Atomic stereophotograph of intercalation compound Fe$_{1/3}$NbS$_2$

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Stereoatomoscope was used to study the atomic arrangements of intercalation compound Fe$_{1/3}$NbS$_2$. The three-dimensional atomic arrangements around different kinds of atoms (Nb and Fe) are visualized by taking the photoelectron angular distribution (PEAD) patterns at clockwise and counterclockwise circularly polarized lights. Atomic distances between the emitters and the scatterers are obtained from the PEAD patterns by measuring the rotation angles of the forward focusing peaks. The applications of stereoatomoscope to intercalation compound show the possibility to build an ultimate microscope for scientist. © 2006 American Institute of Physics.

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I. INTRODUCTION

The stereoatomoscope, which is realized by the combination of display-type spherical mirror analyzer (Diana) and circularly polarized light, opens a way to study crystal structures directly. Different from the scanning probe microscopy method for the topmost surface topology, such as scanning tunneling microscope (STM) or atomic force microscope (AFM), stereoatomoscope can be used to observe three-dimensional atomic arrangements within several layers below the surface directly without Fourier transformation. The basic principle of the stereoatomoscope is the circular dichroism in photoelectron angular distribution (PEAD). Figure 1 shows the spiral constant phase surface for photoelectrons excited by circularly polarized light on which photoelectrons propagate perpendicularly. The forward focusing peaks corresponding to the scatterer atom directions are observed in the PEAD patterns. The rotation angles of forward focusing peaks at circularly polarized light are inversely proportional to the distance between the emitter and the scatterer, which is the same as the parallax for stereoview. Thus, three-dimensional atomic arrangements are observed when viewing the two PEAD patterns taken at clockwise (cw) and counterclockwise (ccw) circularly polarized lights by two eyes simultaneously. Measuring the rotation angles of forward focusing peaks, the atomic distance between the emitter and the scatterer can be obtained. Selecting the photoelectrons emitted from the specific kind of atomic core levels by tuning photon energy and pass energy of the analyzer, stereoscopic photographs of atomic arrangements around different kinds of atoms and the corresponding atomic distance can be obtained. In this paper, we present the stereoscopic photographs of atomic arrangements around Nb and Fe atoms in the intercalation compound Fe$_{1/3}$NbS$_2$, and the concept for crystal structure analysis by using stereoatomoscope.

II. EXPERIMENT AND RESULTS

The experiment was performed at BL25SU/SPring-8 (Japan Synchrotron Radiation Institute), where cw and ccw circularly polarized soft x rays are produced by using twin helical undulator. The photon incident angle was 45° with respect to sample surface normal. The single-crystal Fe$_{1/3}$NbS$_2$ with the lattice constant $a=3.28$ Å and $c=12.08$ Å (Ref. 7) was cleaved in situ in ultrahigh vacuum (10$^{-8}$ Pa) chamber.

FIG. 1. Image of circularly polarized x-ray and the forward focusing peak rotation. The strip describes the constant phase surface on which photoelectrons propagate perpendicularly.

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The hexagonal forward focusing peaks are always observed when using the Nb 3p photoelectrons. The center forward focusing peak is produced by the Fe and Nb atoms lying on top of the emitter Nb atoms. In the lower right corner of the PEAD patterns, a shadow caused by the electron gun in the analyzer, which is used for the low-energy electron diffraction (LEED) measurement, appears and the photoelectrons flying near the electron gun are trapped. In the PEAD pattern at cw circularly polarized light, one of the six inner forward focusing peaks, which is near the electron gun, is weaker than the other five forward focusing peaks. While in the PEAD pattern at ccw circularly polarized light, the forward focusing peak near the electron gun becomes stronger. This is a clear visual evidence that the forward focusing peaks turn right at cw circularly polarized light and left at ccw circularly polarized light. When seeing the two patterns by left and right eyes individually at the same time, three-dimensional atomic arrangements seen from Nb atoms with the magnification of about $2 \times 10^6$ can be observed.

The shift angles of the forward focusing peaks in the PEAD patterns can be expressed by a simple formula $\Delta = m'/(kR \sin^2 \theta)$, where $m'$ is the effective magnetic quantum number that can be approximated as $m \sin \theta$, $k$ is the wave number of photoelectrons, $R$ is the atomic distance between the emitter and the scatterer, and $\theta$ is the angle between the incident photon direction and the outgoing direction of the emitted photoelectrons. Measuring the shift angles $\Delta$ of the forward focusing peaks, the atomic distances between the emitters and scatterers can be obtained by using the formula. This is the only way to measure the atomic distances and viewing the three-dimensional atomic arrangements directly without Fourier transformation process. The peak positions are decided as the center of the circles that are used to match the forward focusing peaks. In order to understand the structure easily, the angle $\theta_{c} (\text{crystal})$ between the surface normal and the scatterer direction in the crystal is also measured through coordinate transformation. The atomic distances between the emitters and scatterers are obtained as an average 7.98 Å, while the angles $\theta_{c}$ are averaged as 15.01° from the inner forward focusing peaks with hexagonal lines as eye guides. Errors are estimated as about 15% of the measured distances.

The measured results show good agreement with the S atoms lying in the upper fifth-nearest-neighbor layer from the Nb emitters, whose corresponding values calculated from the lattice constant that are obtained from the x-ray diffraction method are 7.78 Å and 14.08°, respectively. In the same way, the outer forward focusing peaks are concluded to be the Nb atoms lying in the upper fourth-nearest-neighbor layer. In Fig. 3, the calculated forward focusing peak positions of the S atoms (red ball) and the Nb atoms (red box) at cw and ccw circularly polarized lights are overlapped, respectively. The discrepancies of the outer forward focusing peak positions result from the distortion of the peaks in larger acceptance angles of the analyzer.

Figure 4 shows the PEAD patterns obtained by using the Fe 2p$_{3/2}$ photoelectrons with a kinetic energy of 550 eV at cw and ccw circularly polarized lights, respectively. Though the intensity of Fe 2p in the spectrum is very weak, forward focusing peaks forming a hexagonal arrangement with a center are observed. Moreover, weak forward focusing peaks
lying in the outer space are also visible. The hexagonal arrangements of the Fe 2p_{3/2} photoelectron forward focusing peaks are almost the same as that of the Nb 3p_{3/2} photoelectrons due to the layer crystal structure. The two PEAD patterns also show us the three-dimensional atomic arrangements viewed from Fe atoms. The atomic distances between the emitters and the scatterers are measured from the PEAD patterns by using the same way as that used in the Nb 3p_{3/2} PEAD patterns. Since the forward focusing peaks near the electron gun are difficult to recognize, only the three peaks A, B, and C in the two patterns are used to estimate the atomic distances between the emitters and the scatterers. The average measured atomic distances \( R \) and angles \( \theta_{c} \) from the three peaks are 8.67 Å and 16.65° with about 15% errors, respectively. The inner forward focusing peaks are concluded to be the S atoms lying in the upper fifth-nearest-neighbor layer, while the outer forward focusing peaks are the Fe atoms lying in the upper fourth-nearest-neighbor layer from the photoelectron-emitting Fe atoms. The overlapped red balls and boxes are the calculated positions of the S atoms lying in the upper fifth-nearest-neighbor layers and the Fe atoms lying in the upper fourth-nearest-neighbor layers at cw and ccw circularly polarized lights, respectively. Because there are only 1/10 amount Fe in one unit cell, the forward focusing peaks produced by Fe 2p_{3/2} photoelectrons are weaker than those produced by the Nb 3p_{3/2} photoelectrons. The atomic distance between the emitter Fe atoms and the scatterer S atoms lying in the upper fifth-nearest-neighbor layer is expected to be 7.78 Å due to the known lattice constant. The hard forward focusing peak-position decision because of the weak intensity and the analyzer inhomogeneity are thought to be the main reasons for the discrepancy between the measured and calculated atomic distances.

S 2p PEAD patterns were also taken to observe the atomic arrangements. However, the relatively complicated S arrangements in the crystal and the inhomogeneity of the analyzer make the forward focusing peaks diffuse with strong backgrounds.

III. CONCLUSIONS AND OUTLOOK

Scanning the pass energy of the analyzer, x-ray photoelectron spectrum can be obtained, and thus element specification is realized. By analyzing the intensity of photoelectrons, the amount of different elements can be estimated. Selecting the photoelectrons emitted from different kinds of atoms, the three-dimensional atomic arrangements can be obtained around the selected atoms, and the atomic distances between the emitters and scatterers can be measured by measuring the forward focusing peak positions in the PEAD patterns. For the inner forward focusing peaks in the Nb 3p_{3/2} PEAD patterns, the measured atomic distances show good agreement with those calculated from the known lattice constant. If sharp forward focusing peaks are obtained, the accurate atomic distances and orientations between selected atoms can be measured. This provides us the direct structure information of atomic arrangements in crystal. So far, the stereoatomscope is the only instrument that has the ability to take three-dimensional atomic arrangements around selected elements and to measure the atomic distance directly. The high sensitivity of the stereoatomscope is certified by the observation of the three-dimensional atomic arrangements around Fe atoms despite its small amount in Fe_{1/3}NbS_{2}. When the photoelectrons for selected area are selected, the selected area structures and chemical states analysis can be realized. After improving the transmission of photoelectrons and decreasing the inhomogeneity of the analyzer, the stereoatomscope is expected to be a powerful method for the research of nanoscience.

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