represent the calculated positions of the forward focusing peaks using eq. (12) with $m=2$ for [115] (the four crosses nearest to the center), [113] (the four second-nearest crosses), [112] (the four third-nearest crosses), and [101] (the white crosses outside the pattern in Figs. 3(b) and 3(d)). The [101] peaks are weak in Figs. 3(a) and 3(c), and the peak at the upper-left corner in (c) is not a peak but the discharge of the microchannel plates.

The refraction effect has been taken into account in the calculation of these cross patterns assuming that the inner potential is 12 eV.[14] This effect is limited in the shift along the $\theta$ direction. Its magnitude is at most $2^\circ$ even in the lowest kinetic energy patterns and the largest $\theta$ peaks. Hence, the result is not substantially affected by the inclusion of this refraction effect.

The agreement of these predicted peak positions with the observed ones indicates the propriety of the present analysis. Hence this experiment corresponds to the direct observation of the rotation of the wave front of the photoelectron wave functions.

Now the difference between usual CDAD study and this study is clear. The fact that the orientation in this study is nonchiral is not the essential difference because in this case the orientation of the system is not normal to the surface but in the orientation of each emitter-scatterer pair and they are not in the same plane as the photoelectrons and the incident photons. The essential difference is the mechanism which causes asymmetry, i.e., usual CDAD considers the final-state anisotropy by interference neglecting the diffraction effect, but this study considers a spherically symmetric final state and diffraction. This difference originates mainly from the difference of the kinetic energy of the photoelectrons (20-100 eV in usual CDAD and 150-450 eV in this study). Of course, the combined theory will be required to describe these phenomena over the entire energy region.

Recently, Fadley et al. [15] calculated this pattern using a formula

$$I = |<x> \pm iy>|^2 \quad (16)$$

for left and right circularly polarized light, where $<x>$ and $<y>$ represent the photoelectron amplitudes calculated for $x$- and $y$-direction linearly polarized light. Their calculated patterns are in good agreement with these data especially at 250eV.

On magnetic materials, magnetic circular dichroism (MCD) has been extensively studied by means of photoemission spectroscopy[3,4], measuring the difference of the photoemission intensity when the direction of the magnetic moment and/or the polarization of circularly polarized light are reversed. What is found in the present study is strong circular dichroism of the entire photoelectron diffraction pattern in nonmagnetic materials. In these MCD experiments with angle-resolved photoelectrons, these rotations of the pattern must be taken into account.

This phenomenon can be used to measure a three dimensional surface structure because this pattern tells us the bondlength through eq.(12) as well as the direction of the scatterer through that of the forward focusing peak.

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