Spectroscopic study on chemical ordering of transition metals in decagonal Al-Co-Ni and Al-Co-Cu quasicrystals

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Abstract. Preferred occupation at the transition metal (TM) sites in the building unit cluster of two-dimensional Al-Co-Ni and Al-Co-Cu quasicrystals has been investigated by comparing their experimental electronic structures with those of the unit clusters calculated by a discrete variational Xα method. Analysis of the bonding character and bond energy for local clusters around the TM sites shows that the Al-Co-Cu quasicrystal favours the Cu and Co occupations at the first and second inner TM sites, respectively, and hence the chemical order of these TM's, while the small bond energy difference in the Ni and Co occupations at those TM sites suggests the large chemical disorder of the transition metals in the Al-Co-Ni quasicrystal.

1. Introduction
Decagonal phases of Al-Co-Ni and Al-Co-Cu alloys are typical two-dimensional quasicrystals, where quasiperiodic planes are periodically stacked along a tenfold axis (the c-axis) [1]. The atomic arrangement in the quasiperiodic planes is often viewed as a special tiling such as the Penrose one composed of two unit tiles, a skinny rhombus and a fat one, and it may be regarded as consisting of a single decagonal building unit cluster with overlapping rules [1-3]. However, because of the lack of periodicity, it is still challenging to determine the atomic arrangement and clarify the formation mechanism of the unique quasiperiodic arrangement.

For the Al-Co-Ni quasicrystal, high-resolution transmission electron microscopic (HRTEM) studies show that the various structural modifications are formed as a function of the Co/Ni ratio [4], although it is still hard to distinguish the transition metal (TM) elements, Co and Ni, from each other in the microscopic image. For the Co-rich Al-Co-Ni quasicrystal, the X-ray diffraction (XRD) study of a W-
(AlCoNi) approximant Al\textsubscript{72.5}Co\textsubscript{20}Ni\textsubscript{7.5} has brought a new model with fivefold symmetric Al-TM mixed arrangement for the cluster centre [1,5,6], which also describes well the atomic arrangement of decagonal Al\textsubscript{65}Co\textsubscript{4}Cu\textsubscript{22} quasicrystal [7]. Theoretical studies with use of interatomic pair potentials predict such an Al-TM decagonal ring-like arrangement for the cluster centre of the Co-rich Al-Co-Ni approximant (the decagon tile) [8,9], while they show that the decagonal (pentagonal) symmetry of the cluster centre is broken for the Ni-rich Al-Co-Ni approximant (the hexagon-boat-star (HBS) tiling) [9-11]. Electronic band structure calculations for Al-Co-Ni approximants and a recent \textit{ab initio} study of the W-(AlCoNi) approximant show the importance of the energetically favourable Al-Co and Ni-Ni interactions as well as the contribution of the Hume-Rothery mechanism to the structural stabilization [12,13]. It is also pointed out that the chemical ordering between Al and TM may be an origin of the broken symmetry in the Ni-rich Al-Co-Ni quasicrystal [14,15]. However, the chemical ordering is not so clear in particular for the transition metals because of the difficulty in distinguishing them from each other.

In this paper, we have studied the atomic arrangement of the Al-Co-Ni and Al-Co-Cu quasicrystals by comparing the electronic structure obtained by the soft X-ray photoelectron spectroscopy (XPS) and the TM L\textsubscript{α} X-ray emission spectroscopy (XES) with those calculated theoretically by the discrete variational \(X\alpha\) (DV-\(X\alpha\)) method for the model unit cluster, based on the XRD and electron microscopic observations, in order to specify the sites occupied by Co, Ni and Cu and clarify the chemical nature bringing its unique atomic arrangement with the various modifications. A part of the present study for the Al-Co-Ni quasicrystal has been already reported in detail elsewhere [16].

2. Experimental and Calculating procedures

Specimens were single-grain decagonal quasicrystals Al\textsubscript{72}Co\textsubscript{16}Ni\textsubscript{12} and Al\textsubscript{65}Co\textsubscript{4}Cu\textsubscript{22} grown by the Czochralski method [17,18]. For the XES measurement, their surfaces were mechanically polished just before the measurement, while clean surfaces for the XPS measurement were prepared by \textit{in situ} fracturing specimens perpendicularly to the tenfold axis under the pressure of 1 - 4 x 10\textsuperscript{-8} Pa.

The XES measurement for the Al-Co-Cu quasicrystal was performed at 100 K with a slit-less spectrometer in the depolarized configuration at the beamline BL27SU of SPring-8, the Japan Synchrotron Radiation Research Institute [19,20]. The photon energy of the spectrometer was calibrated with elastically scattered excitation light, whose energy was determined by measuring photoelectron spectra of the Fermi edge and the 4\(f\) core level of an evaporated Au film. The excitation photon energy \(h\nu\) was tuned at 968.83 eV for the present Co and Cu L\textsubscript{α}, XES measurements. In order to represent the XES spectra in terms of the binding energy, we have used the Co and Cu 2\textit{p}\textsubscript{3/2} core level binding energies \(E_{\text{B}}\) of 778.53 and 933.89 eV, respectively, obtained from the XPS measurement. The error in the binding energy scale of the XES spectrum is estimated to be within 0.2 eV.

The XPS measurement for the Al-Co-Cu quasicrystal was performed at 20 K with a high-resolution hemispherical analyzer in the angle-integrated mode at the beamline BL23SU of SPring-8 [21]. The total energy resolution and the origin of the binding energy, the Fermi energy \(E_{\text{F}}\), were determined by measuring the Fermi edge of evaporated Au films. The energy resolution was estimated to be 0.27 eV at \(h\nu = 1200\) eV. The experimental details for the Al-Co-Ni quasicrystal are described elsewhere [22].

The DV-\(X\alpha\) method is one of the real-space first principle molecular orbital calculations, and it is powerful for studying the electronic structure and chemical bonding in the materials including many TM’s without the periodicity [23]. In this method, the Hartree-Fock-Slater molecular equation is solved by the self-consistent charge procedure with the Slater’s \(X\alpha\) potential as the electron exchange-correlation and the random-sampling integration for the matrix elements of Hamiltonian and overlap integrals. For the present calculation, we have modified the available code SCAT [24] for faster calculation with larger cluster than the original one [16].

The model unit cluster has a triple layered structure along the \(c\)-axis with two types of quasiperiodic layers, A and B, shown in figure 1, in the A-B-A or B-A-B stacking sequences with the interlayer distance \(c/2\) of 0.2000 and 0.2074 nm for the Al-Co-Ni and Al-Co-Cu quasicrystals, respectively. The
atomic arrangement in the quasiperiodic layers is based on the model proposed for the W-(AlCoNi) approximant [1,5] and is the same for both the quasicrystals [7]; an underlying Penrose tiling with the fat and skinny rhombi is shown by broken lines in the figure and the quasilattice constant $a_q$, that is, the edge length of the rhombi is taken as 0.250 and 0.230 nm for the Al-Co-Ni [1] and Al-Co-Cu [25] quasicrystals, respectively. In figure 1, open circles represent Al, and closed circles and diamonds stand for two kinds of transition-metals, TM1 and TM2, respectively, i.e. Co or Ni for the Al-Co-Ni quasicrystal and Co or Cu for the Al-Co-Cu one; the total number of TM1 per a pair of A and B layers is set equal to that of TM2, and the occupation of the nearest neighbour TM is avoided for the mixed sites of the proposed model for simplicity. Open squares show hydrogen atoms to reduce the so-called surface effects for the outer TM in the calculation for the Al-Co-Ni quasicrystal, but we could not place these hydrogen atoms for the Al-Co-Cu quasicrystal in the present code. A large thick circle in the figure indicates the size of the unit cluster, ~2 nm, and the nominal composition per a pair of the A and B layers, $\text{Al}_{81}\text{TM1}_{15}\text{TM2}_{15}(\text{H}_{50})$, may correspond to $\text{Al}_{73.0}\text{TM1}_{13.5}\text{TM2}_{13.5}$.

In order to avoid the surface effects, the density of states (DOS) for the model cluster is obtained as the sum of the local DOS’s of the central layers A and B for the respective BIAIB and AIBIA model clusters. The DOS are shown after convoluting their calculated line spectra with a Gaussian function of the 0.17 eV half width at half maximum.

### 3. Results and Discussion

Calculated local TM 3$d$ DOS’s at the various TM sites assigned in figure 1 are shown in figure 2 for the Al-Co-Cu quasicrystal with total and partial DOS’s of the model clusters: (a) a Cu centre model, i.e. a model with TM1 = Cu and TM2 = Co in figure 1, and (b) a Co centre model, i.e. TM1 = Co and TM2 = Cu. As already reported for the Al-Co-Ni quasicrystal [16], the local TM 3$d$ DOS’s at the sites 2 and 3 for both the model clusters have almost the same energy distribution also in the Al-Co-Cu quasicrystal because of the resemblance in their nearest neighbour arrangement, and they are the lowest in energy due to the large Al-TM interaction. The small difference in their distribution may be caused by the different arrangement of the second nearest neighbours. The 3$d$ DOS at the site 4 is distributed over the highest energy region due to the weak Al-TM interaction, while the energy distribution of the 3$d$ DOS at the site 5 is similar to that at the site 1. The dependence of the local DOS on the TM site suggests the importance of the Al-TM interactions or the Al coordination. Thus, we will ignore the sites 4 and 5 below, since their local atomic arrangements are incomplete in the present

**Figure 1.** Atomic arrangement in the quasiperiodic layers A and B of a model unit cluster of Al-Co-Ni and Al-Co-Cu decagonal quasicrystals. Open circles, closed circles and diamonds, and open squares represent Al, the transition metals TM1 and TM2, and H, respectively. The non-equivalent transition metal sites are assigned with numbers. A large thick circle indicates the size of the unit cluster, ~2 nm.
Figure 2. Local density of the Co and Cu 3d states at different transition metal sites of the model unit clusters (a) Cu centre model and (b) Co centre model. The transition metal sites, 1 to 5, are assigned in figure 1. Total and partial densities of the states of the unit model clusters are also shown in the top panel.

calculation. Both the Co and Cu 3d DOS’s at the sites 2 and 3 are located lower in energy than those at the innermost TM site 1, which might imply the preferential occupation at the site 2 (or 3) rather than the site 1. However, the anti-bonding character increases near $E_F$ for the TM-Al bond at the sites 2 and 3 in comparison to the site 1, as observed in the Al-Co-Ni quasicrystal [16]. The energy gain by the Cu occupation at the site 1 may lead to the energy consumption by the Co occupation at the site 2, and vice versa. It should be also noted that the Al partial DOS’s for both models show a pseudogap near $E_F$, implying the contribution of the Hume-Rothery mechanism to the stabilization of this quasicrystal.

In figure 3, we compare the TM 3d partial DOS, calculated by summing up the local DOS’s at the sites 1 to 3, with the experimental XES and XPS spectra for the Al-Co-Ni and Al-Co-Cu quasicrystals. The panels (a) and (b) show the TM 3d DOS’s for the Ni or Cu centre models and for the Co centre model, respectively. The experimental spectra of the Al-Co-Cu quasicrystal shows well-separated Co and Cu 3d bands, while the XPS spectrum of the Al-Co-Ni quasicrystal reveals a single 3d band which is composed of the Co and Ni 3d bands in the low and high binding energy sides, respectively. In the Co centre model, the Cu 3d band is separated largely from the Co 3d one. Thus, as a whole, the calculated energy distributions for the Cu centre model agree fairly well with the experimental results, which suggests the preferential occupation of Cu at the site 1. On the other hand, the Co and Ni 3d bands are distributed over rather wide region for the Co centre model; a single peaked TM 3d band appears for the Ni centre model but the Co 3d band is located at higher binding energy than the Ni one, inconsistent with the experimental results. Instead, it is found in the previous study [16] that the 3d partial DOS for a model with Co and Ni mixed at the site 1 agrees better with the experimental result than the others. This suggests the chemical disordering may occur in the Al-Co-Ni quasicrystal.

In order to compare quantitatively the chemical stabilities at the TM sites 1 (the innermost TM site of the model cluster) and 2 (the second innermost one), we have calculated the local bond energy at the TM sites and bond order of the Al-TM bonds at the TM sites, because the present DV-Xα method does not have enough accuracy, unfortunately, to compare the total energy for the whole system including the deep core levels. The results are summarized in table 1. Here, the local bond energy is defined as the energy gain of the occupied TM band states at the TM site compared to the sum of the relevant occupied orbital energy of an isolated TM atom, and the bond order shows how large the bonding nature in the concerned molecular states [26]. For the Al-Co-Cu quasicrystal, the total bond
Figure 3. Transition metal (TM) 3\textit{d} band calculated with Co and Cu (or Ni) at two types of the sites, 1 and 2(3) shown in figure 1, for (a) Cu (or Ni) centre model and (b) Co centre model for Al-Co-Cu and Al-Co-Ni quasicrystals. The TM \textit{L}\alpha X-ray emission spectra (XES) and valence-band X-ray photoelectron ones (XPS) of Al$_{65}$Co$_{20}$Cu$_{15}$ (left) and Al$_{72}$Co$_{16}$Ni$_{12}$ (right) quasicrystals are also shown in the top panel.

Table 1. Local bond energy at the transition metal (TM) site and Al-TM bond order.

| Model Cluster | Site 1 Bond Energy (eV atom$^{-1}$) / Bond Order | Site 2 Bond Energy (eV atom$^{-1}$) / Bond Order | Total Bond Energy (eV atom$^{-1}$) |
|---------------|-----------------------------------------------|-----------------------------------------------|---------------------------------|
| Al-Co-Ni      |                                               |                                               |                                 |
| (Ni, Co)      | 18.32 / 0.145 Co Ni                           | 19.68 / 0.146 Co Ni                           | 22.16 / 0.135 Co+Ni Ni = 38.00  |
| (Co, Ni)      | 15.90 / 0.155 Co Ni                           |                                               | 22.16 / 0.135 Co+Ni Ni = 38.06  |
| Al-Co-Cu      |                                               |                                               |                                 |
| (Cu, Co)      | 23.16 / 0.137 Cu Co                           | 18.32 / 0.148 Cu Co                           | 27.20 / 0.131 Cu Co+Cu = 41.48  |
| (Co, Cu)      | 12.69 / 0.154 Cu Co                           |                                               | 22.16 / 0.135 Cu Co+Cu = 39.89  |


energy, which is higher by ~1.6 eV for the Cu centre model than for the Co one, clearly indicates the preferential occupation of Cu at the site 1 and Co at the site 2, and the bond order also may favour the Cu centre model in a sense of almost the same bond strength at the various TM sites. These suggest a highly chemical ordering of Cu and Co in the Al-Co-Cu quasicrystal. For the Al-Co-Ni quasicrystal, the bond order may prefer the Ni centre model to the Co one, but the bond energy is slightly high for the Co centre model. The difference in the bond energy is very small and hence the chemical disordering may be expected to occur easily for the Al-Co-Ni quasicrystal.

Although the peripheral part of the unit cluster is not clear yet in the present study, tendency in the TM occupation may provide some hint to the observed Co/Ni dependence of the modifications in the Al-Co-Ni quasicrystal; Hiraga et al. [1,27] have pointed out that the density of unit clusters increases with the Co/Ni ratio, suggesting the increase in the linkage of the unit cluster forming a skinny rhombus, which in turn may contain less Ni than the linkage forming a fat rhombus. The strong Al-Co interaction as well as the chemical disordering might play an important role in forming the various
modifications in a wide composition range.

4. Conclusions

Comparison between the theoretical and experimental electronic structures and analysis of the local bond energy and bond order at the TM sites show that the Al-Co-Cu quasicrystal favours the Cu and Co occupations at the first and second inner TM sites, respectively, and hence the chemical order of Co and Cu, while the small difference in the total of the local bond energy suggests the large chemical disorder of TM’s in the Al-Co-Ni quasicrystal, which might bring its various modifications.

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