

# Electronic structure of the topmost tenfold surface of decagonal Al-Ni-Co quasicrystal

T. Suzuki,<sup>1,2,\*</sup> H. R. Sharma,<sup>1</sup> T. Nishimura,<sup>3</sup> M. Shimoda,<sup>1</sup> Y. Yamauchi,<sup>1</sup> and A.-P. Tsai<sup>1</sup>

<sup>1</sup>National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

<sup>2</sup>PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

<sup>3</sup>Department of Physics, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

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The electronic structure of the tenfold surface of a decagonal Al-Ni-Co quasicrystal was investigated using metastable He\* ( $2^3S, 1s2s$ ) deexcitation spectroscopy, which is extremely sensitive to the topmost surface. It was found that the density of states at the Fermi level was remarkably reduced at the topmost surface. The deexcitation of He\* via a resonance transition followed by Auger neutralization observed on the quasicrystal-line surface indicates the persistence of states within the pseudogap at the topmost surface. The similarity of the electronic structure between the topmost surface and the bulk is consistent with a bulk-terminated structure, as observed by low-energy ion scattering spectroscopy.

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## I. INTRODUCTION

It has been indicated that the density of states (DOS) of quasicrystals has a significant reduction at the Fermi level ( $E_F$ ) (pseudogap). This characteristic of the electronic states of quasicrystals is believed to be one of the origins of their unique transport properties, such as the extremely low electric conductivity for alloys. The formation of this pseudogap has been attributed to their lack of periodicity and high symmetry. Briefly, the Brillouin zone of quasicrystals is close to a sphere compared with crystals because of the high symmetry. The sphere like Brillouin zone interacts strongly with the Fermi surface, and this is interpreted to be the origin of the pseudogap (the Hume-Rothery mechanism).<sup>1</sup>

Although the formation of the pseudogap in quasicrystals seems to be generally accepted, the electronic structure of the topmost surface still remains an open question. The electronic structure of the quasicrystal surface has attracted attention because it has various properties, such as low coefficients of friction, oxidation resistance, and reduced adhesion, which have potential industrial applications.<sup>2,3</sup>

The electronic structure of quasicrystals, in particular, the detailed structure of the valence band, has mostly been observed by photoemission spectroscopy (PES). Since PES involves some contribution from the topmost surface, the electronic states of the topmost surface have also been discussed using PES. However, contradictory results were obtained from PES concerning the similarity of the electronic structure at the topmost surface with that of the bulk.<sup>3</sup> This situation is partly due to the lack of sensitivity of PES to the topmost surface. To our knowledge, no clear evidence for the pseudogap at the topmost surface has been reported by means of electron spectroscopy, although some measurements using tunneling spectroscopy have pointed out the persistence of the pseudogap at the topmost surface.<sup>4-7</sup> In the present study, the electronic structure of the topmost tenfold surface of a decagonal Al-Ni-Co (*d*-Al-Ni-Co) quasicrystal has been investigated using metastable deexcitation spectroscopy (MDS), which is extremely sensitive to the topmost surface.<sup>8</sup>

An inevitable problem when studying surface electronic structure comes from the inconsistency of the formation of the quasiperiodicity at the surface.<sup>9</sup> Indeed, different results for the surface electronic structure have been reported depending on the surface preparation.<sup>3</sup> For this reason, the surface structure has been investigated in parallel with electronic structure analysis using low-energy ion scattering spectroscopy (LEIS) in the present study.

## II. EXPERIMENT

An Al<sub>72</sub>Ni<sub>12</sub>Co<sub>16</sub> quasicrystal was grown by the floating zone method, and the quasicrystal was sliced parallel to the quasiperiodic planes, i.e., perpendicular to the tenfold axis.<sup>10</sup> After mechanical polishing, the substrate was introduced into an analysis chamber (base pressure  $5 \times 10^{-11}$  Torr) equipped with an ion gun for sputtering, an electron gun, a 180° rotatable electrostatic hemispherical sector analyzer (Omicron SHA50), a Stern-Gerlach analyzer, a beamline for He metastable atoms, a beam line for LEIS, a photon source (VSI UVS300A), and reflection high-energy electron diffraction (RHEED). The sample surface was cleaned by several cycles of 3 keV Ar<sup>+</sup> sputtering and annealing at about 1000 K. The composition of the surface after the cleaning procedure was checked by Auger electron spectroscopy as well as LEIS.

In MDS, He metastable atoms [ $\text{He}^*(1s2s, 2^3S)$ ] are projected onto the sample surface, and electrons emitted in the deexcitation of He\* are measured by an electrostatic energy analyzer (SHA50). The deexcitation of He\* occurs only at the outermost surface, and this is the basis for the extremely high surface sensitivity of MDS.<sup>8</sup> A time-of-flight (TOF) technique was employed in combination with a pulsed discharge in the He\* source to separate the contributions of photons to the spectra.<sup>11</sup> The  $2^1S$  atoms, which were simultaneously produced in the source, were deexcited using a quenching lamp positioned between the He\* source and the sample.<sup>12</sup> The ratio of the He\*  $2^3S$  to  $2^1S$  atoms in the beam measured by a Stern-Gerlach analyzer was about 30:1. In both MDS and ultraviolet photoelectron spectroscopy (UPS), the electrons emitted in the direction normal to the sample

surface were measured with a pass energy of 4 eV.

In our LEIS, the scattering angle was almost  $180^\circ$ . This specialized LEIS is often called coaxial impact collision ion scattering spectroscopy (CAICISS).<sup>13</sup> The scattering angle of about  $180^\circ$  eliminates blocking effects, and so the analysis is greatly simplified compared with conventional LEIS. In the CAICISS measurements, a pulsed beam of 3 keV  $\text{Ne}^+$  ions was impinged onto the sample surface, and the scattered particles were analyzed by TOF, where the path length from the sample to the detector (microchannel plate) was 36 cm. The radiation damage of the sample surface during the CAICISS measurements is negligible because of the small duty ratio of 1.5% with an ion current of several nanoamperes at the sample, where the beam diameter was about 2 mm.

### III. COMPUTER SIMULATION FOR CAICISS

In structural analysis using CAICISS, the intensity of scattered particles is measured as a function of the polar or azimuthal angle of a sample. Computer simulation is necessary to discuss the geometrical relationship between the atomic arrangement and the shadow cone, which is the origin of the intensity variation in the CAICISS angle scan measurement.

Trajectory tracing of incident ions based on molecular dynamics simulations is the closest to an ideal method of the various calculating techniques.<sup>14</sup> However, many target atoms must be taken in a calculation for quasicrystals since there is no periodicity. This results in unfeasible computational time. Instead of tracing all trajectories, only the incident trajectories were followed to calculate the close-encounter probabilities of the incident ions on the target atoms in the present study. The concept of the close-encounter probability was introduced by Barrett.<sup>15</sup> On the basis of this concept, the program utilized in the present study was developed by Kido and co-workers.<sup>16,17</sup> Since the blocking effect is negligible in CAICISS as mentioned above, the close-encounter probability is directly related to the backscattering probability of CAICISS in the present simulation.<sup>17</sup>

The *d*-Al-Ni-Co quasicrystal is one of the two-dimensional quasicrystals which have a periodic stacking structure of *ABAB...* type along one direction and quasicrystalline ordering in the plane perpendicular to the periodic direction. Figure 1 shows the atomic arrangement in the quasicrystalline plane of the *d*-Al-Ni-Co quasicrystal, parallel to the sample surface, proposed by Yamamoto and Weber.<sup>18</sup> It is generally accepted that the frame structure of the *d*-Al-Ni-Co quasicrystal consists of columnar clusters of 20 Å diameter, which are located at the vertices of a rhombic Penrose pattern of 20 Å edge length with a certain rule for overlapping between the clusters. The large and small circles indicate atoms in the first and second layers, respectively, in the periodic stacking structure. The full and open circles indicate transition metals (Ni or Co) and Al, respectively. The atomic arrangement in the rhombus taken in the simulation is represented in Fig. 1 by gray

circles. The calculation involves seven atomic layers containing over 3500 atoms and the trajectories of  $3 \times 10^6$  ions. An interatomic potential of the universal type and Ziegler's stopping power formula for electronic energy loss were employed with a Debye temperature of 600 K.<sup>19</sup>

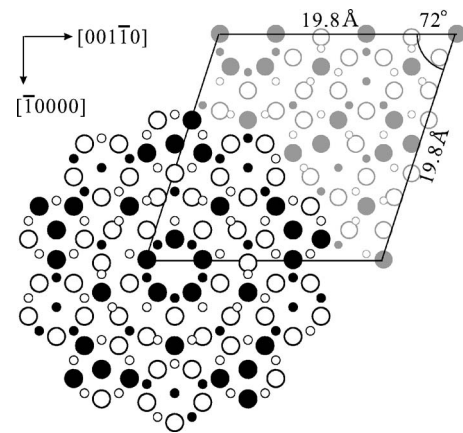


FIG. 1. The atomic arrangement of the *d*-Al-Ni-Co columnar clusters proposed by Yamamoto and Weber (black circles) Ref. 16. The large and small circles indicate the atomic positions of the first and second layer, respectively, in the periodic layer stacking of the *ABAB...* type of *d*-Al-Ni-Co. The full and open circles indicate transition metals (TMS) and Al, respectively. Gray circles indicate the atomic position in a certain rhombus of a Penrose pattern which was taken in the simulation. The vertex of the rhombus is shifted to the top position of the TM atom for convenience of simulation.

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### IV. RESULTS AND DISCUSSION

Figure 2 shows the RHEED patterns and a CAICISS azimuthal angle scan with the fixed polar angle at  $40^\circ$  for the *d*-Al-Ni-Co quasicrystal. In the RHEED patterns for two inequivalent azimuths, the ratios of the spacing between reciprocal rods are very close to the golden mean  $\tau (=2 \cos \pi/5)$

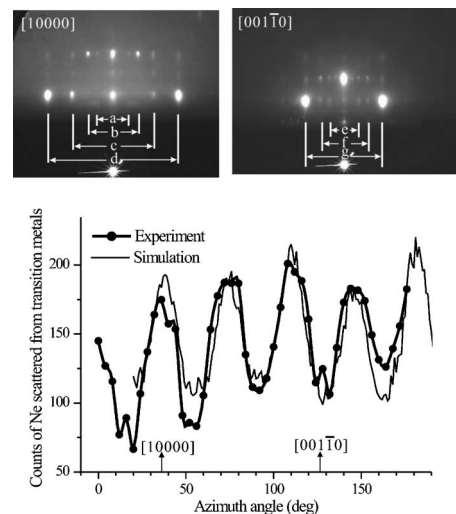


FIG. 2. RHEED patterns obtained for  $[10000]$  and  $[001\bar{1}0]$  azimuths and CAICISS azimuthal angle scan in which the polar angle was fixed at  $40^\circ$  on the *d*-Al-Ni-Co quasicrystalline surface.

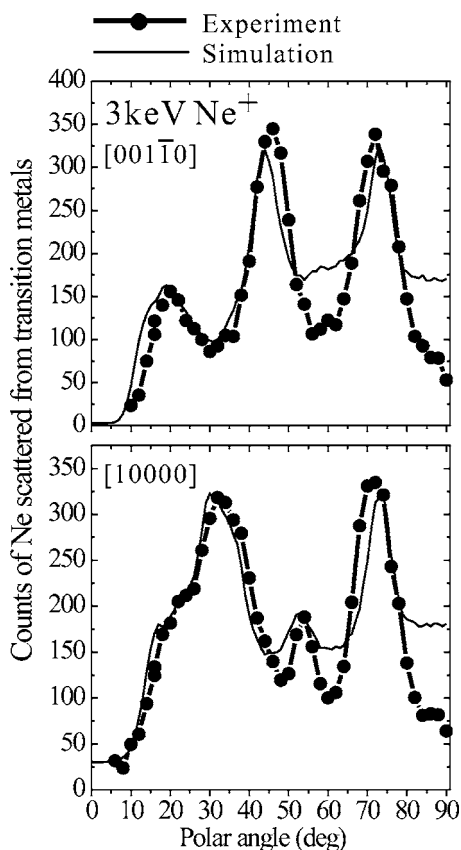


FIG. 3. The polar angle scans of CAICISS along  $[001\bar{1}0]$  and  $[10000]$  azimuths on the  $d$ -Al-Ni-Co quasicrystalline surface.

$=1.618\dots$ ) which characterizes the quasiperiodicity,<sup>20</sup> i.e.,  $b/a \approx c/b \approx d/c \approx f/e \approx g/f \approx \tau$ . This indicates quasicrystalline ordering at the surface. On the other hand, the CAICISS azimuthal angle scan exhibits maxima at almost every  $36^\circ$ , and thus demonstrates that the surface atoms reside in a local tenfold-symmetric environment.<sup>21</sup> The computer simulation for CAICISS reproduces well the tenfold-symmetric intensity variation. The deviation of the intensity variation in the simulation originates from the limitation of the number of ion trajectories and target atoms. From these measurements, it is concluded that the  $d$ -Al-Ni-Co quasicrystal has a quasiperiodic ordering at the surface after our cleaning procedure.

Figure 3 shows the CAICISS polar angle scans for two inequivalent azimuths. Briefly, the polar angle scan of CAICISS is sensitive to the positions of surface atoms which are located within scanning planes, while the azimuthal angle scan detects the symmetry at the surface. The number of layers taken in the simulation for the experiment in Fig. 3 was changed from three to nine in order to estimate the contribution to the CAICISS intensity from deep layers. It is observed that the feature of the intensity variation in Fig. 3 is mostly determined by the structure of the first five layers from the topmost surface (not shown). The simulation in Fig. 3 takes the first seven layers into account. Fairly good agreement of the simulation with the experiments indicates a bulk-terminated structure of the  $d$ -Al-Ni-Co quasicrystal surface.

It is often observed that the quasicrystal surface crystallizes with sputtering. Such structural transition has also been

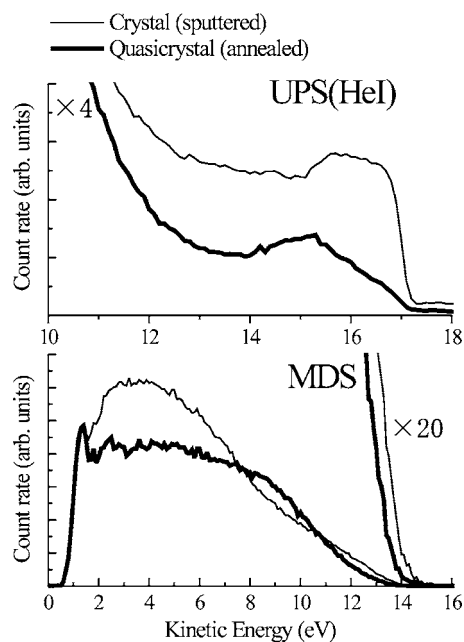


FIG. 4. UPS and MDS spectra on the Al-Ni-Co crystalline (thin line) and quasicrystalline (thick line) surfaces.

observed in the  $d$ -Al-Ni-Co system.<sup>22</sup> This transition from the quasicrystal to the crystal is explained by the compositional change at the surface by preferential sputtering which induces the transition between the crystalline and quasicrystalline equilibrium phases. The structural phase transition with sputtering was also observed by RHEED in the present study. It was observed that the crystallized (quasicrystallized) surface repeatedly quasicrystallized (crystallized) with an annealing (sputtering).

Figure 4 shows UPS and MDS spectra for the crystalline (sputtered) and quasicrystalline (annealed) surfaces of Al-Ni-Co. The UPS spectrum on the crystalline surface shows a sharp Fermi edge at 17 eV. The feature at  $E_F$  results from the overlap of the Co and Ni  $3d$ -like states.<sup>23</sup> With the quasicrystallization of the sample surface by annealing, a remarkable decrease of the states at  $E_F$  is observed in UPS (pseudogap).

On the other hand, the structureless feature of the MDS spectra indicates that  $\text{He}^*$  deexcites via a resonance transition (RT) followed by Auger neutralization (AN). In this deexcitation process, the kinetic energy distribution of the emitted electron basically corresponds to the self-convolution of the surface DOS.<sup>8</sup> In this case, the spectra do not reflect directly the surface DOS, while the emitted electrons which have the largest kinetic energy originate from  $E_F$ . Thus, the emitted electron intensity at the largest kinetic energy region in the spectra (14–15 eV in Fig. 4) is related to the electron population at  $E_F$ . It is clearly observed that the emitted electron intensity drops at  $E_F$  after annealing. Therefore, it is concluded that the DOS is also reduced at the topmost quasicrystalline surface of  $d$ -Al-Ni-Co, as it is in the bulk, observed by UPS in Fig. 4.

In RT, one  $2s$  electron of  $\text{He}^*$  resonantly transfers to the surface. There should be unoccupied states at the same energy level as the  $2s$  electron of the approaching  $\text{He}^*$  in the

RT process. The  $2s$  level of  $\text{He}^*$  (or ionization energy of  $\text{He}^*$ ) is 4.8 eV, although the effective ionization energy may be slightly reduced in front of the surface due to the image potential.<sup>8</sup> On the other hand, the work function on the quasicrystalline surface of  $d$ -Al-Ni-Co measured by the cutoff of secondary electrons in UPS was 4.8 eV. This indicates unoccupied states just above  $E_F$ , which are responsible for the RT of  $\text{He}^*$ . Therefore, it is most likely that some states still remain around  $E_F$  even after the formation of the pseudogap at the outermost surface.

For the purpose of discussing quantitatively the pseudogap in UPS, several approaches have been proposed to simulate the spectra close to  $E_F$ . The simulation of the spectra is typically made by fittings with a linear function multiplied with a Lorentzian, which characterizes the pseudogap.<sup>24</sup> In the UPS of Fig. 4, however, the high arbitrariness in the linear extrapolation poses difficulty for the quantitative estimation of the pseudogap. Indeed, this was suggested to be a major drawback of the fitting simulation.<sup>25</sup> Instead of this fitting simulation, the pseudogap is simply evaluated by the spectrum intensity ratio at  $E_F$  between the crystalline and the quasicrystalline surfaces. The integrated intensity ratio of UPS at  $E_F$  (16.2–17.2 eV) of the crystal to the quasicrystal is about 17.9:1. On the other hand, that of MDS on the crystalline (14.0–15.0 eV) to the quasicrystalline surface (13.8–14.8 eV) is about 1.9:1, where the slight difference of the integral region between the crystal and the quasicrystal comes from the difference of the work function measured in the present study (4.6 eV for the crystalline and 4.8 eV for the quasicrystalline surface). The smaller ratio of the integrated intensity of MDS than that of UPS indicates a rather moderate pseudogap at the topmost surface compared to the bulk, with the assumption that the emitted electron intensity at  $E_F$  is inversely proportional to the dip of the pseudogap.

The difference of the integrated intensity ratio between MDS and UPS is not due to the inhomogeneity of (quasi)crystallinity along the normal direction of the surface. The inhomogeneity has great influence on UPS which detects both the surface and subsurface, and thus reduces the integrated intensity ratio. However, the ratio for UPS is larger than for MDS in the experiment.

The smaller pseudogap at the topmost surface of the  $d$ -Al-Ni-Co quasicrystal surface is consistent with recent tunneling spectroscopy measurements which also detect the electronic states at the topmost surface. The typical width of the pseudogap in the tunneling spectroscopy is several 10 meV,<sup>4–6</sup> while that in PES is in the order of 1 eV.<sup>3</sup> This narrow pseudogap observed by tunneling spectroscopy is sometimes interpreted to correspond to gaps of small width (10–100 meV) superimposed on a broad pseudogap predicted by *ab initio* calculations of the DOS on approximant phases.<sup>1,26</sup>

It has been reported that preferential sputtering occurs on the  $d$ -Al-Ni-Co quasicrystal surface, where the content of Al decreases with sputtering.<sup>27</sup> It may be reasonable to consider that the composition of the sputtered Al-Ni-Co quasicrystal has a gradient normal to the surface, where the content of Al at the surface is smaller than that in the subsurface. A simple linear interpolation by which the work function of an  $\text{Al}_x\text{Ni}_y\text{Co}_{1-x-y}$  alloy is estimated to be  $x\varphi_{\text{Al}}+y\varphi_{\text{Ni}}+(1-x-y)\varphi_{\text{Co}}$ , where  $\varphi_M$  represents the work function of the pure element  $M$ , does not fit with the present experiment. It is estimated that the work function of the crystalline surface is larger than that of the quasicrystalline surface in this linear interpolation, since the work function of polycrystalline Al (4.3 eV) is smaller than those of Ni (5.2 eV) and Co (5.0 eV),<sup>28</sup> while the work function of the crystalline surface (4.6 eV) is smaller than that of the quasicrystalline surface (4.8 eV) in the present experiment.

The smaller work function of the crystalline surface compared with that of the quasicrystalline surface is considered to be due to the surface dipole moment caused by charge transfer. The smaller content of Al may cause charge transfer from Al in the subsurface to transition metals (Ni or Co) at the surface by taking into account the electronegativity. The charge transfer contributes to the surface dipole moment oriented to the vacuum side which reduces the work function on the crystalline surface.

## V. CONCLUSION

The electronic structure of the topmost surface of a  $d$ -Al-Ni-Co quasicrystal was investigated using MDS. The pseudogap at the topmost surface was clearly observed, although some states exist within the pseudogap which cause resonance transition of the  $\text{He}^*2s$  electron to the surface. The pseudogap is found to be smaller at the topmost surface than in the bulk. The slight difference in the work function for the crystalline (4.6 eV) and quasicrystalline surface (4.8 eV) was interpreted in terms of partial charge transfer between Al at the subsurface and transition metals at the surface. The atomic position in the topmost several layers was analyzed by specialized LEIS (CAICISS). The polar angle scan of CAICISS demonstrates the bulk-terminated structure at the  $d$ -Al-Ni-Co quasicrystal surface.

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\*Corresponding author.

Electronic address: suzuki.taku@nims.go.jp

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