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Quantitative adsorbate structure determination for quasicrystals using X-ray standing waves

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Abstract

The quantitative structure determination of adsorbed species on quasicrystal surfaces has so far appeared to present insurmountable problems. The normal incidence standing X-ray wavefield (NISXW) technique offers a simple solution, without extensive datasets or large computations. Its application to quasicrystals raises several conceptual difficulties that are related to the phase problem in X-ray diffraction. We demonstrate their solution for the case of Si atoms adsorbed on the decagonal Co-rich Al-Co-Ni quasicrystal to determine the local structure, comprising 6-atom clusters in particular hollow sites.

The surfaces of quasicrystals exhibit many interesting and unusual properties, including the stability of aperiodic structures at surfaces, their comparatively low friction and adhesion, and their potential for exotic and useful thin films [1-4]. However, obtaining a complete quantitative determination of adsorbed species on a quasicrystalline surface appears to have presented insurmountable problems. Scanning tunnelling microscopy (STM) images can provide information on lateral ordering, but not the quantitative adsorption geometry, nor the elemental identity [5], although particularly when combined with density functional theory calculations it can be used to identify probable structures. Low-energy electron diffraction (LEED) has provided quantitative structures of clean quasicrystalline surfaces [6-9], but the need to treat adsorbate structures by huge model clusters with very many structural parameters renders this approach untenable. X-ray photoelectron diffraction (XPD) has also provided some information on clean quasicrystal surfaces [10] but is ill-suited to the determination of adsorbate geometries. However, the normal-incidence X-ray standing wave (NIXSW) technique offers a solution to this problem. While it has been shown to be possible to investigate the bulk structure of quasicrystals by NIXSW [18], its application to quasicrystal surfaces raises several additional conceptual problems. However, we show how these can be overcome to achieve a local structure determination of Si atoms adsorbed on the 5-fold (5-f) symmetric surface of a decagonal $\text{Al}_{72}\text{Co}_{17}\text{Ni}_{11}$ quasicrystal.

In NIXSW studies from crystalline substrates [11, 12] an x-ray standing wave is established in the substrate through interference of the incident and Bragg-reflected waves at near-normal incidence to the associated scattering planes. The location of the adsorbate atoms in the x-ray standing wavefield can then be determined by measuring the x-ray absorption variation at the adsorbate atom as the standing wavefield is swept through this atom by scanning the x-ray energy. Additional NIXSW measurements using scattering planes inclined relative to the surface plane provide information on the lateral position of the adsorbate atoms by triangulation. However, two complications related to the phase problem in x-ray diffraction [13, 14] emerge in the investigation of the structures of quasicrystals [15, 16]. Firstly, in the system studied here, the diffracted beam *intensities* show 10-fold symmetry as a result of the 10-fold-rotoinversion symmetry of the quasicrystal [15, 17], but the *phase* of the associated structure factors show only the lower 5-fold true rotation symmetry. NIXSW thus probes the quasicrystal structure at a lower symmetry than is evidenced by the diffraction pattern. This was established earlier for XSW from the bulk planes of an icosahedral quasicrystal [18].

Secondly, the phase of a standing wave in a quasicrystal is defined relative to the average periodic scattering planes that give rise to the diffracted beams, not to the actual quasiperiodic atomic planes and not, in particular, to the terminating surface plane. These problems would appear to preclude the use of the XSW technique for surface structure determination on quasicrystal surfaces, but we show here how to overcome these problems.

The quasicrystal used in this study was grown at Ames Laboratory using the melt decantation method [19]. It was cleaned by bombardment with 750 eV Ar⁺ ions, followed by annealing at 800°C (> 30 hours). The 10-fold symmetry of the resulting surface diffraction pattern was verified with LEED. Si was deposited at ~0.25 ML/min from a Knudsen cell, with the sample at room temperature. NIXSW measurements were made from a coverage of ~0.2 ML (estimated from the XPS Si/Al peak ratio and the appearance of the LEED pattern reported previously [20]), using beamline 4.2 of the Daresbury Laboratory's Synchrotron Radiation Source. This beamline was fitted with double crystal (InSb(111)) monochromator and a surface science end-chamber equipped with the usual *in situ* sample preparation and characterisation facilities. A concentric hemispherical analyser (at 40° to the incident photon beam in the horizontal plane) was used to measure the photoelectron energy spectra.

Decagonal Al₇₂Co₁₇Ni₁₁, the Co-rich modification of the decagonal quasicrystal, has the 5D space group symmetry $P\overline{10}2c$ [21, 22], and has aperiodic 5-fold symmetric layers stacked in a periodic arrangement [23]. This periodicity perpendicular to the surface allows us to apply the standard NIXSW technique (normal incidence to the scatterer planes minimises the impact of substrate mosaicity), monitoring the absorption at the (0004) reflection (photon energy ~3053 eV) by measuring the Si 1s photoemission intensity, to obtain the layer spacing of the Si atoms relative to these periodic planes [11, 12]. The amplitude and phase of the standing wavefield for a given set of planes are referred to as the coherent fraction (CF) and coherent position (CP), respectively. The (00004) structure factor required to analyse the data for the planes parallel to the surface was obtained by using a 200 x 200 Å² determination of the structure [21, 22] of this substrate, treated as a periodic unit cell. The results (Fig. 1) yield a CP value of 0.87 in units of the bulk interlayer spacing (2.04 Å) and thus a height above the nearest extended bulk layer of 1.77±0.05 Å. In the absence of any significant surface relaxation of the surface layers, this distance corresponds to the average height of the

Si atoms above the surface layer. The CF value of 0.48 ± 0.05 is significantly less than the unity value that would arise in the absence of any thermal vibrations for a single layer spacing, indicating that there must be a distribution of heights of the adsorbed Si atoms.

To determine the lateral positions of the Si atoms we must confront the problems outlined above associated with diffraction from the quasiperiodic structure in directions other than the surface normal. NIXSW absorption profiles were measured using the $\{0\bar{1}101\}$ planes; these have the second highest scattering amplitudes for Al-Co-Ni, (after the (00004) planes), and are tilted 60.4° from (00004) planes, with an average interlayer spacing of 2.02 \AA . The perpendicular to these planes contains a component parallel to the surface, so for a crystalline substrate this measurement determines the lateral position of the absorber atoms within the unit cell. In the case of a quasicrystal there is no periodic unit cell, but treating the $200 \times 200 \text{ \AA}^2$ structural unit that has been determined previously as a repeating unit cell should provide a rather good description of the structure. The $\bar{10}$ symmetry of the crystal means that the diffracted beam intensities are the same in 10 different azimuthal directions at intervals of 36° , so the structure factors in these 10 directions have the same amplitudes, but not the same phases. The relative phases of these 10 structure factors depend on the choice of the reference origin used in their calculation, but the most symmetric situation is obtained if the reference site is chosen to be a point of local 5-f symmetry in the structure. Using this reference site the calculated structure factors alternate for azimuthal increments of 36° between two distinct values that differ in phase by approximately $\pi/2$ (Fig. 2). An important consequence of this is that experimental measurements in a single azimuth correspond to only one of these structure factors, but the diffracted beam intensities do not allow us to know which value is appropriate. Moreover, NIXSW bulk absorption profiles also fail to distinguish between these two different azimuthal groups; simulations for these two sets of directions lead to the same profiles, both consistent with the experimental data (Fig. 2), because these are sensitive only to the relative positions of the dense scattering planes and the (same) dense absorber planes, and not to the position of these planes relative to some fixed point in the crystal. Distinguishing the two sets of azimuthal directions in our experiments must therefore rely on measurements of atomic positions on the surface. (In studies of *bulk* quasicrystals this phase problem can also be solved by multiple-beam X-ray diffraction [24].)

The sensitivity of NIXSW to absorption at different local adsorption sites on the surface is illustrated by the simulations shown in Fig. 3. The sites chosen for this example are the two different types of local 5-f hollows at the centre of the red and blue circles in Fig. 3(a) that for convenience we label ‘right-side-up’ (RSU) and ‘upside-down’ (USD), highlighting the fact that the local positions of the Al atoms are rotated in azimuth by 180° . Fig. 3(b) shows the results of NIXSW simulations for a single X-ray-absorbing atom at each of these sites in each of the two inequivalent azimuths. Unlike the simulations for bulk absorption, the NIXSW simulations show the true 5-f symmetry of the surface, with quite different results from the two azimuthal groups. Fig. 3(c) shows simulations (in azimuthal group B only) for the absorbing atom at three different RSU sites (i.e. three different sites that are locally-equivalent to the two RSU sites shown in Fig. 3(a)). The resulting NIXSW profiles are identical, showing that the NIXSW technique reflects the self-similarity of these sites that is a feature of the quasicrystalline order. Finally, Fig. 3(d) shows simulated NIXSW profiles for different lateral displacements of the absorbing atom from the RSU site in both x and y directions (as defined in Fig. 3(a)). Clearly the results are sensitive to these arbitrary shifts, but not to lateral shifts between self-similar quasicrystalline sites.

An important consequence of the different azimuthally-dependent structure factors is that it is not possible to analyse experimental NIXSW profiles from these canted scatterer planes by the usual method used crystalline substrate, using a single geometrical structure factor to extract the values of the fitting parameters CP and CF. Instead, we must perform simulations of the expected NIXSW profile for different structural models, averaging over the different symmetry-equivalent incidence azimuths. The resulting iterative trial-and-error determination of the optimum model structure is, of course, the method used in almost all other methods of surface structure determination. Plausible starting models are often informed by the results of studies using complementary techniques.

In the present case, STM images from this adsorption system [20] provide a guide to possible structural models, indicating the presence of six-atom pentagonal clusters of Si, each consisting of a ring of five atoms plus a sixth one at the centre. Clusters having two opposite orientations (azimuthally rotated by 180°) were observed, their spatial distribution being quasiperiodic, consistent with adsorption in specific sites. Simulations of the Si NIXSW absorption profile were therefore performed for structural models comprising six-atom

pentagonal clusters of Si atoms in locations consistent with points of 5-fold symmetry on the model surface, at an average height of 1.77 Å.

The two most favorable 5-f sites are those indicated in Fig. 3. At first sight the obvious way to add a pentagonal Si cluster to these sites is to place one adatom in the central 5-f hollow and the other five adatoms in the surrounding 5-fold coordinated sites intersected by the superimposed circles in Fig. 3(a). However, assuming the Si-Al (or Si-TM) distance is ~ 2.5 Å [25, 26] leads to an average layer spacing of the Si atoms above the extended bulk scatterer planes of only 1.30 Å, much smaller than the value of 1.77 Å determined by the (00004) NIXSW. However, if the outer ring of Si atoms is contracted towards the centre atom until they occupy 3-fold coordinated sites relative to the underlying substrate, the average layer spacing is almost exactly 1.77 Å. Moreover, the fact that the central Si lies significantly lower in the surface than the surrounding Si atoms accounts for the reduced CF value in the (00004) NIXSW. This model is shown in Fig. 4, together with the results of NIXSW simulations for the clusters in the two different (RSU and USD) sites in each of the two azimuthal groups. Superimposed on these simulated profiles are the experimental results. The simulations for pentagonal clusters on the two different sites are quite similar, despite the fact that the simulations for single Si atoms in the centre sites (Fig. 3(c)) differ very significantly.

As STM images show that clusters of the two opposite orientations coexist on the surface, our model should comprise a mixture of RSU and USD site clusters. Fig. 4 includes results for a 1:1 mixture of the two sites and shows clearly that the fit to (quite noisy) experimental data is insensitive to modest variations in the relative occupation of the two sites. These comparisons of experiment and theory also show that while the simulations for the two distinct azimuthal groups are qualitatively similar, both the modulation amplitude and the exact energy of the peak are reproduced significantly better by calculations in azimuthal group B than in azimuthal group A.

We therefore conclude that the pentagonal cluster model shown in Fig. 4 provides a good account of the experimental NIXSW in both (00004) and $\{0\bar{1}\bar{1}01\}$ reflections and that our $\{0\bar{1}\bar{1}01\}$ experiments were performed in one of the five azimuthal group B incidence directions. Moreover, this is the only cluster model we have identified that is consistent with these data and with reasonable values of the adsorbate-substrate bondlengths. The reason for

the formation of the clusters, rather than a wider distribution of the adsorbed Si atoms, is unclear, but this same effect has been seen in STM studies of Al, Pb and Bi adatoms on other 5-f quasicrystal surfaces [5, 27, 28].

We believe this investigation is the first quantitative determination of an adsorbate site on a quasicrystalline surface, as well as the first application of the NISXW technique to investigate a quasicrystal surface. Indeed, NISXW may be the only viable technique for the experimental determination of adsorbate structures on quasicrystalline surfaces. LEED is the most widely used technique for quantitative surface structure determination, but the analysis of intensities relies on crystalline periodicity and requires the use of significant approximations for its application to quasicrystals. Solving an adsorbate structure on a quasicrystal surface with LEED would present a major computational challenge. Surface X-ray diffraction (SXR) would be computationally less challenging due to the relative absence of multiple scattering, but simulations would still require a structural model including all the adsorbate atoms within a very large (e.g. $200 \text{ \AA} \times 200 \text{ \AA}$ as used here) unit cell. NISXW offers the significant advantage that it is a *local* structural probe that does not require calculations over large unit cells or the consequential need to acquire very large data sets to fit a large number of parameters. The technique is based on X-ray diffraction in the substrate, and from periodic crystalline substrates the local structure is obtained relative to a periodic surface mesh. The results presented here, however, show that at a quasicrystal surface, similar local sites lead to similar NISXW absorption profiles, despite the lack of true surface periodicity. As a result, we have been able to identify a clearly-preferred adsorbate structural model based on just two measured NISXW spectra from different planes. Of course, additional spectra recorded at other diffraction conditions could improve the precision of our results.

In surface studies, we are concerned with the phase of the standing wave relative to the atomic terminating plane, but the same distribution only leads to an uncertainty in the height of the adsorbate above the scattering planes, by an amount related to the wavelength of the standing waves. Previous studies have shown that although quasicrystal surfaces, like periodic crystalline surfaces, show atomic steps and thus expose different termination planes, these terminating planes have been found to be self-similar, and not random [29, 30]. In the particular experiment described here, there is no uncertainty in the height of the adsorbate atoms above the surface because the structure of this quasicrystal is periodic perpendicular to

the surface. However, for the other directions used to triangulate the location of the adsorbates, the aperiodic distribution of atom layers relative to the standing wave phase is present. We may therefore expect that our approach is equally viable for the study of materials that show quasicrystalline ordering in all three dimensions.

We have demonstrated that NISXW is a viable technique for quantitative structural studies of adsorbates on quasicrystals, and that it provides a relatively simple method for such studies. It could equally well be extended to the cases of larger molecular adsorbates on quasicrystals such as pentacene [3] or phthalocyanines [31]. It could also be applied to adsorption on periodic but complex structures such as the complex intermetallic alloy $\text{Al}_{13}\text{Fe}_4$ [32], a quasicrystalline approximant that has potential as a catalytic promotor for adsorbed gases. We anticipate that the technique could be used fruitfully to elucidate the early stages of growth of thin films on complex substrates, a topic that has generated much interest recently for its potential in electronic materials [4, 28, 33-35].

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Figure Captions.

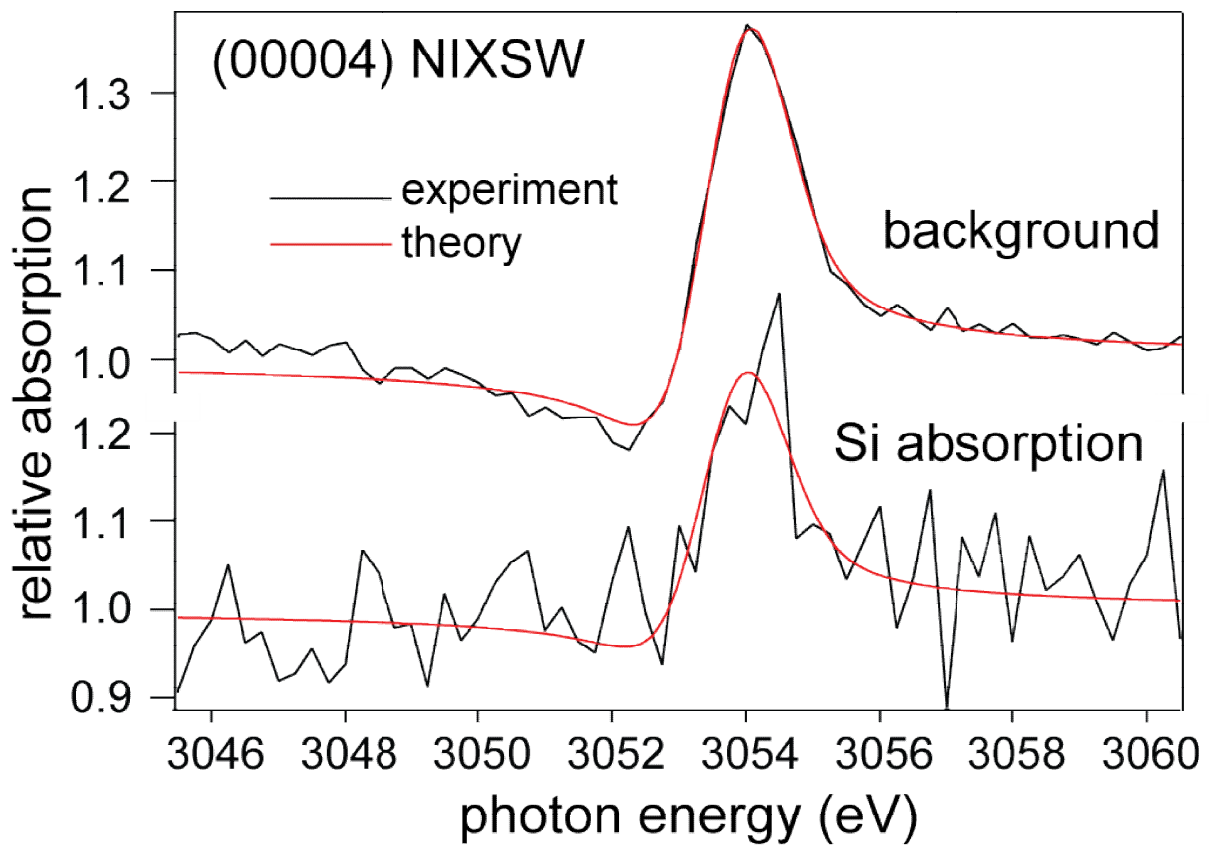


Fig. 1. Comparison of experimental (00004) NIXSW absorption profiles from the substrate and from the adsorbed Si atoms with best-fit calculated spectra.

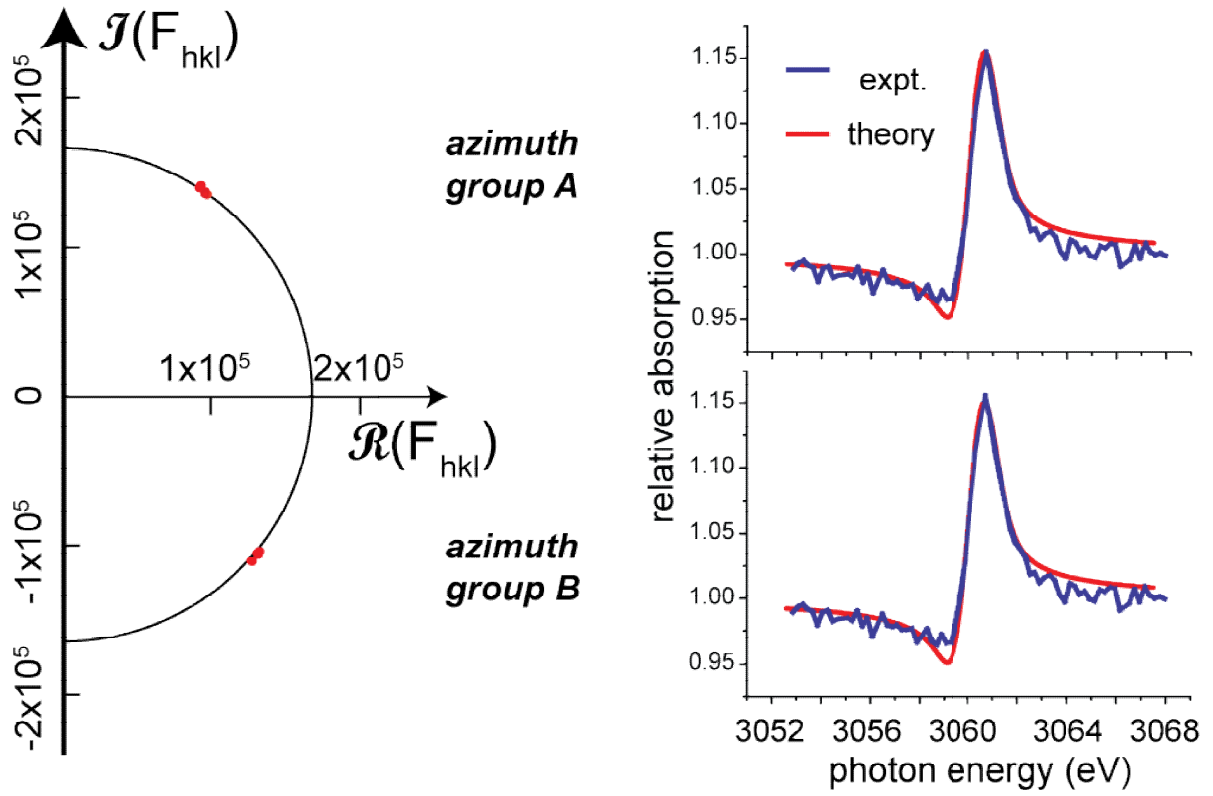


Fig. 2. (left) Argand diagram showing the two groups of structure factors for the $\{0\bar{1}\bar{1}0\}$ reflections, each corresponding to 5 different azimuthal directions. (right) comparison of the experimental NIXSW substrate adsorption profiles with theoretical simulations for each of these two groups of azimuths with different structure factors.

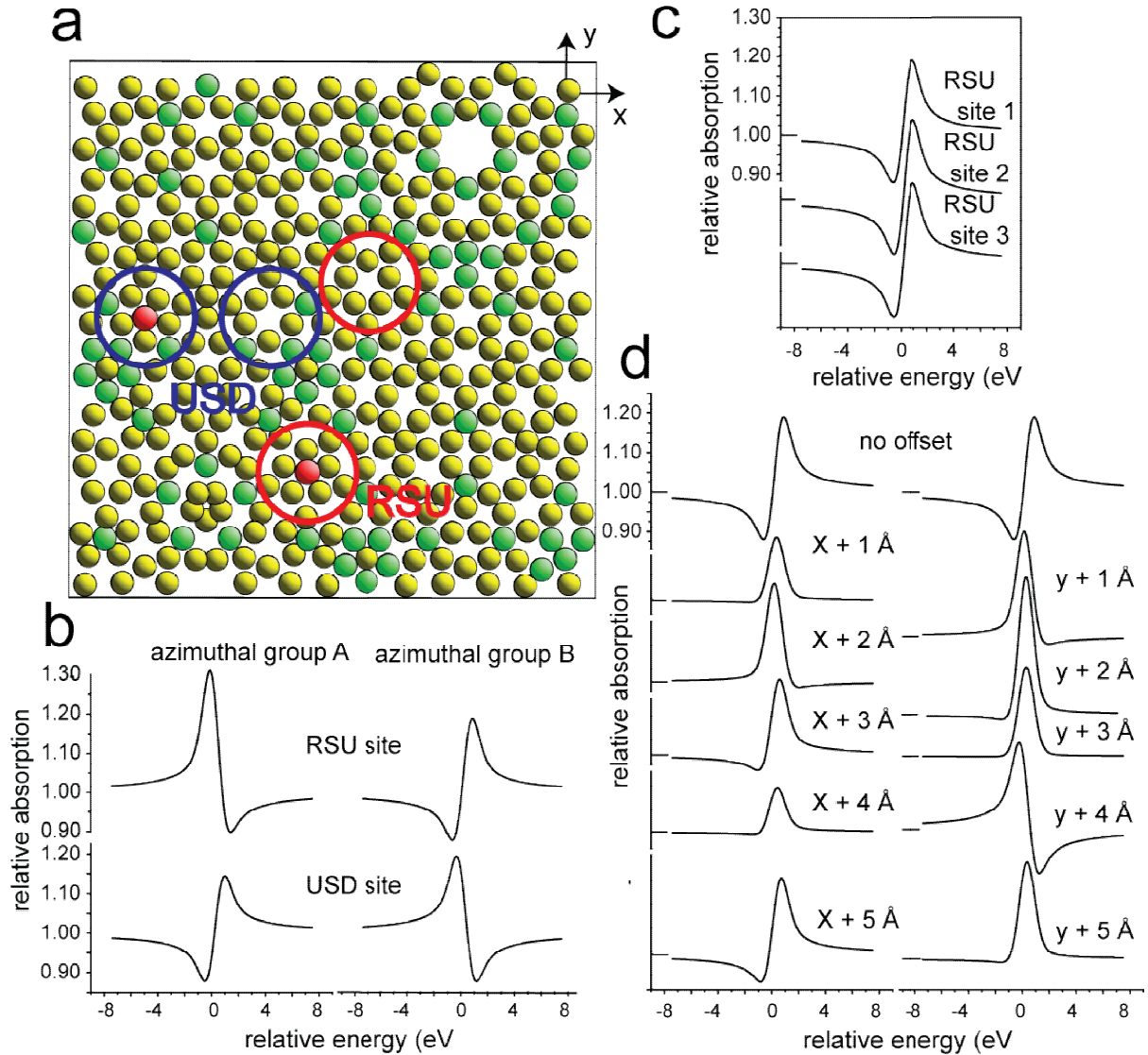


Fig. 3. (a) Plan view of the outermost layer of the clean surface with two different types of local 5-f sites circled. The red and blue circles show sites RSU and USD (see text) sites respectively. Al, TM and adsorbed Si atoms are shown yellow, green, and red, respectively. (b) Simulated NIXSW profiles in each azimuthal group for absorber atoms at RSU and USD central sites. (c) Simulated NIXSW profiles in azimuthal group B for absorbing atoms at 3 different RSU sites. (d) Similar simulated NIXSW profiles at different lateral displacement from the RSU site.

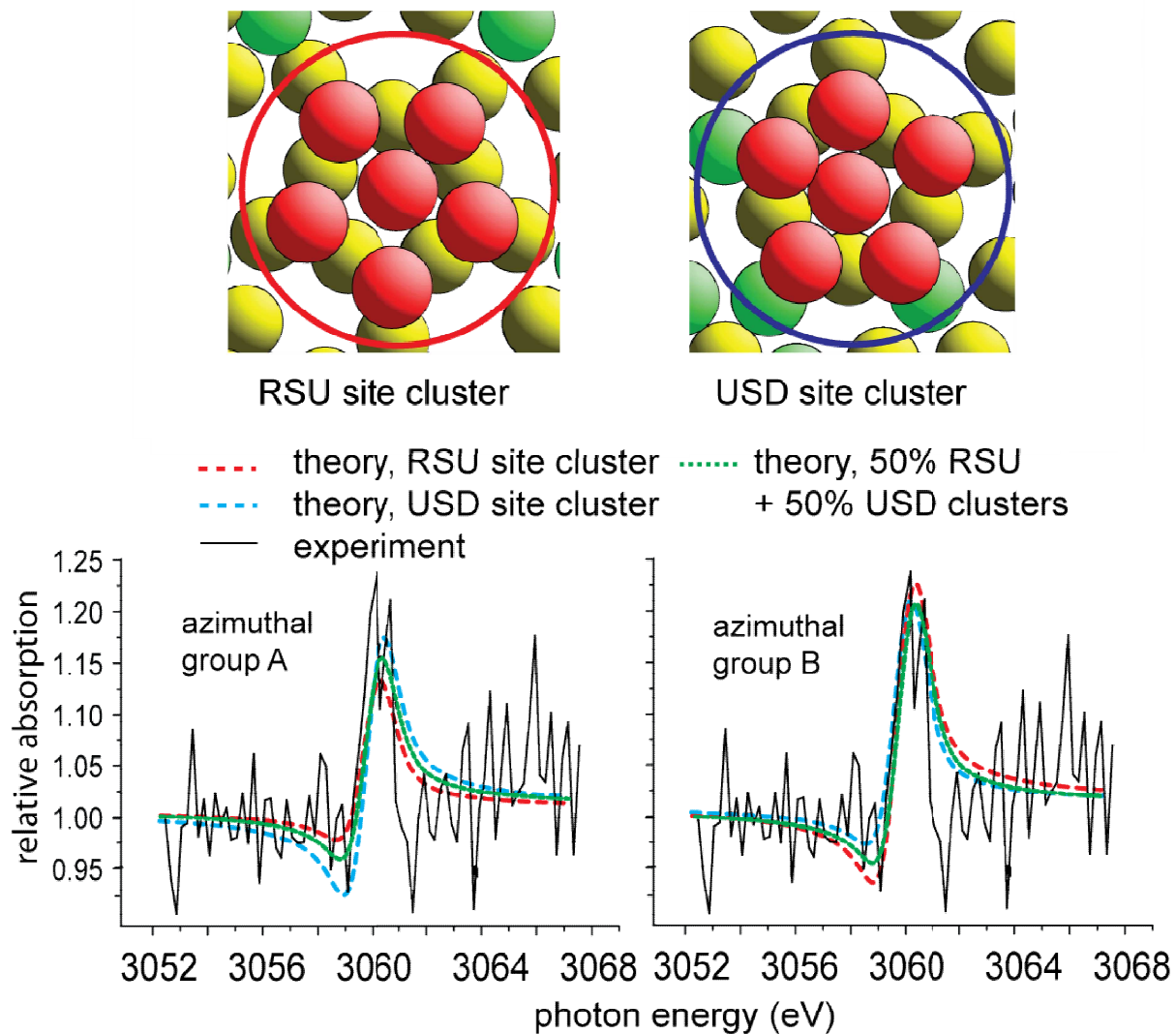


Fig. 4. Schematic diagram of the two Si pentagonal cluster models, together with a comparison of the experimental $\{0\bar{1}\bar{1}01\}$ Si NIXSW absorption profile with simulations based on these models and a mixture of them.

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