Atomic Structure of a Decagonal Al-Co-Ni Quasicrystal

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A structure refinement of the decagonal quasicrystal $Al_{70}Co_{20}Ni_{10}$ with the 5D superspace group $P10/mmm$ was made on the basis of single-crystal x-ray-diffraction data. The structure is a layer structure which consists of two kinds of layers stacked along the c (tenfold) axis with an interval of $c/2$ ($c = 4.08$ Å). The structure has a local atom arrangement similar to that of monoclinic $Al_{13}Fe_4$ but includes stacking disorder of the layers. The model explains well the diffraction intensity, chemical composition, and density. There exists another model with $P10_5mc$ which gives a diffraction intensity similar to that of the above model except for the extinct reflections due to the extinction rule of the superspace group.

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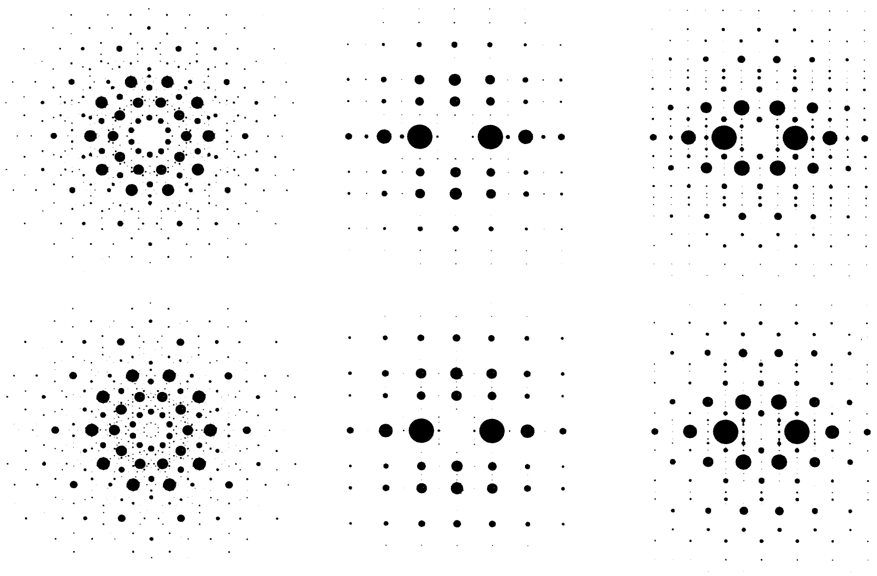
The structures of the decagonal quasicrystals have been extensively studied by electron microscopy, powder x-ray and neutron diffraction, and scanning tunneling microscopy, but the atomic structure is not clear yet.[1-7] Recent progress in the formation of large quasicrystals enables us to investigate quasicrystal structures by means of the single-crystal diffraction method. Several stable quasicrystals have a large enough crystal size for single-crystal x-ray diffraction.[8,9] The method was first applied to the structure refinement of the icosahedral Al-Cu-Li quasicrystal.[9] In the present work, it is applied to the determination of the decagonal Al-Co-Ni structure with an $\cong$4-Å period along the c axis.[7,8] This will be one of the simplest structures among the decagonal quasicrystals with periods of about 4, 8, 12, and 16 Å found in Al-Mn, Al-Fe, Al-Co-Ni, and Al-Cu-T (T denotes transition metal Mn, Fe, Co, or Ni) because it has the shortest period. The periods being multiples of 4 Å suggests that the basic unit has $c \cong 4$ Å and the others are modulated structures or polytypes. Therefore it is important to determine the basic structure with an 4-Å period in order to clarify such a series of structures.

The quasicrystal structure is represented by a three-dimensional section of an appropriate higher-dimensional crystal (the section method). This method has been successfully applied to the icosahedral Al-Mn quasicrystal in order to determine the atomic structure and its efficiency has been shown.[10] It is also applicable to the decagonal quasicrystal. The decagonal quasicrystal is then described as a crystal in five-dimensional space with the occupation domain extended to the two-dimensional internal (pseudo) space as shown by Yamamoto and Ishihara on the decagonal Al-Mn and Al-Fe structures.[11] In their models, the T atoms are located on the vertex position of the Penrose pattern with an edge length of about 4.1 Å when the structure is projected along the c axis. These vertex models explain the observed systematic extinction rules and qualitative diffraction intensities of the electron diffraction. In order to obtain the atomic structure, the electron diffraction, however, does not give sufficient information. The purpose of the present work is to give the atomic structure of $Al_{70}Co_{20}Ni_{10}$ based on single-crystal x-ray-diffraction data.

The decagonal quasicrystal $Al_{70}Co_{20}Ni_{10}$ is thermodynamically stable[8] and we could grow millimeter-sized columnar crystals with the column axis parallel to the periodic direction by a slow solidification from the melt. Single-crystal x-ray-diffraction measurements were carried out on a four-circle diffractometer equipped with Mo $K\alpha$ radiation. The sample is about 0.2 mm in diameter and 3 mm in length. The period is determined to be about 4 Å from the oscillation photograph and refined to be 4.08 Å by the diffractometer data. When we employ the coordinate system used in Ref. 11, the lattice constant a_0 is 4.45 Å but, as is well known, this has an ambiguity of a factor of $\tau = (1+\sqrt{5})/2$. We use $a = \tau^{-1} a_0$ ($=2.75$ Å) instead of a_0 in this paper for convenience. More than 1400 independent reflections were obtained from the $\frac{1}{40}$ region in reciprocal space. The three reciprocal planes shown in Fig. 1 are the diffraction pattern perpendicular to the c axis with indices $h_1h_2h_3h_40$ (zero layer), and the P ($h_1h_2\bar{h}_2\bar{h}_1h_5$) and D ($h_1h_2h_2h_1h_5$) patterns.[2] (The latter two include the tenfold axis.) The P pattern shows the violation of the extinction rule, $h_5 = 2n+1$, characteristic of the superspace groups $P10_5/mmc$ and $P10_5mc$. This indicates that the superspace group is centrosymmetric $P10/mmm$ or its subgroup $P10mm$. The violation of the rule is also confirmed by electron diffraction. Sometimes very weak streaks normal to the c axis are observed in electron-diffraction patterns, implying stacking disorder. If this is



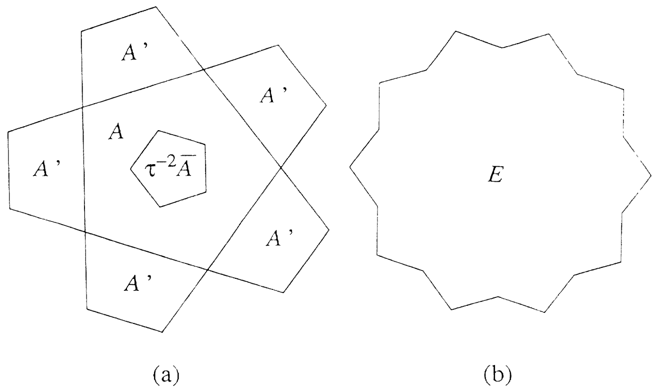
(a) (b) (c)

FIG. 1. The observed (upper) and calculated (lower) diffraction patterns. (a) The zeroth layer normal to the c axis. (b) The P pattern. (c) The D pattern. The tenfold axis is directed horizontally in (b) and (c). The radius of each spot is proportional to the structure factor.

taken into account, the real period becomes 8 Å, but it is neglected in the following. On the other hand, the P pattern reported by Tsai, Inoue, and Masumoto[8] clearly shows the systematic extinction rule consistent with $P10_5/mmc$. This suggests that there are at least two types of Al-Co-Ni quasicrystal structures with $c \cong 4$ Å. The latter case will be briefly discussed later.

An initial structure model can be deduced from the Patterson map and the consideration of the Penrose pattern. The Patterson map shows that the structure consists of two equidistant layers normal to the c axis and these layers are closely related to the Penrose pattern with edge length of $2a/\sqrt{5} = 2.46$ Å: The map drawn with only zero-layer reflections suggests that most atoms are projected onto the vertices of the Penrose pattern by the projection along the c axis. Such a pattern is obtained from the decagonal lattice with lattice constant a. The vertices are classified into four groups by the positions of atoms in the superspace. We call these A, B, C, and D atoms (refer to Refs. 11 and 12 for details). These come from the pentagonal occupation domains A, B, C, and D placed at $(i,i,i,i,0)/5$ $(i=1,2,3,4)$ of the five-dimensional decagonal lattice. It is noted that the A and C or the B and D atoms have a nearest-neighbor distance (corresponding to the short face diagonal of the skinny rhombus) of $2\tau^{-1}a/\sqrt{5} \cong 1.5$ Å. This is too short for the Al-T or Al-Al distance. Therefore the A and C or the B and D atoms must be on different layers. Then the nearest A-C and B-D distances become 2.5 Å since the layer interval is $c/2 = 2.04$ Å. On the other hand, the nearest A-B or C-D distance is $2a/\sqrt{5} \cong 2.5$ Å. This allows us to place the A and B atoms or the A and D atoms on the same layer. Thus we obtain $(A+B)$ $(C+D)$ or $(A+D)$ $(B+C)$ stacking along the c axis, where $(A+B)$ means the layer consisting of the A and B atoms. Since the occupation domains A and B are transformed by the tenfold rotation into D and C, these give the superspace groups of noncentrosymmetric $P10_5mc$ and centrosymmetric $P10/mmm$. We employ the latter as the basic structure for the decagonal $Al_{70}Co_{20}Ni_{10}$ because the violation of the extinction rule due to $P10_5mc$ is observed in the present case as mentioned before. In this model, the A and B atoms placed at $(\frac{1}{5},\frac{1}{5},\frac{1}{5},\frac{1}{5},0)$ and $(\frac{2}{5},\frac{2}{5},\frac{2}{5},\frac{2}{5},\frac{1}{2})$ in the five-dimensional decagonal lattice are independent. The site symmetry of these sites is $5m$, so that the space-group symmetry generates another equivalent site for each one, at which the occupation domain D or C is located. The real structure is the modification of this structure as shown below.

When we consider the realistic atom arrangement of the quasicrystal, the crystal approximant plays an important role. For the decagonal quasicrystals, monoclinic $Al_{13}Fe_4$ seems to be a good crystal approximant.[13] This is related to the Penrose pattern with edge length of 2.5 Å and consists of four layers normal to the twofold axis. The cell dimensions, $a = 12.48$, $b = 8.08$, $c = 15.49$ Å, and $\beta = 107°$, show that the twofold (b) axis corresponds to the tenfold axis.[7] The structure is related to a fictitious quasicrystal structure with $(A+A'+E+\tau^{-2}\bar{D})$ $(B+C)$ $(D+D'+E+\tau^{-2}\bar{A})$ $(B+C)$ stacking, where $\tau^{-2}\bar{A}$ and $\tau^{-2}\bar{D}$ are atoms coming from the central part of the A and D domains, A' and D' are atoms from the trapezoids around the A and D domains [Fig. 2(a)], and E atoms are generated with the occupation domain shown in Fig. 2(b). The A, B, C, and D domains are



(a) (b)

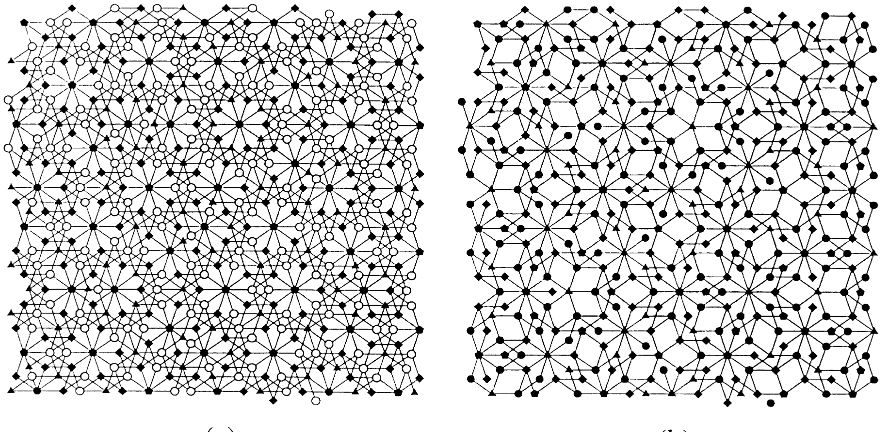
FIG. 2. (a) The occupation domains for the A' atoms (outer five trapezoids), the A atoms (large pentagon), and the $\tau^{-2}\bar{A}$ atoms (small pentagon). (b) The occupation domain for the E atoms. The occupation domain for the C atoms is the regular pentagon τ times larger than A. The occupation domains for B and D (D') atoms are obtained from those of C and A (A') atoms by the inversion operation.

placed at $(i,i,i,z)/5$ ($i=1,2,3,4$), while E is at $(0,0,0,z)$. In $Al_{13}Fe_4$, Fe positions are derived from $\tau^{-2}\bar{B}$, $\tau^{-2}\bar{C}$ (τ^{-2}-times-smaller subdomain in B denoted by ⟨22222⟩, ⟨2211211⟩, ⟨222211⟩ and their conjugates in Ref. 14), and E. Al positions are obtained from the remaining parts of the occupation domains.

The fictitious quasicrystal has the superspace group $P10_5/mmc$ and gives a reasonable point density of 0.0680 Å^{-3}, which is nearly equal to the observed point density 0.0681 Å^{-3} and that of $Al_{13}Fe_4$, 0.0678 Å^{-3}. Its chemical composition is $Al_{71}Fe_{29}$. This structure is, however, not directly related to the decagonal phase of Al-Co-Ni because of the doubling of the c axis. In order to obtain the structure with $c \cong 4$ Å, we consider the stacking disorder. In the above model, the $(A+A'+E+\tau^{-2}\bar{D})$ and $(D+D'+E+\tau^{-2}\bar{A})$ layers appear alternately with the insertion of the $(B+C)$ layer between them. If several $(A+A'+E+\tau^{-2}\bar{D})$ $(B+C)$ $(A+A'+E+\tau^{-2}\bar{D})$ $(B+C)$ or $(D+D'+E+\tau^{-2}\bar{A})$ $(B+C)$ $(D+D'+E+\tau^{-2}\bar{A})$ $(B+C)$ layers are inserted randomly within the coherence length of the x ray, we will observe a structure represented as $(A+A'+D+D'+2E+\tau^{-2}\bar{A}+\tau^{-2}\bar{D})/2$ $(B+C)$, where the $\frac{1}{2}$ means the layer with the occupation probability of $\frac{1}{2}$. This model has the superspace group $P10/mmm$.

In the decagonal quasicrystal $Al_{70}Co_{20}Ni_{10}$, we assume that Co and Ni randomly occupy the Fe sites in the above model because it is difficult to distinguish Co and Ni by x-ray diffraction. The diffraction intensity is calculated by using the structure-factor formula in Ref. 11. Since it is not expected that the model without relaxation of the atom from the ideal position retrieves weak reflection intensity accurately, the refinement of the overall isotropic temperature factor B was made by using strong 41 reflections. The R factor was 0.110 with $B=1.1$ Å^2. As is clear from Fig. 1, the model explains the prominent diffraction intensities very well.

The structure projected along the c axis is given in Fig. 3(a). The characteristic feature of the structure is that there are many tenfold atom clusters, of which five atoms forming the regular pentagon are on the same layer as the cluster center and the other five are on a different layer. The cluster centers are classified into two groups. The first group consists of the $\tau^{-2}\bar{A}$ and $\tau^{-2}\bar{D}$ atoms [solid circles in Fig. 3(a)], while the second one consists of the $\tau^{-2}\bar{B}$ and $\tau^{-2}\bar{C}$ atoms (pentagons). For the first group, the nearest-neighbor atoms are transition metals (triangles). Around the cluster center there are five other Al atoms in the upper and lower layers (squares). Consequently, there exist columnar atom chains along the c axis. On the other hand, for the second group, there are five nearest Al atoms (squares) on the same layer and five other Al atoms in either the



(a) (b)

FIG. 3. (a) The structure of $Al_{70}(Co,Ni)_{30}$ projected along the c axis. (b) The model with the symmetry $P10_5mc$. Circles and triangles represent the Al and transition-metal positions at $z=0$ and squares and pentagons are those at $z=\frac{1}{2}$. Open and full symbols mean half-filled and fully occupied sites.

upper or lower layer (open circles). The nearest-neighbor distance is $2a/\sqrt{5} \cong 2.5$ Å. (It should be noted that the shortest distance between open circles corresponds to the nearest A-D' or A'-D distance and therefore the corresponding atoms are at different layers in the real crystal as is clear from the fictitious quasicrystal $Al_{71}Fe_{29}$ mentioned above.) Such a planar pentagonal atom cluster is found in monoclinic $Al_{13}Fe_4$. The characteristic feature of the model is that there are no edge center atoms, in contrast to icosahedral quasicrystals.

We consider another model for the case of $P10_5mc$. This is described as $(A+A'+B)$ $(D+D'+C)$, in which the T occupies the A, D, $\tau^{-2}\bar{B}$, and $\tau^{-2}\bar{C}$ sites. The remaining sites are occupied by Al [Fig. 3(b)]. The characteristic feature of the structure is that there are many atom clusters forming the regular pentagon. The cluster centers are occupied by T atoms (triangles and pentagons) and their five nearest neighbors are occupied by Al or T. There are ten (Al or T) atoms forming the columnar atom chain as in the above model. The chains are located only around the $\tau^{-2}\bar{B}$ and $\tau^{-2}\bar{C}$ atoms in contrast to the above case. The model gives almost the same point density and chemical composition (0.0689 Å^{-3} and $Al_{72}T_{28}$) and slightly larger R factor ($R = 0.134$). As stated before, the electron-diffraction patterns of an Al-Co-Ni quasicrystal reported by Tsai, Inoue, and Masumoto are consistent with this model. It should be noted that T atoms are on the vertex position with an edge length of 4.1 Å as in the previous model for Al-Mn or Al-Fe.

The structure of the decagonal quasicrystal $Al_{70}Co_{20}Ni_{10}$ is closely related to that of monoclinic $Al_{13}Fe_4$ and a decorated Penrose pattern with edge length of about 2.5 Å as stated above. The result implies that a static atom displacement of about 0.1 Å from the ideal position can be expected from the temperature factor. The displacement is smaller than that of icosahedral Al-Mn-Si.[10] No effect of the random phason was detected by the refinement of an additional temperature factor $\exp\{-B'(\mathbf{q}^i)^2/4\}$.[10] These suggest that decagonal $Al_{70}Co_{20}Ni_{10}$ is a quasicrystal with higher perfectness compared with icosahedral Al-Mn-Si. This is quite natural because decagonal $Al_{70}Co_{20}Ni_{10}$ is a stable phase and can be obtained by slow solidification. This will release the random-phason strain. On the other hand, icosahedral Al-Mn-Si needs a quick solidification. The linear phason distortion may, however, exist because the long-wavelength phason relaxes very slowly,[15,16] but it is not estimated in the present study because the powder-diffraction method is rather sensitive to the linear phason. The present study has clarified the existence of atom clusters in the decagonal phase as in the icosahedral one. This may be related to the matching rules or the growth ability of quasicrystals.[16] Further studies on this point are expected.

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