

### 10-1 Structure Analysis of Low-Dimensional Structures – Analysis of Resonant-Diffuse X-Ray Scattering Spectra

Recent developments in synchrotron-based X-ray diffraction techniques combined with modern analysis methods such as the maximum entropy method and resonant X-ray scattering, enable us to discuss the electronic states of materials. Knowledge of local structure – the atomic arrangement of a specific small volume – is sometimes essential for understanding the functions of materials, since the electronic states are often reflected in the local structures. This is the reason why structure analysis, which provides three-dimensionally ordered atomic positions with excellent spatial resolution and accuracy, is important in solid state physics. Unfortunately, the local structure formed by an electronic state does not necessarily have three-dimensional (3D) ordering. This means that most diffraction-based methods, including ordinary structure analysis, do not always provide information sufficient to clarify the electronic states; most of them are based on the 3D ordering of the atomic arrangement and can not provide information on low-dimensional orderings, or orderings with short correlation lengths which produce rod or plane-shaped scattering or diffuse X-ray scattering.

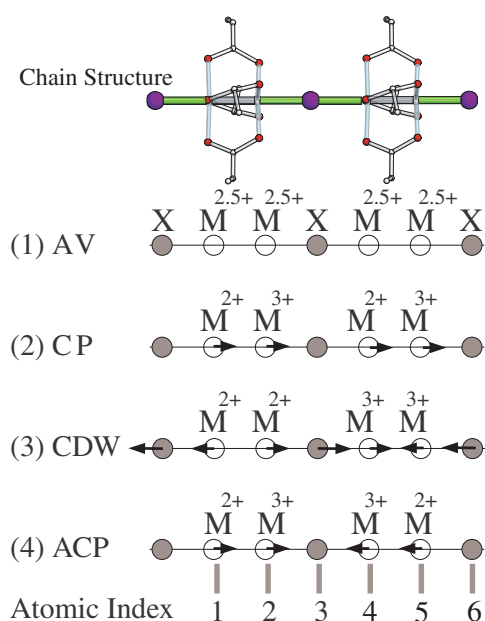


Figure 1  
Traditional models for the valence arrangement of metal-metal-halogen (MMX) complexes. The atomic displacement vectors are also shown.

In order to clarify the local structure for low-dimensional systems, we have developed a new method of analyzing diffuse X-ray scattering intensity [1]. As a model sample for demonstrating the technique, we study halogen-bridged quasi-one-dimensional metal complexes, which have possible applications as high-performance optical devices due to their huge third-order nonlinear optical susceptibilities [2] and anomalous quasi-one-dimensional conduction [3]. Several types of valence arrangements consisting of chains composed of metal-metal-halogen (MMX) units (Fig. 1) have been proposed in order to explain the properties of these complexes. Currently no method has been successful in clarifying their low-dimensional structure.

Synchrotron X-ray scattering measurements were performed at BL-1A, 1B and 4C. At BL-1A and 1B imaging-plate Weissenberg cameras were used for sample characterization and to observe the overall features of the diffuse scattering distributions. At BL-4C a standard four-circle diffractometer was used for measurements of the energy spectra of the diffuse intensity. Reflecting the low-dimensionality of the structures, diffuse X-ray scattering was clearly observed, as shown in Fig. 2.

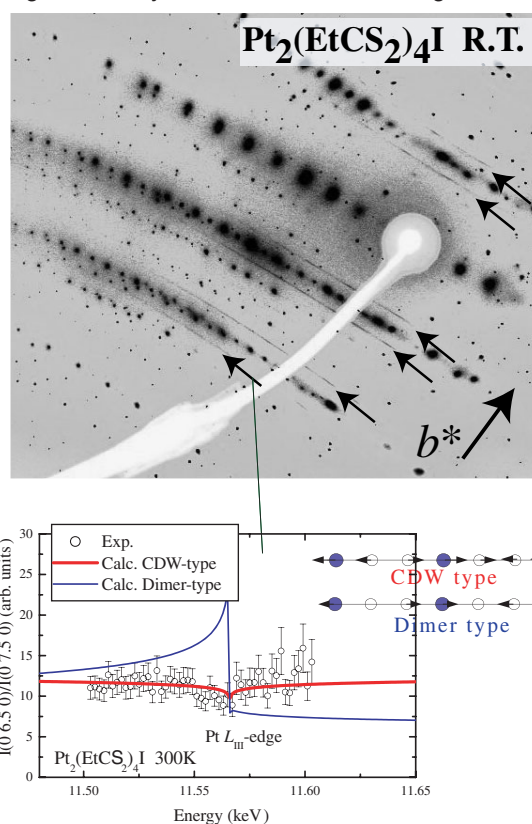


Figure 2  
Oscillation photograph of  $Pt_2(EtCS_2)_4I$  ( $Et = CH_3CH_2-$ ) at room temperature, along with the energy spectrum of the diffuse scattering intensity. The calculated spectra for CDW-type and dimer-type atomic displacement models are also shown.

Each possible valence arrangement shown in Fig. 1 produces a different diffuse scattering intensity distribution. Some of the electronic structures could be rejected by comparing the measured diffuse intensity to the model calculations, although it has not yet been possible to obtain a unique solution. The difference between the models becomes more prominent when we extract the scattering amplitude of the Pt ions using the technique of resonant X-ray scattering. Figure 2 shows the energy spectrum of the diffuse scattering intensity near the Pt  $L_{III}$  absorption edge, together with the calculated spectra for two different one-dimensional structures producing almost the same Q-dependence of the diffuse scattering distribution. The energy spectra confirm that a CDW-type structure is present in the material. This result provides us with further insights [1] as to the origin of the anomalous conductivity which has been reported for this material [3]. Application of the new method to other low-dimensional systems will provide useful new information for solid-state physics and chemistry.

**Y. Wakabayashi<sup>1</sup>, A. Kobayashi<sup>2</sup>, H. Sawa<sup>1</sup>, H. Ohsumi<sup>3</sup>, N. Ikeda<sup>3</sup> and H. Kitagawa<sup>2</sup>** (<sup>1</sup>KEK-PF, <sup>2</sup>Kyushu Univ., <sup>3</sup>JASRI/SPring-8)

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## 10-2 Development of an Electron Electron Ion Coincidence Apparatus for Auger-Photoelectron Coincidence Spectroscopy (APECS) and Electron Ion Coincidence (EICO) Spectroscopy

Auger-photoelectron coincidence spectroscopy (APECS) is a unique and powerful technique for elucidating the correlation between a specific photoemission and the resultant Auger processes [1]. Since Auger electrons reflect electronic states in the vicinity of the core-excited atom, APECS has been applied for the study of the local electronic structures at a specific site [2]. On the other hand, electron ion coincidence (EICO) spectroscopy is widely used for the study of ion-desorption stimulated by Auger processes (Auger-stimulated ion desorption (ASID), Fig. 3) [3]. Since ASID plays important roles in many disciplines, including surface science, astrophysics, radiation biology, and surface

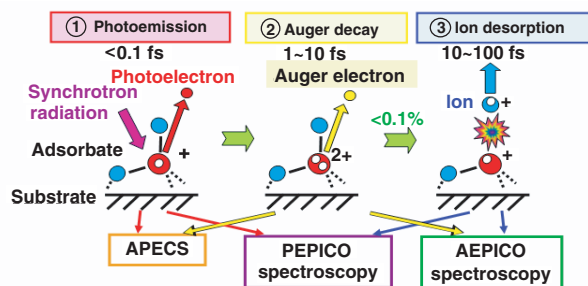


Figure 3 Auger-stimulated ion desorption (ASID) mechanism, and APECS, PEPICO, and AEPICO spectroscopy.

analysis, study of the phenomenon has attracted large numbers of researchers for decades. To study ASID, APECS as well as photoelectron photoion coincidence (PEPICO) and Auger-electron photoion coincidence (AEPICO) measurements are essential, as shown in Fig. 3.

Recently, we have developed an electron electron ion coincidence (EEICO) apparatus that can be used for both APECS and EICO measurements. An overview of the apparatus is given in Fig. 4 and described fully in reference [4]. The EEICO analyzer consists of a coaxially symmetric mirror analyzer (ASMA) with an electron energy resolution ( $E/\Delta E$ ) of  $\sim 50$ , a cylindrical mirror analyzer (CMA) with an  $E/\Delta E$  of  $\sim 20$ , a time-of-flight ion mass spectrometer (TOF-MS), an xyz stage, a tilt-adjustment mechanism, and is mounted on a conflat flange with an outer diameter of 203 mm. During irradiation of the sample with synchrotron radiation, the emitted electrons are energy-analyzed and detected by the ASMA and the CMA, and the desorbed ions are detected by the TOF-MS. The performance of the EEICO analyzer was tested at BL-8A.

Figure 5 shows Si- $L_{23}VV\text{-Si}^0\text{-}2p$  and Si- $L_{23}VV\text{-Si}^{1+}\text{-}2p$  APECS of Si(111)7 $\times$ 7 exposed to water ( $H_2O$ ) at room temperature.  $H_2O$  is known to be dissociatively ad-

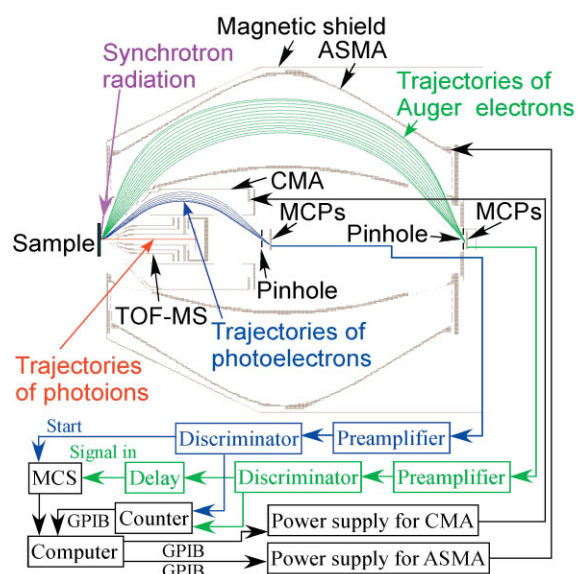


Figure 4 EEICO analyzer for APECS and EICO spectroscopy. The measurement system for APECS is also shown. "MCPs" represent microchannel plates, and the "MCS" is a multichannel scaler.

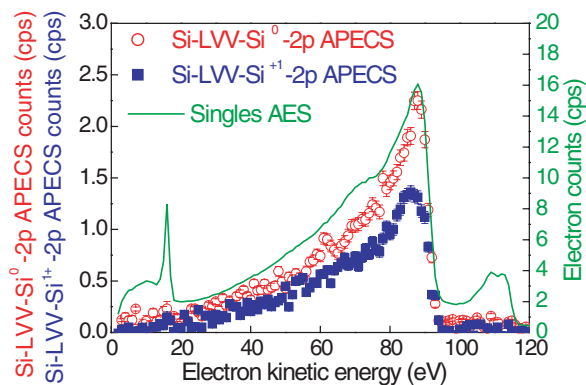


Figure 5  
Si-L<sub>23</sub>VV-Si<sup>0</sup>-2p (open circles) and Si-L<sub>23</sub>VV-Si<sup>+1</sup>-2p (filled squares) APECS at  $h\nu = 120$  eV of Si(111)7×7 covered with dissociated H<sub>2</sub>O. The thick solid line represents the singles AES.

sorbed on Si(111)7×7, forming Si-OH and Si-H surface species. The Si-L<sub>23</sub>VV-Si<sup>+1</sup>-2p APECS reflects the Si L<sub>23</sub>VV Auger electron spectrum (AES) at the Si-OH site, while the Si-L<sub>23</sub>VV-Si<sup>0</sup>-2p APECS reflects the Si L<sub>23</sub>VV AES at the Si-H and the bulk Si sites. The peak position of the Si-L<sub>23</sub>VV-Si<sup>+1</sup>-2p APECS was shifted by 2 eV to the lower electron-kinetic-energy (KE) side compared to the Si-L<sub>23</sub>VV-Si<sup>0</sup>-2p APECS. This result indicates that the valence electronic states in the vicinity of the Si-OH site are shifted to larger binding-energies in comparison with those of the Si-H and the bulk Si sites.

Figure 6 shows a H<sup>+</sup> AEPICO spectrum and a singles AES (AES measured with the ASMA) of condensed water (H<sub>2</sub>O) recorded at the 4a<sub>1</sub> ← O 1s resonance ( $h\nu = 532.9$  eV). Major, medium, and minor peaks appear at KEs of 510, 490, and 470 eV in the H<sup>+</sup> AEPICO spectrum. These positions are shifted by several eV to higher KEs compared to the singles AES. These results indicate that the following four-step mechanism is responsible for H<sup>+</sup> desorption; 1) 4a<sub>1</sub> ← O 1s resonant transition of a surface H<sub>2</sub>O molecule, 2) extension of the HO-H distance in the (O 1s)<sup>-1</sup>(4a<sub>1</sub>)<sup>1</sup> state within the lifetime of the O 1s hole, 3) spectator Auger transition leav-

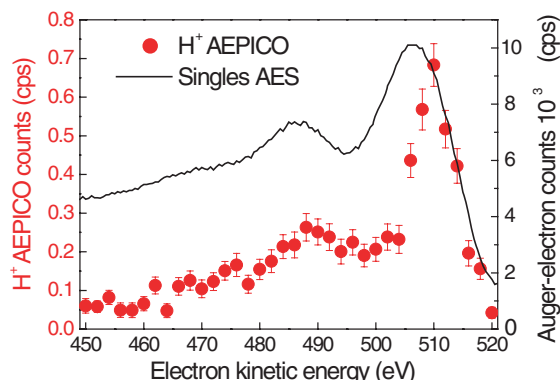


Figure 6  
H<sup>+</sup> AEPICO spectrum (filled circles) and singles AES (solid line) of condensed H<sub>2</sub>O at the 4a<sub>1</sub> ← O 1s resonance ( $h\nu = 532.9$  eV).

ing a (valence)<sup>-2</sup>(4a<sub>1</sub>)<sup>1</sup> state, and 4) H<sup>+</sup> desorption along the repulsive potential surface of the (valence)<sup>-2</sup>(4a<sub>1</sub>)<sup>1</sup> state [3].

The EEICO apparatus is now available for users of the Photon Factory. The advantages of the apparatus are high detection efficiency, relatively high energy resolution, easy alignment, easy operation, and low cost.

**T. Kakiuchi<sup>1</sup>, E. Kobayashi<sup>2</sup>, N. Okada<sup>3</sup>, K. Oyamada<sup>3</sup>, M. Okusawa<sup>3</sup>, K. K. Okudaira<sup>4</sup> and K. Mase<sup>1,2,5</sup>** (<sup>1</sup>The Grad. Univ. for Adv. Stud., <sup>2</sup>KEK-PF, <sup>3</sup>Gunma Univ., <sup>4</sup>Chiba Univ., <sup>5</sup>JST-PRESTO)

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