High-Resolution Electron Microscopy and Atomic Arrangements of Al-Mn-Si and Al-Li-Cu Icosahedral Quasicrystals

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Two types of icosahedral quasicrystals of Al-Mn-Si and Al-Li-Cu were examined with a 400 kV high-resolution electron microscope having a resolution of 0.17 nm. Their images taken with the incident beam parallel to the fivefold symmetry axis clearly show a structure model formed by the aggregation of atom clusters with icosahedral symmetry. The observed image contrast of Al-Mn-Si was reproduced by an image calculation of the structure model using the multislice method. The calculation demonstrated that high-resolution images taken with the 400 kV electron microscope faithfully represent projected potential of the quasicrystals.

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I. Introduction

High-resolution electron microscopy of icosahedral quasicrystals has provided valuable information about structures of quasicrystalline alloys; *e.g.* the existence of fivefold symmetry and long-range quasiperiodicity in real space⁽¹⁾, and interesting defects such as quenched phason strains⁽²⁾ and dislocations⁽³⁾. However, almost all the images observed so far are so-called lattice images taken with electron microscopes having a poor resolution of about 0.23 nm, and so have given us little information about atomic arrangements of the quasicrystals. The purpose of this work is to observe so-called high-resolution structure images which faithfully represent projected potential of the quasicrystals, by using a 400 kV electron microscope having a resolution of 0.17 nm, and to discuss atomic arrangements of Al-Mn-Si and Al-Li-Cu quasicrystals.

II. Experimental Procedures

Samples of the Al-Mn-Si quasicrystal were prepared by a melt-quenching method using an alloy with a nominal composition of Al₇₄Mn₂₀Si₆. For Al-Li-Cu, a part of the single quasicrystal prepared by the Bridgeman method in the Nanao group, Institute of Industrial Science, the University of Tokyo, was used. The quasicrystals are so brittle that the samples for electron microscopy were prepared by dispersing crushed materials on microgrids with holey carbon films. High-resolution observations were performed with a 400 kV electron microscope (JEM-4000EX) equipped with a top-entry type of goniometer, which has a theoretical resolution of 0.17 nm.

III. Results and Discussion

1. Al-Mn-Si

Figure 1 shows a high-resolution electron micrograph of the Al-Mn-Si quasicrystal taken with the incident beam parallel to the fivefold symmetry axis, together with an electron diffraction and a Fourier transformed pattern of the image. The Fourier transformed pattern reproduces well an intensity distribution of the electron diffraction pattern, considering that the intensity of weak spots in the Fourier transformed pattern is enhanced by the effect of multiple scattering in the electron diffraction pattern taken from a relatively thicker region than that of the high-resolution image. It was confirmed from the Fresnel fringes observed at the edge of an amorphous film that the image was taken under the condition of near Scherzer defocus. Thickness of the region of the image is considered to be less than 10 nm. Thus, the observed image is a so-called structure image and is considered to represent projected potential of the quasicrystal along the fivefold axis, and accordingly the dark and bright regions in the image correspond to the high- and low-potential regions, respectively. In the image, we notice characteristic image contrasts composed with a bright ring and surrounding ten bright dots. Hereafter, the characteristic image contrast is called the decagon contrast. Note that most of the rings in the decagon contrasts are observed to be divided into three parts with un-homogeneous contrast.

The decagon contrast can be interpreted by an icosahedral atom cluster shown in Fig. 2(a). The atom cluster called the Mackey icosahedral cluster was proposed by Elser and Henley⁽⁴⁾ to interpret atomic arrangement of the Al-Mn quasicrystal. The atom cluster can be constructed by placing atoms with an octahedral type of arrangements (Fig. 3(b)) on a fundamental icosahedral

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Fig. 1 High-resolution electron micrograph of the Al-Mn-Si quasicrystal (a) and electron diffraction pattern (b) taken with the incident beam parallel to the fivefold symmetry axis. (c) is a Fourier transformed pattern of the image.

Fig. 2 Icosahedral atom cluster (a) and atomic arrangement projected along the fivefold symmetry axis (b).

atom cluster of Fig. 3(a). On the other hand, the construction with tetrahedral arrangements (Fig. 3(c)) leads to the other type of atom cluster (Fig. 8(a)) which was proposed for atomic arrangement of the Al-Li-Cu quasicrystal. Atom positions in those atom clusters can be related to the Penrose lattices as follows. It is known that a polyhedron (Fig. 4(a)) formed with twenty acute rhombohedra appears at vertices of the Penrose lattices inflated with a scaling parameter of τ^3 . The polyhedron has icosahedral symmetry, and so atom clusters with icosahedral symmetry can be formed by placing atoms at special positions in the twenty acute rhombohedra.

Fig. 3 (a): Fundamental icosahedral atom cluster, (b): octahedral arrangement on the icosahedral atom cluster, and (c): tetrahedral arrangement.

Fig. 4 Atomic decorations for the icosahedral and triacontahedral atom clusters. (a): Polyhedron formed with twenty acute rhombohedra, (b): atomic decoration for the icosahedral cluster in one of the twenty acute rhombohedra, and (c): for the triacontahedral cluster. Numbers in (b) and (c) indicate the order of successive atomic shells.

Fig. 5 Two types of connections of the icosahedral atom clusters; an edge contact (a) and a plane contact (b). Glue atoms placed at the positions indicated with arrows in (a) make octahedral atomic arrangements.

Atomic decorations in one of the twenty rhombohedra for the two types of atom clusters of Fig. 2(a) and Fig. 8(a) are shown in Fig. 4(b) and 4(c), respectively. Note that most of the atom positions in the clusters must be accurately shifted from the special positions. In the decorations, the successive atomic shells centering the 0 atom form various types of polyhedra with icosahedral symmetry.

In the projection of the icosahedral atom cluster (Fig. 2(b)), there are a ring-shaped channel around the centered atom and ten channels outside double atom rings. Their channels are expected to be represented as bright regions in the observed image; *i.e.* the ring channel becomes a bright ring and the ten channels are ten bright dots in the image. For the icosahedral quasicrystal of Al-Mn, Yamamoto and Hiraga⁽⁵⁾ proposed a structure model that the icosahedral atom clusters are placed at special positions in the three-dimensional Penrose lattices, namely, twelvefold positions proposed by Henley⁽⁶⁾. The twelvefold positions can be considered to be the sites that the icosahedral atom clusters are densely packed in space with three types of connections. The connections are shown in Fig. 5, *i.e.* an edge contact (a), a plane contact (b) and a connection by sharing a pentagon indicated in (b). Note that the octahedral atomic arrangements appear in the plane contact (Fig. 5(b)), and if glue atoms are placed at positions indicated with arrows in Fig. 5(a), the octahedral arrangements appear near the edge contact.

Figure 6 shows a projection of the twelvefold positions in the three-dimensional Penrose lattices along the fivefold axis. An atomic arrangement formed by placing the icosahedral atom clusters (Fig. 2(b)) at the twelvefold positions is shown in Fig. 7(a). Taking account of dynamical effect with the multislice method, a high-

Fig. 6 Twelvefold positions in the three-dimensional Penrose lattices, projected along the fivefold symmetry axis. Large and small circles correspond to the twelvefold positions and vertices of the fundamental rhombohedra forming the Penrose lattices, respectively.

Fig. 7 (a): Atomic arrangement formed by placing the icosahedral atom clusters (Fig. 2(b)) at the twelvefold positions (Fig. 6), projected along the fivefold axis. (b): Calculated image of the atomic arrangement under a defocus value of 45 nm and at a thickness of 6 nm.

resolution image of the atomic arrangement was calculated, using a periodic continuation approximation with an unit cell of $a=3$ nm, $b=3$ nm and $c=15$ nm, where the c -axis is parallel to the fivefold symmetry axis. The quasicrystal is assumed to be arranged periodically with vacuum boundaries of 0.5 nm in width between them along the a - and b -directions. Thickness of one slice was set to be 0.5 nm. The image of Fig. 7(b) was calculated under the Scherzer defocus of 45 nm and at a thickness of 6 nm. The calculated image reproduces well the image contrast expected from the projected atomic arrangement; the ring-shaped channel and ten channels surrounding it are represented as the bright ring and ten bright dots, respectively. Also we can see that almost of the bright rings are divided into three parts with unhomogeneous contrast, as seen in the observed image of Fig. 1. Consequently, the calculated image shows a good correspondence with the observed image of Fig. 1, though the observed image includes a few phason strains which are always observed in the icosahedral quasicrystals prepared by the melt-quenching method. Our calculation revealed that high-resolution images taken from thinner regions than about 10 nm faithfully represent projected potential for the Al-Mn quasicrystal. The result provides a significant way for the interpretation of observed high-resolution images of quasicrystals.

2. Al-Li-Cu

As for the Al-Li-Cu icosahedral quasicrystal, a triacontahedral atom cluster formed with 137 atoms (Fig. 8(a)) was proposed by the similarity of the R-AlLiCu crystalline phase⁽⁷⁾⁽⁸⁾. In the atomic cluster, two sizes of atoms are closely packed, and the large atoms placed on the threefold axes are considered to correspond to Li atoms and small atoms at the other positions are Al and Cu atoms. Projected atom positions of the

triacontahedral atom cluster along the fivefold symmetry axis is shown in Fig. 8(b). If the triacontahedra with an edge length of a (a is an edge length of the fundamental rhombohedra forming the Penrose lattices) are placed at the twelvefold positions, three-dimensional space may be filled up with three types of connections by sharing a rhombic plane, an obtuse rhombohedron and a rhombic icosahedron, which are shown in Fig. 9. In the projected atomic arrangement (Fig. 8(b)), we can see the existence

Fig. 8 Triacontahedral atom cluster (a) and atomic arrangement projected along the fivefold symmetry axis (b).

Fig. 9 Three types of connections appearing in the packing of triacontahedra in space, by sharing a rhombic plane (a), an obtuse rhombohedron (b) and a rhombic icosahedron (c).

Fig. 10 High-resolution electron micrograph of the Al-Li-Cu quasicrystal (a) and electron diffraction pattern (b), taken with the incident beam parallel to the fivefold symmetry axis. (c) is a Fourier transformed pattern of the image. White arrows indicate the displacement of arrays of the decagon contrasts.

of a ring-shaped channel and ten channels, like the case of the icosahedral atom cluster (Fig. 2(b)), though there are the other ten channels outside the ten channels. Considering that the outer ten channels are always overlapped with those in the other atom clusters in an actual structure, the image contrast for the triacontahedral atom cluster is expected to be similar to that for the above icosahedral atom cluster.

Figure 10 is a high-resolution electron micrograph of Al-Li-Cu taken with the incident beam parallel to the fivefold symmetry axis. In the image, we can see the decagon contrasts similar to those observed in Fig. 1. Since Al-Li-Cu is a stable quasicrystal and has less effect of multiple scattering due to a smaller average atomic number, the observed image shows homogeneous contrast with few defects in a wide region. In the image, we can see a long-range correlation of the decagon contrasts; *i.e.* the decagon contrasts are arrayed along the straight lines parallel to the fivefold directions and with three types of distances related with the golden ratio, τ , as indicated by small arrows. The characteristic feature of the arrangement of the decagon contrasts in the image is in good agreement with that of the twelvefold positions; the straight arrays of the twelvefold positions and the distances related with τ in Fig. 6. So we can say that the structure of an ideal icosahedral quasicrystal is that the

atom clusters are placed at the twelvefold positions. The twelvefold positions are the special sites that the atom clusters can be packed most densely with the three types of connections and with icosahedral symmetry. Break of icosahedral symmetry in the arrangement of the atom clusters produces the phason strains which are often formed in the quasicrystals. In the image, we can see few phason strains which give rise to displacements of the arrays of the decagon contrasts, indicated by white arrows. The phason strains which were observed as displacements of lattice fringes in the lattice images of the previous work⁽²⁾ are interpreted by the displacements of the arrays of atom clusters from the straight lines in the projected arrangement.

IV. Conclusion

High-resolution structure images taken with an electron microscope having a resolution of 0.17 nm proposed the structure model to understand an outlined structure of quasicrystals. In the model, the atom clusters with icosahedral symmetry, which have various atomic arrangements depending on quasicrystalline alloys, are packed most densely with icosahedral symmetry. The image calculation demonstrated that high-resolution images of quasicrystals taken from thinner regions than about

10 nm, using an electron microscope having a resolution of 0.17 nm, faithfully reproduces projected potential.

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