Cluster study of Al-Co-Ni decagonal quasicrystal

Manabu Inukai, Kazuo Soda*, Masahiko Kato, Shinya Yagi, Yoshihiko Yokoyama

[I] Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.
[II] Institute of Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan.

Received; accepted

Decagonal quasicrystal / Cluster modelling / Electronic structure

Abstract. The electronic structure and atomic arrangement of a decagonal Al-Co-Ni quasicrystal have been investigated in terms of a model unit cluster by using a discrete variational $X\alpha$ (DV-$X\alpha$) cluster calculation. The partial electronic density of states (DOS) and overlap population analysis for local clusters around the constituent transition-metals (TM's) show the energy reduction of both the Co and Ni 3*d* states but the increase in the anti-bonding character for their TM-Al bonds at the second inner ring TM site of the model cluster in comparison to the most inner ring TM site. Comparing the calculated DOS with the observed valence-band photoelectron and TM $L\alpha$ X-ray emission spectra, we discuss the occupation at the transition metal sites by Co and Ni.

Introduction

Decagonal phase of an Al-Co-Ni alloy is one of typical two-dimensional quasicrystals; quasiperiodically arranged atomic layers are stacked periodically along a crystal axis [1]. The atomic arrangement in the quasiperiodic layer is often viewed as a special tiling such as the Penrose one of two unit tiles, a skinny and fat rhombi, while it may be regarded as consisting of a single unit cluster with overlapping rules [2,3]. An electronic band structure study for Al-Co-Ni model approximants [4] shows the strong dependence of the transition metal (TM) 3*d* electronic structures on their atomic arrangement, predicting that a decagonal Ni ring-like arrangement is preferentially formed at the center of a cluster-like unit at the vertex of its rhombic tiles and that its Co 3*d* states are located unusually lower in energy than Ni ones because of a strong Co-Al interaction. However, this predicted electronic structure is inconsistent with the experimental partial density of TM 3*d* states (3*d*-DOS) studied by x-ray emission (XES) and

* Correspondence author
(e-mail:j45880a@nucc.cc.nagoya-u.ac.jp)

photoemission (XPS) measurements [5]. Although it is still hard to distinguish the Co site from the Ni one, new models with Al atoms incorporated in the cluster center [1, 6, 7] have been also proposed by using the crystal structure of a W-(AlCoNi)-phase approximant $Al_{72.5}Co_{20}Ni_{7.5}$ [6]. An *ab initio* study of the surface electronic structure of a W-(AlCoNi)-phase model approximant $Al_{70.78}Co_{14.61}Ni_{14.61}$ shows fairly good agreement with the experimental observations by ultraviolet photoemission spectroscopy (UPS) and scanning tunneling microscope (STM) of Al-Co-Ni quasicrystals, suggesting the similarity in the atomic arrangement between the approximant and the quasicrystals [8]. Theoretical studies with use of interatomic pair potentials, where some constraints are enforced about the atomic sites and the obtained atomic arrangement is characterized in terms of a special tiling, predict such an Al-TM decagonal ring-like arrangement for the cluster center of the Co-rich Al-Co-Ni approximant (the decagon tile) [9, 10], while they show that the decagonal (pentagonal) symmetry of the cluster center is broken for the Ni-rich Al-Co-Ni approximant (the hexagon-boat-star (HBS) tiling) [10, 11, 12]. However, the chemical ordering is not so clear in particular for Co and Ni; the chemical ordering between Al and TM may be an origin of the broken symmetry [13].

In this paper, we have studied the electronic structure and atomic arrangement of the decagonal Al-Co-Ni quasicrystal by discrete variational $X\alpha$ (DV-$X\alpha$) cluster calculation [14] and comparison of the calculated electronic structure with the experimental one [5], in order to specify the sites occupied by Co and Ni and to clarify the chemical nature bringing its unique atomic arrangement with the variety depending on the composition. The DV-$X\alpha$ method is one of the real-space first principle molecular orbital calculations and it is powerful for investigating the electronic structure and chemical bonding in the materials including many TM's [14] without the periodicity.

Calculating procedure

The DV-$X\alpha$ method is based on the Hartree-Fock-Slater molecular equation, which 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 [14]. For the present calculation, we have modified the available code SCAT [15] for faster calculation with larger cluster than the original one and have applied it to a 2 nm decagonal model unit cluster.

The model cluster has a triple layered structure along the periodic direction with two quasiperiodic unit layers A and B in the A-B-A or B-A-B stacking sequences with the interlayer distance of 0.2 nm. As shown in Fig. 1, the atomic arrangement in the quasiperiodic layers A and B is based on a recent model proposed from the model of the W-(AlCoNi) approximant [1, 6] but the Co and Ni sites are explicitly distinguished in this study for the TM sites of the proposed model. Here, closed circles and diamonds stand

for two kinds of transition-metals, TM1 and TM2, respectively, *i.e.* Co or Ni; 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 neighbor TM is avoided for the mixed sites of the proposed model [1] for simplicity. In order to avoid the so-called surface effects, the hydrogen atoms (open squares) are put in the peripheral part of the cluster, in particular around TM, and the DOS shown later is obtained as the sum of the local DOS's of the central layers A and B for the respective B-A-B and A-B-A model clusters. The overlap population is estimated also for TM in the central layer. The DOS and overlap population are shown after convoluting their calculated line spectra with a Gaussian function of the 0.17 eV half width at half maximum. In Fig. 1, a large thick circle indicates the size of the unit cluster, 2 nm, and the nominal composition per a pair of the A and B layers is $Al_{81}TM1_{15}TM2_{15}H_{50}$, which may correspond to an $Al_{73.0}TM1_{13.5}TM2_{13.5}$ quasicrystal.

Results and Discussion

Obtained DOS's are shown in Fig. 2 with the TM $L\alpha$ XES and valence-band XPS spectra: (a) a Ni inner ring model, *i.e.* a model with TM1 = Ni and TM2 = Co for the TM sites in Fig. 1, and (b) a Co inner ring model, *i.e.* TM1 = Co and TM2 = Ni. Except for the detailed differences discussed later, DOS's for both the present models agree well with the experimental spectra as a whole; in the previous calculation for double-layered small unit clusters [5], the calculated features appear at higher energy by about 1 eV than the experimental ones, which is probably due to the surface effects or the Madelung potential. In fact, the DOS for the Ni inner ring model is similar to that obtained by the band structure calculation for the Al-Ni innermost ring model [4], which possesses the close similarity of their TM arrangement in the central part of the decagonal cluster. Thus the present procedure will properly present the bulk electronic structure of the model quasicrystal. For the Ni inner ring model, the Co 3*d* band is slightly lower than or almost the same as the Ni one, while the Co and Ni 3*d* bands are separated and broadened for the Co inner ring model. Similar trends are recognized in the band structure calculation for the approximants [4]. The Al partial DOS shows the decrease around the Fermi energy (the origin of the binding energy E_B = 0 eV), *i.e.* the formation of a pseudogap, which is also consistent with the band structure calculation [4] and the Hume-Rothery-type behavior in the quasicrystal phase formation [16].

In order to see the contribution to the total DOS and the chemical properties of the TM at the various TM sites, 1 to 5, assigned in Fig. 1, we show the local 3*d*-DOS at the TM sites for the Ni and Co inner ring models in Fig. 3(a) and (b), respectively, and the overlap population between TM and Al in the local clusters, TM_3Al_9 around the most inner ring TM site (the site 1 in Fig. 1) and (b) $TMAl_{11}$ around the second inner ring TM site (the site 2) in Fig. 4(a) and (b), respectively. Here, the local cluster is composed of the first, second, and third nearest neighbors around the central TM, and the overlap population is estimated by summing

the conventional overlap population for the bond between two atoms, TM and Al, over the TM-Al bonds of the local cluster. The local 3*d*-DOS's at the second inner ring sites 2 and 3 are almost the same, as expected from the fact that the local atomic arrangements or local clusters around these TM's are similar to each other. While TM at the site 5 shows the local DOS distributed over nearly the same energy region as the site 1, TM at the site 4 causes a peak or hump at the low binding energy side of the main TM 3*d* band. At present, it is uncertain whether TM's at the outer sites 4 and 5 may present the bulk DOS properly or not, since these TM's are surrounded partially with H. Thus we will not further deal with these sites in this paper.

As seen in Fig. 3, the 3*d* states of both Co and Ni at the sites 2 and 3 are located lower in energy than those at the most inner ring 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 for the TM-Al bond at the sites 2 and 3, compared to the site 1. Since the present DV-$X\alpha$ method does not have enough accuracy, unfortunately, to compare the total energy for the whole system including the deep core levels, we have calculated the total energy for the occupied valence band and found that the total valence band energy is slightly lower in the Co inner ring model than in the Ni inner ring model, in contrast to the band structure calculation [4], where the Ni innermost ring model, though it is slightly different from our model, shows the lowest total energy.

As already seen in Fig. 2, neither Ni inner ring model nor Co one shows detailed agreement with the experimental results; the Co 3*d* band is located slightly lower than the Ni one in the Ni inner ring model, while they are separated and hence the TM 3*d* band is broadened in the Co inner ring model. Taking into account the possible small difference in the total energy and the experimental energy position of the TM 3*d* band, we have tentatively calculated the TM 3*d* band by simply adding the local DOS's at the sites 1 and 2 of the two model unit clusters with their equal weights, as shown in Fig. 5(c). Obtained spectrum shows fairly good agreement with the experimental results in spite of rough estimation. This may imply the large chemical disordering or the random occupation of the available TM sites by Co and Ni in the quasicrystal. Or this may be induced by TM in the peripheral part of the unit cluster disregarded in this study.

In the present study, we have concentrated on the Co and Ni sites rather for the Co-rich quasicrystals partly because of simplicity to derive the TM site characteristics. For the Ni-rich quasicrystals having the symmetry broken or the HBS tiling unit clusters, we have not calculated the electronic structure with the triple-layerd unit clusters but the double-layered small ones, whose atomic arrangements are derived from the models proposed by Mihalkovič *et al*. [11] and Abe *et al*. [12]. Although the overall shift towards the low binding energy is recognized as already mentioned, the ordering and seperation of the Ni and Co 3*d*-DOS's is similar to those of the mixed occupation model. This is probably due to the mixed occupation of Co and Ni in the cluster center of the proposed models. Further study is also necessary on the detailed electronic structure of the $TMAl_m$

local clusters and the effects of the neibouring TM or the TM-Al mixed occupation on the electronic structure of the local cluster.

Conclusions

In order to determine the Co and Ni sites consistently with both the experimental microscopic and spectroscopic observations for the decagonal Al-Co-Ni quasicrystal, we have compared the calculated valence band electronic structures with the transition metals $L\alpha$ XES spectra and the valence band XPS spectra [5]. We have found that the experimental TM 3*d* band can be explained by the mixed occupation of Co and Ni at the TM sites.

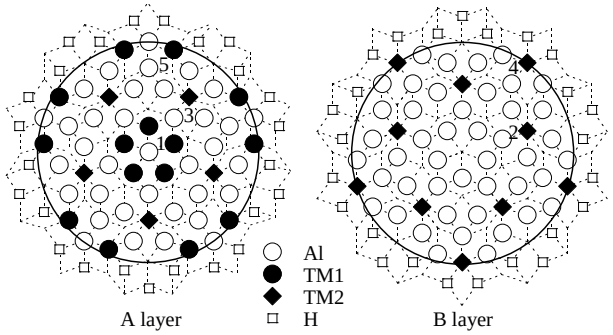

Fig. 1. Atomic arrangement in the quasiperiodic layers A and B of a model unit cluster of Al-Co-Ni decagonal quasicrystal. Open circles, closed circles and diamonds, and open squares represent Al, the transition metals TM1 and TM2, and H, respectively. The non-equivalent tranistion metal sites are assigned with numbers.

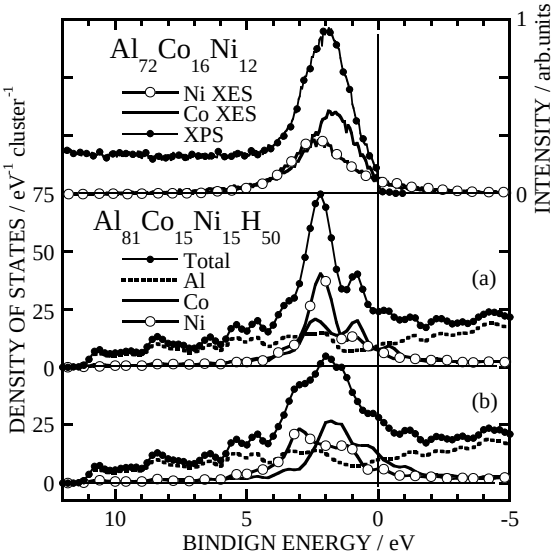

Fig. 2. Total and Al, Co, and Ni partial densities of states for model unit clusters $Al_{81}Co_{15}Ni_{15}H_{50}$ of (a) Ni inner ring model, *i.e.* a model with TM1 = Ni and TM2 = Co in Fig. 1, and (b) Co inner ring model, *i.e.* that with TM1 = Co and TM2 = Ni. The Co and Ni $L\alpha$ X-ray emission (XES) and valence-band X-ray photoelectron (XPS) spectra of $Al_{72}Co_{16}Ni_{12}$ quasicrystal are shown for comparison [5]. For XES spectra, the ratio of their integrated intensities is normalized with their composition ratio.

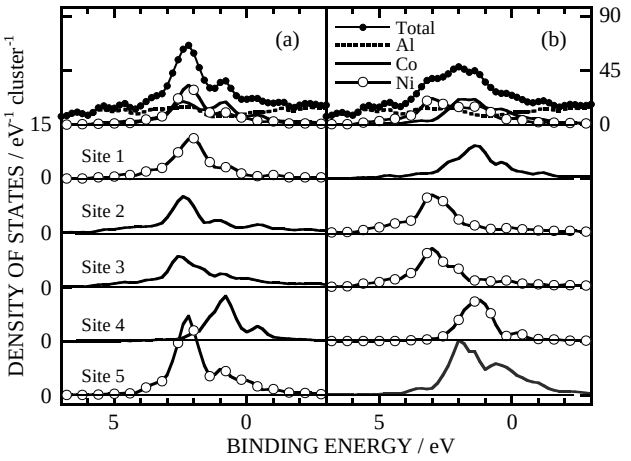

Fig. 3. Local density of the Co and Ni 3*d* states at different transition metal sites of the model unit clusters, (a) Ni inner ring model and (b) Co inner ring model. The transition metal sites, 1 to 5, are assigned in Fig. 1.

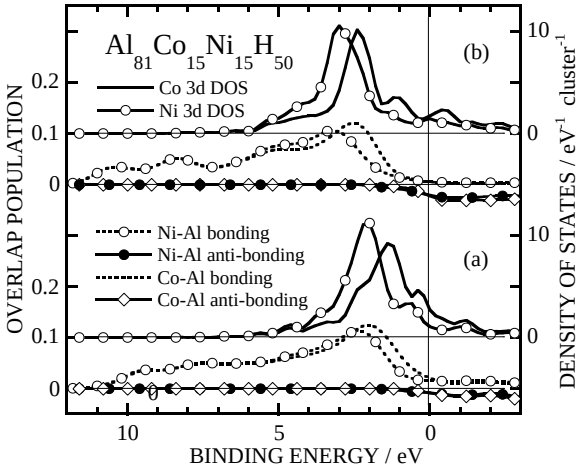

Fig. 4. Overlap population between transition metal (TM) and Al for local clusters (a) TM_3Al_9 around the most inner ring TM site (the site 1 in Fig. 1) and (b) $TMAl_{11}$ around the second inner ring TM site (the site 2). Local densities of the TM 3*d* states at these sites are also shown for comparison.

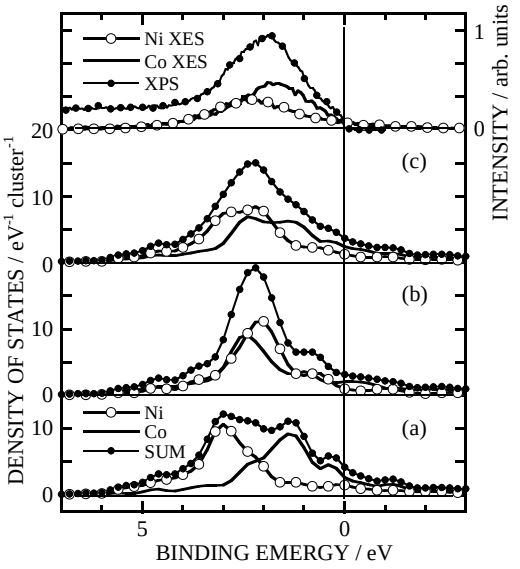

Fig. 5. The transition metal 3*d* band calculated with the transition metals Co and Ni at two types of the sites, 1 and 2(3) shown in Fig. 1, for (a) Co inner ring model, (b) Ni inner ring model, and (c) random occupation model. The transition metal $L\alpha$ X-ray emission spectra (XES) and the valence-band X-ray photoelectron one (XPS) are also shown in the top panel for comparison.

Acknowledgements. We would like to appreciate Prof. H. Wasada and Mr. I. Takahashi at Information Technology Center, Nagoya University for their valuable advice in the modification of the calculating code. This work was partly supported by the 21st Century COE program, Isotopes for the Prosperous Future – Isotope Science and Engineering from Basics to Applications.

References

[1] Hiraga, K.: The structure of quasicrystals studied by atomic-scale observations of transition electron microscopy. Adv. Imaging and Electron Phys. **122** (2002) 1-86.

[2] Zhang, X.; Fu, X.: Electronic spectral properties of a two-dimensional quasicrystal model. Phys. Lett. A **351** (2006) 327-330.

[3] Jeong, H.-C.; Steinhardt, P.J.: Constructing Penrose-like tilings from a single prototile and the implications for quasicrystals. Phys. Rev. B **55** (1997) 3520-3532.

[4] Krajči, M.; Hafner, J.; Mihalkovič, M.: Atomic and electronic structure of decagonal Al-Ni-Co alloys and approximant phases, Phys. Rev. B **62** (2000) 243-255.

[5] Inukai, M.; Soda, K.; Ota, S.;Miyazaki, H.; Suzuki, T.; Kato, M.; Yagi, S.; Tezuka, Y.; Yokoyama, Y.: Energy distribution of Co and Ni 3d states of decagonal quasicrystal $Al_{72}Co_{16}Ni_{12}$. Phil. Mag. **87** (2007) 3003-3010.

[6] Sugiyama, K.; Nishimura, S.; Hiraga, K.: Structure of a W-(AlCoNi) crystalline phase related to Al-Co-Ni decagonal quasicrystals, studied by single crystal X-ray diffraction. J. Alloys Comp. **342** (2002) 65-71.

[7] Deloudi, S.; Kobas, M.; Steurer, W.: 5D modeling of decagonal Al-Co-Ni based on the W-approximant. Phil. Mag. **86** (2006) 581-585.

[8] Krajči, M.; Hafner, J.; Mihalkovič, M.: *Ab initio* study of the surface of a decagonal Al-Co-Ni quasicrystal. Phys. Rev. B **73** (2006) 134203-1-11.

[9] Hiramatsu, S.; Ishii, Y.: Theoretical prediction of phase diagrams for Al-Co-Ni decagonal quasicrystals. J. Phys. Soc. Jpn. **75** (2006) 054602-1-6.
[10] Gu, N.; Henley, C.L.; Mihalkovič, M.: Co-rich decagonal Al-Co-Ni: predicting structure, orientational order and puckering. Phil. Mag. **86** (2006) 593-599.
[11] Mihalkovič, M.; Al-Lehyani, I.; Cockayne, E.; Henley, C.L.; Moghadam, N.; Moriarty, J.A.; Wang, Y.; Widom, M.: Total energy prediction of a quasicrystal structure. Phys. Rev. B **65** (2002) 104205-1-6.
[12] Abe, E.; Saitoh, K.; Takakura, H.; Tsai, A.P.; Steinhardt, P.J.; Jeong, H.-C.: Quasi-unit-cell model for an Al-Ni-Co ideal quasicrsytal based on clusters with broken tenfold symmetry. Phys. Rev. Lett. **84** (2000) 4609-4612.
[13] Yan, Y.; Pennycook, S.J.: Chemical ordering in $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals. Phys. Rev. Lett. **86** (2001) 1542-1545.
[14] Adachi, H.; Tsukuda, M.; Satoko, C.: Discrete Variational $X\alpha$ Cluster Calculations. I. Application to Metal Clusters. J. Phys. Soc. Jpn. **45** (1978) 875-883.
[15] http://www.dvxa.org/
[16] Tsai, A. P.: Quasicrystals as Hume-Rothery Phases, In: Physical Properties of Quasicrystals (Ed. Z. M. Stadnik), p. 23-26. Springer-Verlag, Berlin 2000.