Circularly polarized X-ray photoelectron diffraction—Stereo photograph of atomic arrangement

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1. Introduction

Two-dimensional photoelectron angular distribution (PEAD) in XPS from the core-level contains structural information because the emitted electrons are scattered by nearby atoms and produce a photoelectron diffraction pattern in PEAD. Hence a two-dimensional PEAD is often used to analyze atomic structure by the photoelectron diffraction (PED) or by the photoelectron holography (PH) method. Usually the forward-focusing peaks (FFP) appear in a PED pattern in the direction from the emitter to the scatterer. FFPs are very strong and often disturb the PED or PH analysis. These methods are not direct methods to reveal a three-dimensional atomic arrangement, and require a model in the PED or require Fourier transform in PH, hence some ambiguity remains.

Here we describe a new direct method of three-dimensional structure analysis of surface atoms, with which one can realize three-dimensional atomic arrangement directly by the naked eyes. It was found that the FFP rotates around the direction of the incident photon when the photon is a circularly polarized light [1–3]. This is a new type of circular dichroism. Usually circular dichroism is the difference of absorption coefficient between counterclockwise (cw) and clockwise (cw) circularly polarized light. So far this phenomenon has been observed in chiral or magnetic systems. This phenomenon is the circular dichroism in non-chiral and non-magnetic systems.

The azimuthal shift is in good agreement with that estimated by the orbital angular momentum of photoelectrons, which has a close relationship to the classical idea of impact parameter. A simple formula for the angular shift was derived including the quantum number of the angular momentum (magnetic quantum number), m, of the photoelectron. The effective m value, which is an average of possible final state m values at a certain polar angle, is discussed in the analysis. The azimuthal shifts of FFPs in the PEAD obtained by left and right helicity light are the same as the parallax in a stereo view. Taking advantage of this phenomenon, a "stereo atomoscope" was invented [4]. The display-type spherical mirror analyzer (DIANA) [5] can display stereoscopic photographs directly on the screen without any conversion process. The element- and chemical-state-selective
stereo photographs are obtained directly and reproduce the atomic arrangement in real space directly.

From a different point of view, this experiment corresponds to the observation of the orbital angular momentum of an electron. The quantization of orbital angular momentum is an essential feature in quantum mechanics, but it has never been observed directly so far. The quantum of the orbital angular momentum is too small to be measured macroscopically. Classical orbital angular momentum of an electron is a product of the momentum and the impact parameter. The impact parameter, which is the distance between a nucleus and the line of trajectory of an electron, is usually less than 1 Å. The photoelectrons excited by a circularly polarized light have ccw or cw orbital angular momentum given by ccw or cw light, respectively. The difference of the direction between these two kinds of electrons at a certain position is, however, less than $10^{-9}$ in the macroscopic world, say at 10 cm apart, and it is too small to be observed easily. In this study we used a nearest neighbor atom as a detector (or observer), which results in an exaggeration of the direction enabling measurement even when the angular resolution is around $1^\circ$.

In this paper, we describe the “rotation of forward scattering peaks”, the analyzer used in the measurement, and the “stereo photographs of atomic arrangements”.

2. Two-dimensional photoelectron angular distribution (PEAD)

Fig. 1 shows a schematic diagram of the photoelectron angular distribution (PEAD) for core-level photoelectrons at kinetic energies of several hundred electron volts. An X-ray produces a photoelectron wave $\psi^0$ from the core-level of the emitter atom O. $\psi^0$ produces a scattered wave $\psi^S$ when it hits a scatterer atom, for example A. The photoelectron diffraction pattern is described by the square of the sum of $\psi^0$ and all $\psi^S$'s from nearby atoms. When the kinetic energy of a photoelectron is higher than several hundred electron volts, a strong forward scattering peak (FP) appears along the direction that connects the emitter and the scatterer [6]. The characteristic feature of the PEAD consists of strong FPs and weak diffraction rings around each FP.

![Fig. 1. Schematic diagram of photoelectron angular distribution.](image)

2.1. Surface photoelectron diffraction

Fig. 2(a) and (b) are examples of diffraction rings and FFPs. They are the photoelectron diffraction patterns of O 1s and W 4f photoelectrons from the top and first-layer atoms on the W(110) $\times 1$ -O surface [7]. Fig. 1 shows the schematic side view of this surface, and Fig. 2(c) shows its top view. The photoelectrons from the first-layer W atoms are easily distinguished from those of the bulk W atoms due to a large chemical shift (0.73 eV). Fig. 2(a) and (b) are plotted by the stereographic projection method. The center of the pattern corresponds to the surface normal direction and the edge corresponds to the polar angle of 90°. The excitation light is Al Kα.

In Fig. 2(a) we can see diffraction rings along the direction connecting the oxygen atoms in Fig. 2(c). We cannot see any FFP here because the FFP should appear at the polar angle of 90°, which is outside the measured region. However the concentric diffraction rings show that we expect FFP at the center of each ring. In Fig. 2(b) we can see six strong FFPs. The directions of the peaks A, B, C, A', B', and C' correspond to the direction of the oxygen atoms seen from the first-layer W atoms. In Fig. 2(b), we cannot see any diffraction rings clearly because FFPs are much stronger than diffraction rings. This big difference of intensity

![Fig. 2. Photoelectron diffraction pattern of (a) O 1s photoelectrons from the top layer oxygen atoms and (b) W 4f photoelectrons from the first-layer W atoms on W(110) $\times 1$ -O surface. (c) shows the structure of this surface [7].](image)

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between FFPs and diffraction rings makes photoelectron holography analysis difficult. Because these FFPs have information about the direction from the emitter to the scatterers, the positions of the atoms can be obtained easily in this simple case [7].

2.2. Rotation of forward-focusing peaks

Although FFPs have information about the direction from the emitter to the scatterers, they do not have information about the distance between them. Recently, strong circular dichroism in photoelectron diffraction (CDPD) was found for non-chiral and non-magnetic materials [1–3]. The positions of the forward scattering peaks in the two-dimensional, photoelectron-diffraction pattern which was excited by a circularly polarized light rotated in the same direction as the rotation of the electric vector of the light.

2.2.1. W(110) × 12-O

Fig. 3 shows an example of circular dichroism in a two-dimensional diffraction pattern of the chemically shifted W 4f peak from the first-layer W atoms of W(110) × 12-O surface [2]. The sample is the same as that in Fig. 2, but the excitation photons are polarized synchrotron radiation from the advanced light source (ALS) and the photoelectron kinetic energy is 317 eV here. Fig. 3(a) and (b) show the results for linearly polarized (LP) and left circularly polarized (LCP) light, respectively. Here the LCP is defined as the ccw-rotation direction of the electric vector of the photon in the planes of Fig. 3(b). The stereographic projection method was also used to plot these figures. The photons were incident normal to the surface. The polar take-off angle range was almost the same as that over which the forward-focusing peaks in Fig. 2(b) were observed. We can see basically six forward scattering peaks in each of the patterns of Fig. 3, as in the case of Fig. 2(b). In this case, the emitter atom is the first layer W atom and the scatterer atoms are the O atoms above it. Hence the forward peaks in Figs. 2(b) and 3 are considered to be dominated by single scattering.

The azimuthal angles of the peaks for LP light are the same as those observed in high-energy XPD [7] (Fig. 2(b)). It is clear that there is a tendency for the pattern to shift counterclockwise with LCP excitation in Fig. 3(b). The rotation angle of the peak C (at the bottom) and A (at the sides) in the LCP data is 12° and 14°, respectively. Such peak “rotations” were observed for the first time on Si(001) surface [1].

3. Theory

3.1. Simple formula for the rotation angle

All these shifts are considered to be rotations of the forward-focusing peaks with respect to the photon incident direction. This rotation has been explained as being due to the transfer of the angular momentum of the photons to the photoelectrons, whose z component ratio has been biased while being excited by the circularly polarized light.

The rotation angle Δ of the peak around the photon incident axis is reproduced well by the simple formula [1]:

\[
\Delta = \tan^{-1} \left( \frac{m}{kR \sin^2 \theta} \right) \approx \frac{m}{kR \sin^2 \theta}
\]

Detailed theoretical works [8–10] support this formula. Here, \( m \) is the magnetic quantum number (z component angular momentum) of the photoelectron, \( k \) is its wave number, \( R \) is the internuclear distance between the emitter and the scatterer, and \( \theta \) is the angle between the photon incident direction and the outgoing photoelectron direction. When the position vector of the scatterer is described as \((R, \theta, \phi)\), the peak position observed by using ccw and cw circularly polarized light appears at \((\theta, \phi \pm \Delta)\). This relation is shown in Fig. 4. Using this formula, we can measure \( R \) from the azimuthal shift of the forward-focusing peaks and can construct three-dimensional atomic structures directly [11].

3.2. Rotation angle and the orbital angular momentum

The characteristic feature of the photoelectron excited by circularly polarized light is that it has an orbital angular momentum around the incident light axis. Here, we consider the photoelectrons from an initial core state \( \psi_i \) with the quantum number of the angular momentum \( l' \) and its z component \( m' \). Its angular component can be described by a spherical harmonic \( Y_{l'm'}(\theta, \phi) \).

Fig. 3. Rotation of forward-focusing peaks excited by (a) LP and (b) LCP.
Fig. 4. Rotation of the forward-focusing peaks excited by cew circularly polarized light.

\[ \Phi \propto \frac{e^{ikr}}{r} Y_{lm}(\theta, \phi) \propto \frac{e^{ikr}}{r} \Theta_{lm}(\theta) e^{im\phi}, \]  

where \( \Theta_{lm}(\theta) \) is the \( \theta \)-function in the spherical harmonic.

The propagation direction of this final state wavefunction is intuitively calculated considering the wavefront of Eq. (2). The phase of the wave is expressed as

\[ \exp[i(kr + m\phi)]. \]  

The equation of the constant phase surface is expressed as

\[ r = \frac{m\phi}{k} + C, \]  

where \( C \) is a constant. This curve is a spiral, as shown in Fig. 5 by the solid and broken lines. The wave propagates perpendicular to these lines, which represent the wavefront, as shown by the thick arrow in Fig. 5. The shift of the forward direction \( \Delta \) from the OA direction is expressed as

\[ \Delta = \tan^{-1} \frac{m}{kR \sin^2 \theta} = \frac{m}{kR \sin^2 \theta}. \]  

The physical base of the azimuthal shift is summarized as follows: the forward-focusing peak appears because the phases of all wavelets on the wavefront which are scattered by each

infinitesimal atomic potential coincide in the forward direction. This "forward direction" is perpendicular to the wavefront, and when the wave has an angular momentum, the wavefront hits the scatterer at an angle; hence, the forward direction of the photoelectron wavefunction is inclined at the scatterer. In other words, the peak does not shift from the forward direction, but the forward direction has already changed before the scattering.

In Fig. 5, the arrow is bent near the emitter O, which may look strange in the classical picture because there is no field to bend the trajectory. However, in the quantum mechanical formula there is no wave there because the intensity of the spherical Hankel function \( h_1^{(1)}(kr) \), which represents an outgoing spherical wave, has no contribution below around \( r = \hbar k \). This radius nearly corresponds to the classical impact parameter \( b \) in Fig. 5.

This formula (5) for the forward scattering peak direction is exact when the photoelectron wavefunction can be expressed by only one component of the angular momentum. This condition is satisfied in the excitation of an s core electron, where the final \( m \) should be \pm 1. In the following, we describe a more general case of excitation.

The probability of transition to the \( l + 1 \) final state is much higher than that to the \( l - 1 \) final state. In the case of photoexcitation from the Si 2p (\( l = 1 \) core state by a photon of \( \sigma_{\text{po}} = +1 \), as in the case in Ref. [11], the final \( l \) is either 2 or 0, and the final \( (l, m) = (2, 2), (2, 0), \) and \( (0, 0) \). The probability of realizing these three \( l = 2 \) final states is much higher than that for \( l = 0 \), being about 13:1 at a photon energy of around 350 eV [12].

The probabilities of realizing these three final \( m \) values are not equal. For example, the probabilities for \( (l, m) = (2, 2), (2, 0), \) and \( (0, 0) \) are \((6:3:1)\), respectively. When \( \sigma_{\text{po}} = -1 \), the ratio for \( m = (-2, -1, 0) \) is also \((6:3:1)\); even when the spin-orbit interaction of the core state is considered, this ratio is unchanged for each spin-orbit split component \( p_{1/2} \) and \( p_{3/2} \). This ratio, however, is that of the total cross-section over \( 4\pi \) steradians, and it depends on the emission angle \( \theta \) (but does not depend on \( \phi \)). In the next section we discuss the angular dependence of \( m \).

3.3. Effective \( m \) value

The effective \( m \) value as a function of \( \theta \), \( m_0(\theta) \), which is an expectation value of the possible final state \( m \) at a certain polar
angle, is discussed in Ref. [11]. The angular dependence of the contribution of each $m$ state in the final state is shown in Fig. 6 for $l = 3$ (i.e., core initial state). The effective $m$ value $m^* (\theta)$ is also shown in the figure. The neglect of the $l - 1$ channel causes an error of small percentage. This neglect is convenient because $m^*$ depends only on the initial angular momentum $l$ and does not depend on energy or atomic species. The applicability of this analysis was discussed in a typical example of W(1 1 0) surface [11].

4. Display-type spherical mirror analyzer

A two-dimensional photoelectron angular distribution (2D-PEAD) provides plenty of information, not only for structural analysis, but also for electronic state analysis, such as Fermi surface mapping. The 2D-PEAD can be measured either by the rotating-sample, rotating-analyzer, or display analyzer methods. The relation between the orientation of the sample and the direction of a photon are preserved only in both the rotating-analyzer and in the display analyzer methods.

A display-type spherical mirror analyzer (DIANA) (Fig. 7) was invented in 1988 [5] and was gradually improved upon [13–16]. Compared to the Eastman-type display analyzer [17,18], this analyzer has two advantages. One is that the emission and detection angles of the photoelectrons are exactly parallel; hence the pattern displayed on its screen is not distorted. The other is that the acceptance angle can be made infinitely wide because the convergence to the exit aperture is exact irrespective of the angle, and has no higher order terms. Therefore, one can measure the angular distribution of particles of one particular kinetic energy up to about $2\pi$ steradians at a time. As the analyzer has evolved, the energy analysis method has been changed from “focus–de-focus” [5] to “high-pass and low-pass filtering” [13,14]. The energy resolution of the latest DIANA [15,16] is about 0.3% of the pass energy.

Fig. 7 shows a schematic view of the new DIANA [16]. It consists of a hemispherical main grid (G), outer sphere, and guard rings (Gd). There are 160 obstacle rings (Ob) on the inner surface of the outer sphere. The Ob’s are axially symmetric with respect to the axis connecting the sample and the center (O) of the hemisphere. G is usually grounded. The potential $V(r)$ of Ob’s and guard rings are biased according to their radii $r$ from O by the formula $V(r) = -2E_0(1 - r/A)$, where $E_0$ is the pass energy and $A$ is the radius of the main grid G. The electrostatic field in the space surrounded by the electrodes G, Ob and Gd is thus made spherically symmetric with respect to the center O. The orbits of the emitted electrons from the sample are subjected to this field after passing through G, and their loci are ellipses obeying Kepler’s law. Their trajectories inside G are straight lines.

The electrons converge exactly to the exit aperture A, which is located at the symmetric position of S with respect to O. Their incident angles are exactly parallel to their emission angles. The Ob’s play essential roles in energy analysis by cutting unnecessary electrons that have higher kinetic energies than the pass energy $E_0$ [13,14]; an electron having slightly higher energy travels slightly outside the locus, collides with the electrodes and is absorbed or scattered. It is unlikely to pass through the small aperture A. Thus the Ob’s work as a “low-pass filter”. On the other hand, the retarding grid R works as a “high-pass filter”, which retards the electrons that have lower kinetic energies than the applied potential.

The electrons, having passed through the retarding grid, are amplified by a pair of microchannel plates (MCP), M, and are converted by a phosphor screen (P) to light pulses, which are detected from outside the vacuum chamber by a cooled CCD camera. The two-dimensional photoelectron intensity angular distribution (2D-PIAD) on the screen is the same as the original 2D-PEAD in front of the sample. An electron gun is mounted for the purpose of LEED measurement. Synchrotron radiation (SR) or excitation light is introduced through a hole. The acceptance angle is limited by the solid angle of the plane MCP and is $\pm 60^\circ$. The energy resolution $(\Delta E/E_0)$ of the present analyzer has been estimated to be 0.3% of the pass energy.

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5. Stereoscopic photographs

A stereoscopic photograph consists of a pair of photographs; one is that would be seen by the left eye, the other seen by the right eye. The positions of an object in the two photographs differ by a parallax, which is inversely proportional to the distance from the observer. Assume that the observer is facing the direction r and looking at an object A with the right and left eye at E and F, respectively, as shown in Fig. 8. When the position of the object A is described as \((R, \theta, 0)\) by polar coordinates, the relation between the distance \(R\) and the azimuthal shift \(\Delta\) of the object A in the two photographs is described as

\[
\Delta = \tan^{-1} \frac{b}{R \sin \theta}
\]

(6)

where \(b\) is half of the distance between the two eyes (OE and OF in Fig. 8).

5.1. Stereo photography of atomic arrangements

Two photographs of an atomic arrangement satisfying the condition of Eq. (6) can be obtained by using a display-type spherical-mirror analyzer described above in the measurement of circular dichroism in a 2D-PEAD. For example, the 2D-PEAD of W(110) surface at a kinetic energy of 800 eV is shown in Fig. 9(a) and (b) [4]. These patterns were observed on the analyzer's flat screen. Fig. 9(a) and (b) were taken with cw and ccw circularly polarized light, respectively. The center of the figure nearly corresponds to the surface normal direction, which is the [1 1 0] axis, and the horizontal direction is [0 0 1]. The ccw and cw incident excitation light is inclined 45° to the surface normal, which is the [0 1 0] direction, as shown in Fig. 9(d). We can see five forward-focusing peaks, such as A, B and C, in the directions shown in Fig. 9(c). These forward peaks are produced by the nearest-neighbor atoms A, B and C in Fig. 9(d). In XPD [7], the positions of these forward peaks are the same as the direction shown in Fig. 9(c), but their positions in Fig. 9(a) and (b) are slightly different from the direc-

![Fig. 9. (a) and (b) Stereo photograph of W crystal. (c) Three-dimensional configuration of atoms imaged by stereo photograph of (a) and (b). (d) Structure of W crystal.](image-url)
tion shown in Fig. 9(c). The patterns obtained by clockwise and
clockwise light are symmetric with respect to the central
vertical line. For example, the [1 0 0] peak A is slightly off cen-
ter to the right in (a) and left in (b), as shown by the dots in the
figure.

These patterns can be considered as stereoscopic photographs
because, in both cases (Eqs. (5) and (6)), the angular shift $\Delta$ of
the object is inversely proportional to the interatomic distance
$R$ from the emitter. The necessary condition is that the direction
of the photon be parallel to the $z$-axis in stereoscopic photogra-
phy. Consequently, if we view the cw circularly polarized-light,
photoelectron-diffraction pattern (Fig. 9(a)) with the left eye
and the ccw pattern (Fig. 9(b)) with the right eye, we can pro-
duce an image of a three-dimensional arrangement of atoms in
a W(1 1 0) crystal, as shown in Fig. 9(c). The A atom looks
closer, and the B and C atoms look farther away, and the others
look the farthest. Moreover, nearby atoms appear strongly while
more distant atoms look faint just as in a real view. The elonga-
tion of atom A is due to the projection of the pattern onto a flat
screen.

To properly recognize the three-dimensional arrangement,
it is necessary that the fields of vision of both images be the
same as that in the measurement. The solid angle of these pic-
tures is about $\pm 60^\circ$ in the measurement, whereas it is only
$\pm 15^\circ$ when these pictures are viewed by using a conventional
stereo viewer. Special projection methods, such as a combina-
tion of polarized light projection and polarized glasses for individ-
ual image, are necessary to realize the $\pm 60^\circ$ field of vision. If
this is realized, the oval of atom A should be seen as a circle,
and the inter-atomic relation should be proportional to the real
relation.

When Eqs. (5) and (6) are identical, there is no distortion.
The necessary condition is that $m(k \sin \theta)$ be constant in Eq. (5).
For the objects in the $x$-$y$ plane, there is no distortion because
$m(k \sin \theta)$ is constant. In this case, the magnification ratio is
$bk/m$. When $b = 3\, \text{cm}$, $k = 14\, \text{Å}^{-1}$ (for the kinetic energy
of 800 eV), and $m = 4$, the magnification ratio is about $10^5$, which
is 1000 times higher than in a conventional electron microscope.
When $\theta$ is not $90^\circ$, the sine function in the denominator of Eq. (5)
would make the atoms appear closer to the viewer; however, this
distortion is hardly present in the actual case because the value
of $m$ in Eq. (5) is not constant, and the $\theta$ dependence of $m'(\theta)$ is
close to $\sin \theta$ [11], as shown in Fig. 6.

### 5.2. Example of stereo photograph

Many stereo photographs have been measured for single crys-
tals and surface layers [19–23]. Fig. 10(a) and (b) show an ex-
ample of a stereo photograph of a single crystal of Cu(0 0 1)
[22]. The square which consists of A atoms is closest to the
viewer and the fcc structure can be realized directly. The peaks
around the bottom A atom is not bright because the excitation
light is incident from this direction and the excitation probability
of photoelectron is low in this direction.

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Fig. 10. (a) and (b) Stereo photograph of Cu(0 0 1). (c) Directions of FFPs from scatterers shown in (d).

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5.3. Stereoscope

Because the stereo photographs are presented directly on the screen of the display-type spherical-mirror analyzer, real-time observation is possible. The problem in all atomic structure analysis methods so far (electron diffraction, X-ray diffraction, photoelectron diffraction and holography, fluorescent X-ray holography) is that the data obtained are that of reciprocal spaces, and a real-space structure cannot be imaged before conversion. In this method, the obtained data is not reciprocal but it is a real-space image similar to a projection microscope. When the time required to switch the helicity of circularly polarized light is reduced and the signal intensity increases, we expect that this display analyzer will provide opportunities for real-time stereoscopic observation around specific atoms. Recently 0.1 Hz switching and 15 s acquisition time for one image have become possible.

Because this technique uses photoelectrons, this photography is element- and chemical-state-selective by selecting the kinetic energy of the photoelectrons. On a DIANA screen, the stereo photographs for the right eye and the left eye will be displayed alternately by switching the helicity of the light. Special glasses allow transmission of each image to each eye by switching the transmittance of each viewing point synchronously. In this way one will be able to view three-dimensional atomic arrangements, as shown in Fig. 11, in real time in the near future. Because this method does not need a regular array, a single molecule or a single nano particle could be viewed in principle.

6. Conclusion

Although the experiment is done within the framework of photoelectron diffraction, the obtained data does not belong to “diffraction”. In other words, this phenomenon is that of real space (scattering) but not of reciprocal space (diffraction). When the structure is known, we can observe orbital angular momentum directly by measuring the rotation angle of forward scattering peaks. The similarity between the angular momentum and the stereo view resulted in the successful application of this phenomenon to stereoscope of atomic arrangement. The possibility of real-time stereo observation was suggested.

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