

3-1 A Structural Study of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag Surface at Low Temperature by X-Ray Diffraction

The Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag surface has been attracting interest since its first observation by low-energy electron diffraction in 1967. Its structure had been controversial until a honeycomb-chained triangle (HCT) model was proposed based on surface X-ray diffraction studies [1]. Figure 1(a) illustrates the atomic arrangements of top three layers projected on the surface in the HCT model. Ag atoms on the top of the surface are shown in orange, the first layer of Si in dark blue, and the second layer of Si in light blue. The unit cell is represented by the mirror lines in gray. In this model, Ag atoms make large triangles, indicated in the figure by broken red lines. As a result of this arrangement, small triangles with equal sizes (shown in light green in Fig. 1(a)) are chained in a honeycomb pattern.

Recently, however, based on first-principles calculations and scanning tunneling microscopy (STM) experiments at low temperatures [2], it has been suggested that the most stable structure of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag surface is not an HCT structure but an inequivalent triangle (IET) structure. This IET model is characterized as a structure in which the large triangles of Ag atoms (indicated by broken red lines in the HCT model) rotate slightly around their centers, losing mirror symmetry. As a result of these rotations, the equal-sized small triangles of the HCT model change into two triangles with different sizes in the IET model, as shown in light green and pale light green in Fig. 1(b). Although a hexagonal lattice pattern (light green) suggesting an IET structure is observed in STM images [2], the existence of the IET structure is still controversial and its atomic arrangement is yet to be determined.

The proposal of the IET model also casts some questions about the structure at room temperature (RT), and suggests the possibility of a model in which Ag atoms thermally fluctuate at RT between two IET structures rotated in opposite directions, as shown in the lower left part of Fig. 1(b).

In this work [3], we investigate the in-plane structure of the surface both at RT and at low temperature using surface X-ray diffraction in grazing incidence geometry. We have observed the intensities of diffraction spots peculiar to the $\sqrt{3}\times\sqrt{3}$ structure both at RT and at low temperature (50 K). The experiments were done at BL-15B2 using a six-circle diffractometer equipped with an ultra-high vacuum chamber. Integrated intensities were accumulated for 26 spots at both temperatures.

Figures 2(a) and (b) show the Patterson maps calculated from the observed intensities at RT and 50 K, respectively. Since peaks in the Patterson map correspond to the interatomic vectors between two atoms, peak A observed at RT is assigned to the interatomic vector between Ag atoms making large triangles in Fig. 1(a) as marked by A. In contrast, peak A splits into two peaks A1 and A2 at 50 K as shown in Fig. 2(b). This split indicates the existence of twin domains in which triangles of Ag atoms are rotated in opposite directions. This result is also supported from the observation of diffuse scattering originating from twin domains at low temperatures.

We have also determined the phase transition temperature to be about 150 K by observing the temperature dependence of the diffuse scattering. Detailed analyses using least-squares fits show that the rotation angle of the Ag triangles is about 6°, consistent with first-principles calculations [2]. Peak B in Figs. 2(a) and (b) corresponds

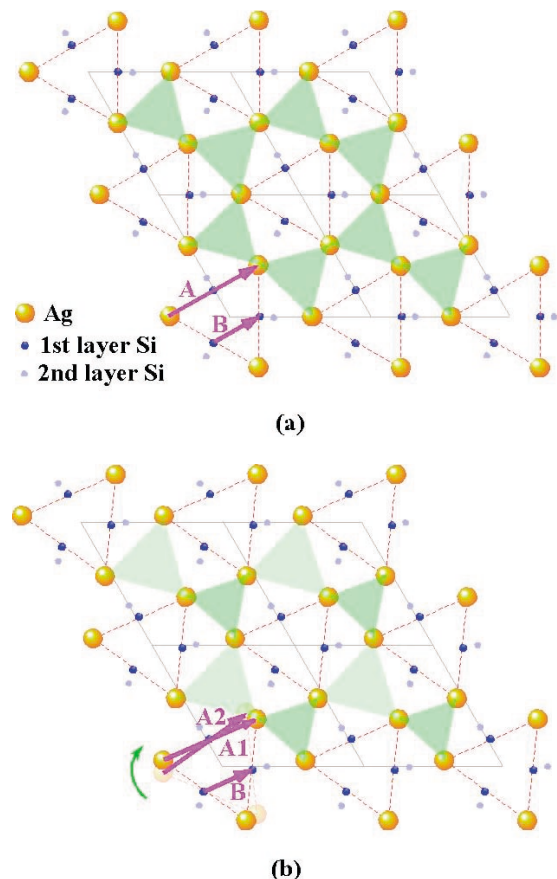


Figure 1 Illustration of the HCT model (a) and IET model (b). Gray lines show the unit cell. In the IET model, the large triangles indicated by broken red lines rotate slightly from their symmetric positions in the HCT model. This rotation changes the size of the small triangles indicated by light green. In the IET model, there exists a domain structure in which the large triangles are rotated in the opposite direction, as illustrated in the lower left part of the figure.

3-2 An Angle-Resolved Photoemission Study of the Near Surface Electronic Structure of Cr(001)

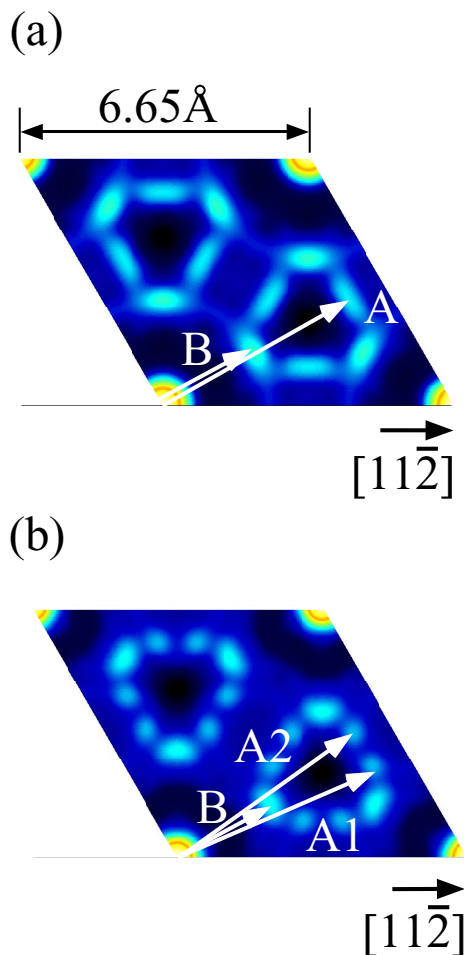


Figure 2
Patterson maps calculated from observed intensities at RT (a) and at 50 K (b). Peak A at RT, corresponding to interatomic vectors between Ag atoms, splits into two peaks A1 and A2 at 50 K. Peak B corresponds to the interatomic vectors between the first-layer of Si atoms.

to the interatomic vectors between the first-layer Si atoms in Figs. 1(a) and (b). Analysis shows that the Si atoms form trimers of almost the same size at both temperatures, suggesting that the Si trimers rotate around their centers in a similar way to the Ag triangles at low temperature.

Measurements of the temperature dependence of some of the diffraction spots indicate that the phase transition is accompanied by structural changes. This means that the structure at RT can not be explained by a model in which Ag atoms thermally fluctuate between the two IET structures rotated in opposite directions. The analysis of the data observed at RT also supports the HCT model.

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The (001) surface of antiferromagnetic Cr metal is theoretically predicted to be ferromagnetic. Surface ferromagnetism of Cr(001) is a basic but challenging problem. The possibility that a ferromagnetic sheet is barely exposed on the surface is still under debate. Nowadays understanding of the magnetic and electronic structure of thin Cr films, including surface ferromagnetism, is a longed-for necessity for a complete explanation of novel features such as giant magnetoresistance and oscillatory interlayer exchange coupling in Fe/Cr superlattices [1].

An angle-resolved photoemission experiment for Cr(001) has previously been performed [2], and two peaks just below the Fermi level (E_F) were observed and interpreted as being due to ferromagnetic exchange-split surface states. On the other hand, a spin-polarized photoemission experiment concluded no ferromagnetism of Cr(001). Since the surface cleaning procedure of Cr(001) is difficult, these features have so far been only poorly examined. We have therefore reexamined the surface electronic structure of Cr(001) [3].

The experiments were performed at BL-3B using ARPES-II equipment. Figure 3 presents normal-emission spectra just below E_F for $25 \text{ eV} \leq h\nu \leq 70 \text{ eV}$ measured at $\theta_i = 30^\circ$. Peak 1 exhibits slight energy dispersion, suggesting that this peak can be assigned to a surface state,

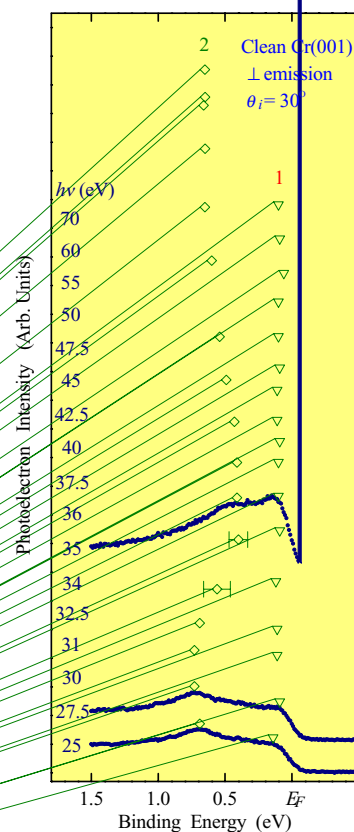


Figure 3
Normal-emission spectra of clean Cr(001) for energies between E_F and 1.5 eV, measured at $\theta_i = 30^\circ$ as a function of $h\nu$.

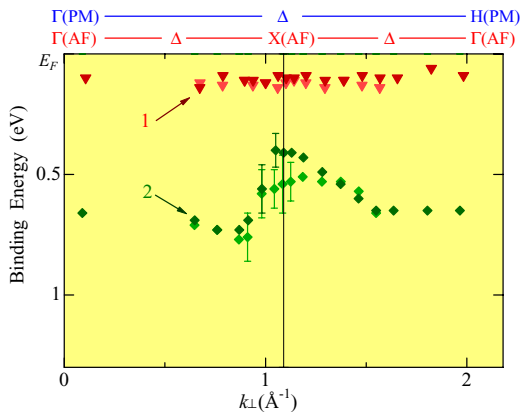


Figure 4
Experimentally observed band dispersion along the Δ -symmetry line. The two points for $h\nu = 70$ eV are folded back to the left hand side of the figure.

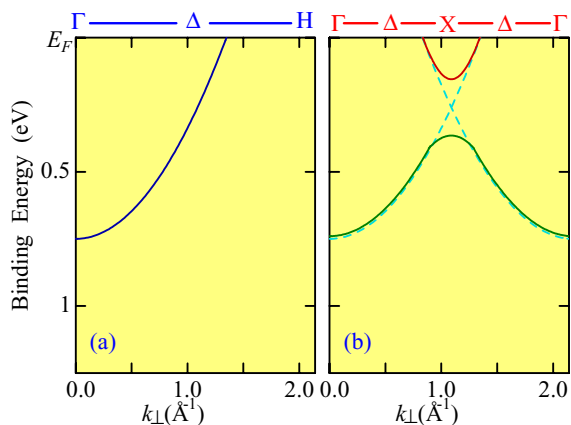


Figure 5
Schematic band structure of (a) PM and (b) AF phases along the Δ -symmetry line. (a) Only one Δ_5 band is found in the calculated band of PM Cr for $E_f \leq E_b \leq 1.5$ eV [4]. (b) In the AF phase, the band is folded back at point X (dashed curves) and an energy gap appears. The solid curves are the resultant bands.

since a surface state has a two-dimensional nature. On the other hand, peak 2 clearly shows an energy shift between 0.4 eV and 0.7 eV. This is conclusive evidence that peak 2 can be no longer ascribed to a surface state but must be due to a bulk state.

Together with the results of spectra taken with $\theta_i = 60^\circ$ (not shown), all the observed peak positions along the [001] direction in the bulk Brillouin zone (BZ) are plotted in Fig. 4. Symmetry points of the BZ for both paramagnetic (PM) and antiferromagnetic (AF) phases are indicated at the top of the figure. To interpret Fig. 4 a schematic band structure of Cr along the Δ line is shown in Fig. 5. Only the relevant Δ_5 band is found in the PM phase [4] [Fig. 5(a)]. The experimentally determined dispersions (Fig. 4) are completely different from theoretical predictions based on a PM phase. In the AF phase, the PM Γ -H Δ symmetry line is folded back at the center. The folded energy bands are also shown by dashed curves in Fig. 5(b). An energy gap appears at X, the point where bands cross. The solid curves in Fig. 5(b) are the resultant schematic energy bands for the AF phase. The dispersion of peak 2 follows approximately the lower band

of Fig. 5(b). This indicates that the band structure of the Cr(001) surface has the same periodicity as the AF bulk band. The upper band of Fig. 5(b) ranges over limited k_\perp and cannot be directly assigned to peak 1. We tentatively assign peak 1 as a surface state split off from this upper bulk band and/or a mixture. Our results show that the generally accepted simple picture that these peaks 1 and 2 are exchange-split surface states is no longer valid, although the appearance of surface ferromagnetism of Cr(001) is still undeniable.

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3-3 Metal-Induced Gap States at Well Defined Alkali-Halide/Metal Interfaces

There is growing interest in the nature of insulator/metal interfaces, since they provide fascinating possibilities for the study of metal-insulator transitions and superconductivity as well as technological applications such as catalysis and magnetic tunneling junctions. Despite these interests, electronic structures characteristic of the insulator/metal interface have not yet been studied satisfactorily. In the present study, we prepared atomically well-defined alkali halide (insulator)/metal interfaces [1], and measured the electronic structures at the interface by near edge X-ray absorption fine structure (NEXAFS) spectroscopy [2] at BL-11B.

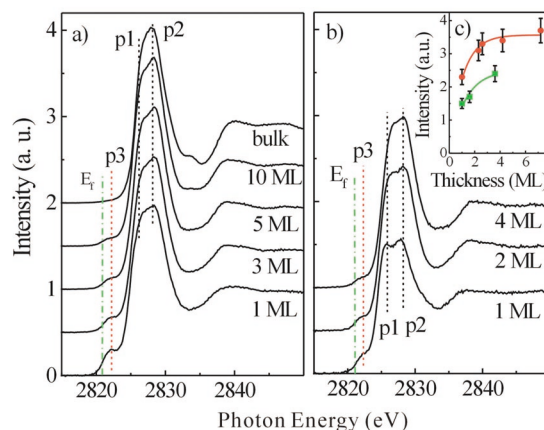


Figure 6
Cl-K edge NEXAFS spectra in LiCl films grown on (a) Cu(001) and (b) Ag(001) for various thicknesses of the LiCl layer. All spectra are normalized by their edge-jump heights. E_f indicates the position of the Fermi level as determined from XPS. The X-ray incidence angle is 15° . Inset (c) shows the intensity of the pre-peak unnormalized versus the film thickness, and the curves are least-squares fits. The intensity of the pre-peak for the LiCl film was obtained by subtracting the bulk component from the raw spectra.

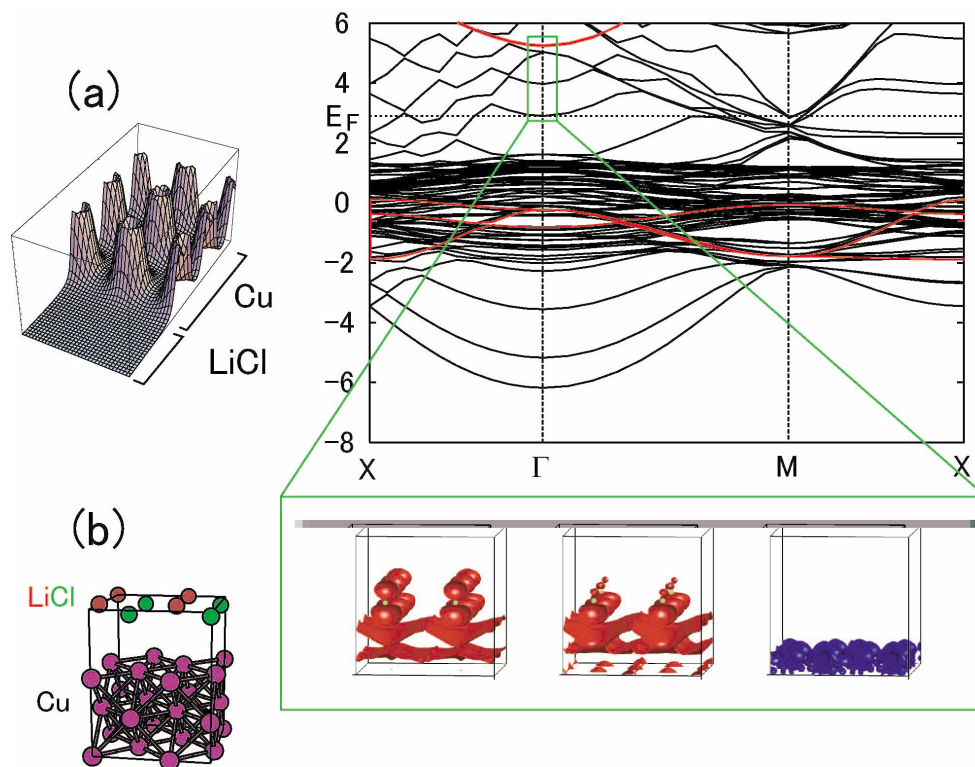


Figure 7

(a) The band structure of 1 ML LiCl/Cu(001) (black) as compared with that for an isolated 1 ML LiCl (red). (b) Contours of the absolute value of the LDA wave functions for the in-gap states (enclosed by a green square) are shown along with the atomic configuration. Wave functions having amplitudes on both Cl and Cu atoms are shown in red. The top left inset shows the charge distribution difference between LiCl/Cu(001) and isolated LiCl.

Figure 6 shows the Cl-K edge NEXAFS results for LiCl/Cu(001) and LiCl/Ag(001). As the thickness of the LiCl layer decreases, a pronounced pre-peak (p3) emerges below the bulk edge onset. The appearance of the pre-peak indicates that new states are formed at the LiCl/metal interface. There are two points to note. Firstly, the pre-peak is observed even for the 10 ML (26 Å) LiCl on Cu(001), indicating that the new states are characteristic of the interface rather than specific to 1 ML. Secondly, the pre-peak is observed for both LiCl/Cu(001) and LiCl/Ag(001), in spite of the difference in the interface structure [1].

To investigate the chemical bonds at the interface, we have investigated the electronic structure of the LiCl film and the metal substrate with X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES). The XPS and AES results showed the absence of chemical bonds at the interface. An additional point to be noted relates to the position of Fermi level, which can be estimated from the binding energy of Cl 1s XPS. As indicated in Fig. 6, the pre-peak crosses the Fermi level, that is, there is a finite density of states at E_F . Therefore, LiCl is *metallized* at the interface. The NEXAFS, XPS, and AES results described above reveal that the pre-peak originates not from chemical bonds at the LiCl/metal interface, but from the gap states formed by the proximity to a metal. The gap states can be qualitatively understood as *metal induced gap states* (MIGS).

From the dependence of the intensity of the pre-peak

on the LiCl thickness, the decay length is determined to be 2.6 ± 0.3 Å for LiCl/Cu(001) and 2.9 ± 0.7 Å for LiCl/Ag(001) [Fig. 6(c)], indicating that the MIGS are indeed localized within a few Å of the interface. In addition, the polarization dependence of the NEXAFS study clearly shows that the MIGS correspond to states extending along the normal to the interface direction. An ab initio electronic structure calculation supports the existence of the MIGS that are strongly localized at the interface (see Fig. 7).

Finally, let us point out that MIGS have interesting implications for superconductivity. The observation of MIGS at insulator/metal interface implies that we do have a coexistence of excitations and carriers at the interface. To have a high T_c , the carriers and the excitons have to interact strongly, which is envisaged to be possible due to the penetration of MIGS into the insulating layer. So we may expect that insulator/metal interfaces such as those discussed here may provide possible grounds for superconductivity.

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3-4 Structure of Methylthiolate Adsorbed on Au(111) Studied by Photoelectron Diffraction

Self-assembled monolayers (SAMs) are highly-ordered monolayers that are spontaneously formed on various solid surfaces and have potential applications such as molecular recognition, biosensors, nanofabrication, and single-molecular electronic devices. In particular, alkanethiolate ($\text{CH}_3(\text{CH}_2)_n\text{S}$) SAMs on Au(111) have attracted much attention because of their simplicity, stability, and high ordering. The structure of the alkanethiolate SAMs, however, has been a long-standing issue, although understanding the structure is quite important for atomistic-level applications. In this work, we measured and analyzed scanned-energy and scanned-angle S 2p photoelectron diffraction (PD) pattern for $\text{CH}_3\text{S}/\text{Au}(111)$, which is the simplest but one of the most thoroughly-studied SAM systems both from experimental and theoretical points of view. We propose from the PD analyses an unambiguous structure model [1], which will contribute to the fundamental understanding of this promising nanomaterial.

The PD experiments were performed at BL-7A [2] with an ultrahigh vacuum end-station equipped with a high-resolution electron energy analyzer. Saturated methylthiolate monolayers on a single-crystal Au(111) surface with

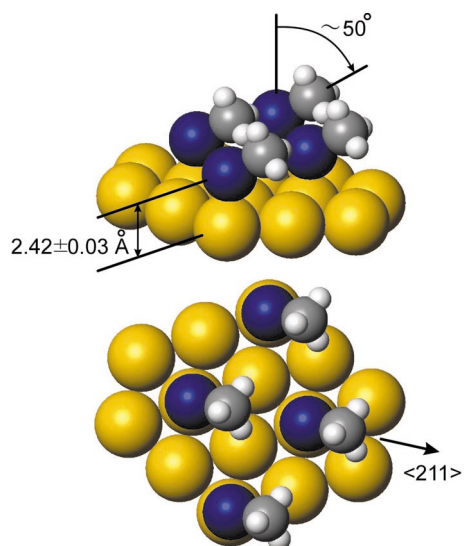


Figure 9 Schematic side and top view of the best-fit adsorption geometry of methylthiolate adsorbed on Au(111). The hydrogen atoms are shown at tentatively assumed positions.

a commensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure were used for the PD experiments. Figure 8(a) shows the modulation function of scanned-energy photoelectron diffraction pattern taken at several emission angles (black curves) and best-fit simulated functions based on an atop model shown in Fig. 9 (green curves). The normal-emission ($\theta = 0^\circ$) function exhibits strong oscillations with almost a single period, while the grazing-emission ($\theta = 60^\circ$) functions show a significant decrease in oscillation amplitude. Since single-period strong oscillations are characteristic of 180° back scattering from a near neighbor, the angular dependence suggests the existence of an Au atom beneath the S atom, *i.e.* atop adsorption. R-factor analyses for the scanned-energy data as a function of S-Au distance give further support for atop adsorption; only the atop model exhibits a clear minimum in the R-factor at an S-Au distance of 2.42 Å, whereas the other models show no apparent minimum, as shown in Fig. 8(b).

Scanned-angle PD data were also measured along the three major azimuths, as shown in the inset of Fig. 8(b), to obtain information on the orientation of the S-C bond. The polar-angle dependence of the PD intensity indicates that the S-C bond of the methylthiolate prefers to be tilted by approximately 50° from the surface normal towards the $[\bar{2}11]$ and $[\bar{1}2\bar{1}]$ azimuths, *i.e.* the nearest-neighbor directions of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ lattice. The resultant structure model for the $(\sqrt{3}\times\sqrt{3})R30^\circ\text{-CH}_3\text{S}/\text{Au}(111)$ system is shown in Fig. 9.

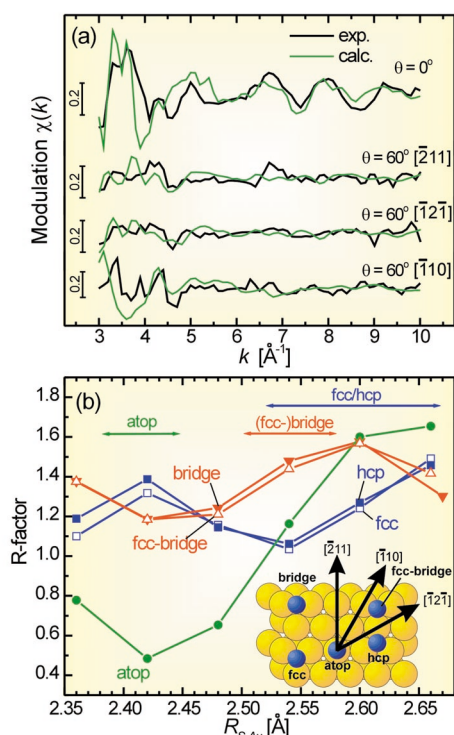


Figure 8 (a) Modulation functions of scanned-energy photoelectron diffraction (black curves) and simulated curves based on the atop model shown in Fig. 9. (b) R-factors of the simulations for the normal-emission curve assuming five high-symmetry sites plotted as a function of S-Au distance. Inset: Schematic illustration for the high-symmetry sites on the unreconstructed (111) surface of Au. Horizontal arrows indicate the possible range of S-Au distance for each site obtained from density functional calculations.

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