Covalent Bonds in AlMnSi Icosahedral Quasicrystalline Approximant

K. Kirihara,[1] T. Nakata,[2] M. Takata,[2,4] Y. Kubota,[3] E. Nishibori,[4] K. Kimura,[1,5] and M. Sakata[4]

[1]*Department of Materials Science, the University of Tokyo, 113-8656, Japan*
[2]*Department of Material Science, Shimane University, 690-8504 Matsue, Japan*
[3]*Department of Natural Science, Osaka Women's University, 590-0035 Sakai, Japan*
[4]*Department of Applied Physics, Nagoya University, 464-8603 Nagoya, Japan*
[5]*Department of Advanced Materials Science, the University of Tokyo, 113-0033 Tokyo, Japan*
(Received 24 February 2000)

Electron density distributions were obtained using the maximum entropy method with synchrotron radiation powder data. In the metallic $Al_{12}Re$, metallic bonding was observed for the icosahedral Al_{12} cluster with central Re atom. In the nonmetallic α-AlMnSi 1/1 approximant, covalent bonds were found in the electron density distribution of the Mackay icosahedral cluster without central atom. Rather than the Hume-Rothery mechanism, the covalency of Al (Si) icosahedron and that between Al (Si) and Mn atoms is considered to be the origin of the pseudogap and nonmetallic behavior of α-AlMnSi.

Unlike crystalline and amorphous metals, stable and structurally ordered icosahedral Al-based quasicrystals exhibit "nonmetallic" properties [1–3]. The term "nonmetallic" means high values of electrical resistivity and a large negative temperature coefficient of resistivity. These characteristics have been explained by a combination of a Hume-Rothery pseudogap in the electron density of states at Fermi level (E_F) and the localization tendency of electrons near E_F [1–4]. Approximant crystalline phases are known to exist in many icosahedral alloy systems, having a composition close to that of icosahedral phases. Among such approximant phases, most can be described as a periodic arrangement of the icosahedral cluster, e.g., the Mackay icosahedral (MI) cluster [5] or Bergman cluster [6] considered to be the basic space-filling units of icosahedral phases.

Detailed research on the electrical properties of approximants has clearly shown that higher-order approximant phases possess quasicrystalline-like, i.e., nonmetallic, properties [7]. In Al transition-metal (TM) icosahedral phases, properties of the 1/1 approximant phases with a lattice constant a of about 1.2 nm are important because such a lattice constant plays a critical role in determining nonmetallic and metallic behavior. For instance, the α-AlMnSi phase [8] ($a = 1.266$ nm) and AlCuFeSi phase [9] ($a = 1.233$ nm) exhibit the former behavior, while the AlCuRu phase [10] ($a = 1.24$ nm) exhibit the latter. Also, the properties of 1/0 approximant phases whose lattice constants are τ times shorter than 1.2 nm, e.g., AlCuRu [10] and $Al_{12}Re$ [11], are metallic; where τ [$= (1 + \sqrt{5})/2$] is the golden mean number.

Molecular orbital calculations have shown metallic bonding for group-III elements in a 13-atom icosahedral cluster with center atom, whereas a 12-atom cluster without a center atom has covalent bonding [12]. Kimura *et al.* surmised that metallic-covalent bonding conversion in icosahedral clusters of aluminum or boron is closely related to the metal-nonmetal transition in both Al-based

icosahedral quasicrystals/approximants and B-based approximants [13,14]. In addition, results of photoemission spectroscopy and soft-x-ray emission spectroscopy (SXES) suggest that strong p-d hybridization between Al-TM atoms plays a crucial role in enhancing nonmetallic properties [15,16].

Therefore, the x-ray charge density study should be required to reveal a bonding nature in order to give a better understanding for the electronic structure of a quasicrystal approximant.

In this Letter, we use the maximum entropy method (MEM) with synchrotron radiation powder data to examine the bonding nature of icosahedral clusters of 12 atoms in nonmetallic α-AlMnSi 1/1-cubic approximant phase and 13 atoms in metallic $Al_{12}Re$ phase, respectively.

Briefly, ingots of $Al_{12}Re$ and $Al_{72}Mn_{16}Si_{12}$ alloys were prepared from elemental constituents (3N) by arc melting under Ar atmosphere. To obtain single-phase bulk samples of $Al_{12}Re$ crystal phase, Al-Re alloy ingots were placed in an evacuated quartz tube and heated to 1023 K, which is slightly below the peritectic point, and held for 5 h. The samples were then cooled to 975 K over 16 h. Sample homogenization of Al-Mn-Si alloy ingots was achieved by remelting via inductive melting, after which single-phase bulk samples of α-AlMnSi crystal phase were prepared by annealing the ingots at 953 K for 17 h under Ar atmosphere. The structures and the local compositions of the samples were observed by using a scanning electron microscope and measured by energy dispersive x-ray spectroscopy, respectively, in order to ensure the sample homogeneousness. X-ray powder diffraction patterns were measured with synchrotron radiation and a diffractometer with six detector arms [17], being carried out at KEK Photon Factory BL-4B$_2$. The wavelength of incident x rays was fixed at 1.3978 Å using a common step width of 0.006° in 2θ. Count time was 9 and 11 s per step for $Al_{12}Re$ and α-AlMnSi, respectively.

Diffraction data were analyzed by the MEM/Rietveld analysis [18]. The space groups, lattice constants, and number of atoms in a unit cell are, for $Al_{12}Re$, Im3, $a = 0.753219(1)$ nm, 26, and, for α-AlMnSi, Pm3, $a = 1.266139(1)$ nm, 138, respectively. Figure 1(a) shows the resultant crystal structure and the (200) plane in $Al_{12}Re$ determined by Rietveld analysis, where atoms of [1(b)] 13-atom icosahedral cluster correspond to those positioned at the body center and at the unit cell origin. In Fig. 1(c), the resultant crystal structure in α-AlMnSi is shown, and the section of MI cluster at the center, glue atom sites G_1 and G_2, containing Al and Si atoms, are present on the (100) plane [1(d)]. The details of crystal data and refined structural parameters for both samples have been published elsewhere [11]. Note that the fundamental structure of α-AlMnSi is the same as that of Sugiyama *et al.* [19] in that Si atoms are distributed in three Al sites and their occupancies are 0.53(3) and 0.73(3) for A_1 sites of MI clusters at the body center and origin, and 0.82(4) for G_2 sites. This disordered distribution, or chemical disorder, of Si atoms may cause the localization tendency of electrons near E_F even for the crystalline structure of α-AlMnSi. The MEM analysis after pre-Rietveld analysis was performed using the MEED [20] computer code with $100 \times 100 \times 100$ pixels per cubic lattice. The MEM/Rietveld analysis succeeded in revealing a peculiar covalent bond in α boron, i.e., multicenter bond in B_{12} cluster and a bent inter-B_{12} cluster bond [21]. The d values of highest-angle reflection corresponding to spatial resolution of the electron density distribution were 0.761 Å for both $Al_{12}Re$ and α-AlMnSi, while the R factor based on structure factors, R_F, was 0.88% and 1.71% for $Al_{12}Re$ and α-AlMnSi, respectively.

Figure 2(a) shows a section contour map of the electron density distribution for $Al_{12}Re$ in the (200) plane. Note that no covalent bond exists for inter-Al atoms of the 13-atom icosahedral cluster. The result differs from a multicenter covalent bond in the 12-atom icosahedral boron cluster. The variation in the bonding nature of the icosahedral cluster is discussed later. The value of minimum electron density of $Al_{12}Re$ is 0.118 $e/\text{Å}^3$, being about a hundred times larger than that of α-AlMnSi (0.001 $e/\text{Å}^3$). This significant feature of charge density may virtually correspond to that of a free electron model, hence this large value is apparently related to the metallic behavior of electrical resistivity and its temperature coefficient. Although $Al_{12}Re$ is surmised to have metallic bonding, it exhibits weak hybridization between each Al atom of the icosahedron and the central Re atom.

Figure 2(b) shows corresponding mapping results for α-AlMnSi in the (100) plane. In contrast with the charge density of $Al_{12}Re$, the α-AlMnSi crystal has a strong directional Mn-Al covalent bond (Mn-A_2) in the second shell of the MI cluster, with similar covalent bonds (Mn-G_1) existing between the Mn atom in the second shell and the

Al atom at G_1 sites; together representing the crystal's strongest bonds. Interatomic Al(or Si)-Al(or Si) covalent bonds for the first shell and Al(or Si)-Mn covalent bonds (A_1-Mn) connecting the first and second shells were observed as well. The characteristics of the bonds for the MI cluster at the body center are the same as those at the origin, i.e., the Mn-Al covalent bonds constitute the second shell of the MI cluster as a cage with high electron density distribution.

Towards understanding the stability of the α-AlMnSi crystal, the bonds between Mn and Al atoms are considered to play an important role in that the Mn-Al covalent bonds in the second shell may contribute to the stabilization of the MI cluster. The Al atoms at glue site G_1 are strongly bound to Mn atoms in the MI cluster, being connected to it such that they form its body-center packing. Based on the results of band structure calculations on a crystal of α-AlMn, where Si atoms in our study are replaced by Al atoms, Fujiwara reported similar characteristics [22], finding that the Mn $3d$ band is split at its middle near E_F and that the binding peak of the density of states (DOS) is slightly below E_F. This binding peak is mainly due to the local projected DOS of the Mn d state, the Al p state of the first shell, and the second shell of MI cluster, which together are responsible for the stability of the MI cluster. As mentioned previously, SXES measurements by Belin *et al.* showed that hybridization between the Al p band and Mn d band is responsible for the opening in the pseudogap near E_F [15]. Our real-space image of electron density distributions enables the strong covalent Mn-Al bond in α-AlMnSi to be described using their band structure calculation and X-ray spectroscopic measurements.

Variation in the bonding nature of the icosahedral cluster could well depend on the center occupancy of the icosahedral cluster, i.e., the 12-atom icosahedron in α-AlMnSi has covalent bonding, whereas that of the 13-atom icosahedron in $Al_{12}Re$ has metallic bonding. Realizing that the atomic radius (Goldschmidt radius) of the Mn atom is smaller than that of the Re atom, a question naturally arises as to why the former atom cannot occupy the icosahedron center in α-AlMnSi, whereas the latter atom can occupy it in $Al_{12}Re$. Molecular orbital calculations [12] indicate that, even though the energy gain is sufficiently large for placing an atom at the center of a 12-atom icosahedron, only a small gain is realized for an icosahedron having 12 hydrogen atoms which terminate 12 dangling bonds sticking along fivefold axes. If a cluster exhibits metallic bonding nature due to having an atom placed at its center, then such occupation would act to stabilize it. On the other hand, if the cluster is forced to have covalent bonding nature due to its environment, then the center site should be empty.

The origin of the pseudogap in Al-based icosahedral phases is considered to be due to a Fermi surface–Jones zone interaction such as that exhibited in Hume-Rothery
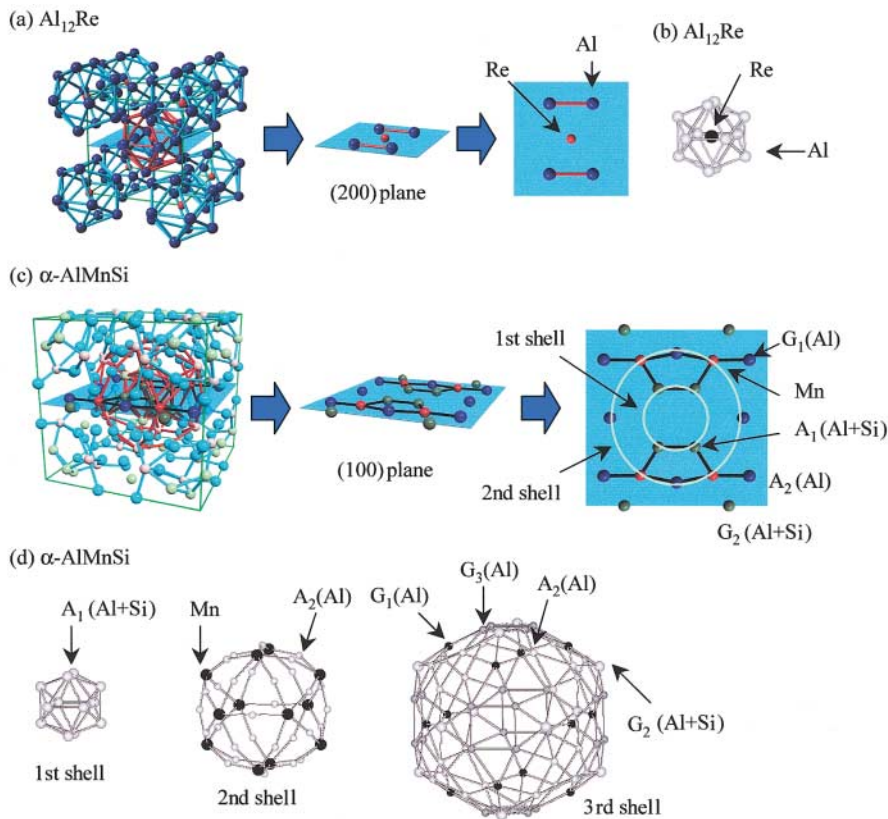
FIG. 1 (color). (a) Refined crystal structures of $Al_{12}Re$ and (b) icosahedral clusters in the crystal. (c) Refined crystal structures of α-AlMnSi. (d) The clusters in (c) are at the origin of cubic unit cell. Clusters up to the second shell, called the MI cluster, are also positioned at the body center. Occupancy of Al and Si in the MI cluster at the body center is slightly different from that at the origin.

alloys; an interaction enhanced when the Fermi-sphere diameter $2k_F$ matches the wave number of the intense Bragg peak K_p. By estimating $2k_F$ from the valence electrons per atom ratio (e/a), we found that $2k_F$ in α-AlMnSi is quite close to K_p of the intense (530) peak corresponding to the pseudofivefold direction.

The Hume-Rothery picture, however, applies to a nearly free electron system in which the potential of the valence electron is rather weak. In the case where $2k_F$ is close to K_p, one of two standing waves created from two plane waves is stabilized and occupied by the electron while the other is empty so that the electron density distribution
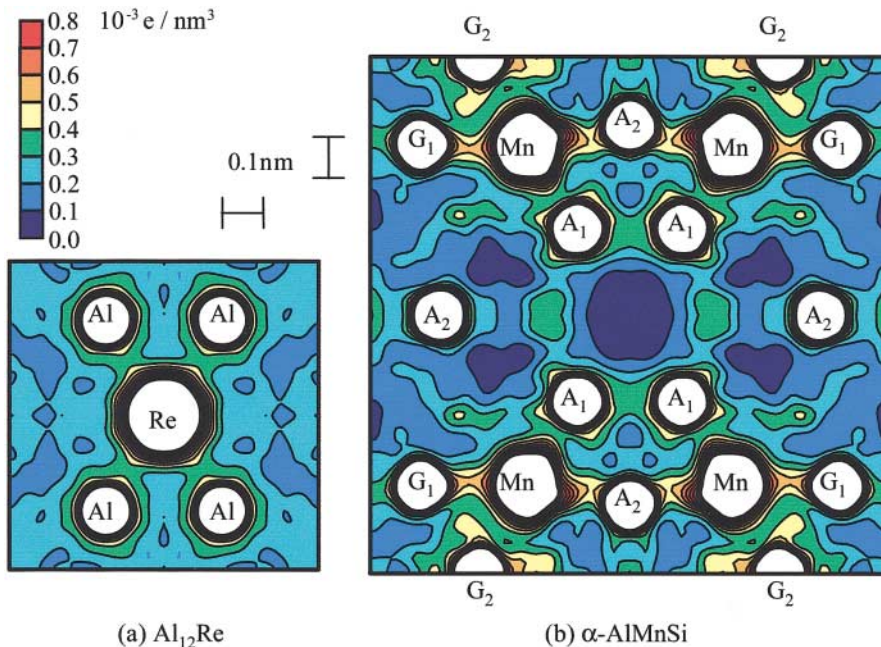

FIG. 2 (color). Section contour maps for (a) $Al_{12}Re$ and (b) α-AlMnSi in the range of $0.00-1.25$ $e/Å^3$ with a step of 0.10 $e/Å^3$. The maps in the range of $0.00-0.80$ $e/Å^3$ are colored. A_1 is Al or Si in the first shell of the MI cluster, while A_2 (Al) and Mn are in the second shell of the MI cluster. Glue atom sites are G_1 (Al) or G_2 (Al or Si). Site names correspond to those indicated in Fig. 1.

becomes inhomogeneous and dense regions appear. The energy difference between two standing waves, the depth of the pseudogap, and the inhomogeneity of the electron density distribution increase with increasing potential. Accordingly, for a sufficiently deep pseudogap, it is easy to see dense regions of valence electrons as covalent bonds as in α-gallium, a metallic molecular crystal [23]. Regarding α-AlMnSi, it is similar to that of α-gallium in that the origin of the pseudogap is considered to be due to the covalent bonds rather than the Hume-Rothery mechanism. In the AlPdRe icosahedral phase, the enhancement of electrical resistivity with increasing concentration of transition metals is due to the enhanced covalency between Al and TM [16,24]. Such hybridization-induced band gaps also exist in Al-Ru and Al-Fe alloys, with the real gap being formed at E_F in Al_2Ru intermetallic compound [25].

The covalency of Al icosahedron and that between Al and TM give rise to extremely low carrier density and small DOS at E_F in α-AlMnSi and perhaps in icosahedral phases. As performed here, high-resolution direct observation of such covalent bonds provides a strong foundation for subsequent research. The MEM/Rietveld analysis for AlCuRu 1/1 and 1/0 approximant phases is in progress. The icosahedral cluster in both metallic phases may be 13-atom ones with a center atom. Such systematic study, including that of icosahedral boron-rich solids, should lead us to a fundamental understanding, e.g., the relation between Hume-Rothery mechanism, hybridization, and covalent bonding, of these unique icosahedral cluster-based solids.

———

[1] K. Kimura *et al.,* J. Phys. Soc. Jpn. **58**, 2472 (1989).
[2] T. Klein *et al.,* Europhys. Lett. **13**, 129 (1990).
[3] B. D. Biggs *et al.,* Phys. Rev. Lett. **65**, 2700 (1990).
[4] K. Kimura and S. Takeuchi, in *Quasicrystals: the State of the Art,* edited by D. P. Divincezo and P. J. Steinhardt (World Scientific, Singapore, 1999), 2nd ed., p. 325.
[5] V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985).
[6] C. L. Henley and V. Elser, Philos. Mag. B **53**, L59 (1986).
[7] T. Shibuya, K. Edagawa, and S. Takeuchi, in *Proceedings of the 6th International Conference on Quasicrystals,* edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998), p. 700.
[8] B. D. Biggs, F. S. Pierce, and S. J. Poon, Europhys. Lett. **19**, 415 (1992).
[9] A. Quivy *et al.,* J. Phys. Condens. Matter **8**, 4223 (1996).
[10] R. Tamura *et al.,* in *Proceedings of the 5th International Conference on Quasicrystals,* edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995), p. 539.
[11] K. Kirihara *et al.,* in *Proceedings of the 7th International Conference on Quasicrystals* (Mater. Sci. Eng. A, to be published). If you need the information rapidly, please contact kirihara@phys.mm.t.u-tokyo.ac.jp
[12] M. Fujimori and K. Kimura, J. Solid State Chem. **133**, 310 (1997).
[13] K. Kimura *et al.,* in *Proceedings of the 5th International Conference on Quasicrystals* (Ref. [10]), p. 730.
[14] K. Kimura *et al.,* in *Proceedings of the 6th International Conference on Quasicrystals* (Ref. [7]), p. 595.
[15] E. Belin *et al.,* J. Phys. Condens. Matter **4**, 1057 (1992).
[16] T. Takeuchi *et al.,* in *Proceedings of the 5th International Conference on Quasicrystals* (Ref. [10]), p. 534.
[17] H. Toraya, H. Hibino, and K. Ohsumi, J. Synchrotron Radiat. **3**, 75 (1996).
[18] M. Takata *et al.,* Nature (London) **377**, 46 (1995); M. Takata *et al.,* Phys. Rev. Lett. **78**, 3330 (1997).
[19] K. Sugiyama, N. Kaji, and K. Hiraga, Acta Crystallogr. Sect. C **54**, 445 (1998).
[20] S. Kumazawa *et al.,* J. Appl. Crystallogr. **26**, 453 (1993).
[21] M. Fujimori *et al.,* Phys. Rev. Lett. **82**, 4452 (1999).
[22] T. Fujiwara, Phys. Rev. B **40**, 942 (1989).
[23] X. G. Gong *et al.,* Phys. Rev. B **43**, 14 277 (1991).
[24] H. Sawada *et al.,* in *Proceedings of the 6th International Conference on Quasicrystals* (Ref. [7]), p. 329.
[25] M. Weinert and R. E. Watson, Phys. Rev. B **58**, 9732 (1998).