Five-Dimensional Superstructure Model of Decagonal Al-Ni-Co Quasicrystals

Akiji Yamamoto[1] and Steffen Weber[1,2]
[1]*National Institute for Research in Inorganic Materials, Tsukuba, 305, Japan*
[2]*Institute of Applied Physics, University of Tsukuba, Tsukuba, 305, Japan*
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The superstructure in decagonal Al-Ni-Co has a unit cell in 5D space 5 times larger than that of the normal structure. A 3D model of this structure proposed recently [K. Hiraga, W. Sun, and A. Yamamoto, Mater. Trans. JIM **35**, 657 (1994)] has a 20 Å cluster on each vertex of the Penrose pattern with an edge length of 20 Å. This Letter shows a corresponding 5D model. There are 20 occupation domains in a unit cell, two of which are independent under the symmetry of $P10_5/mcm(10^71mm)$. This 5D model shows diffraction patterns similar to those of the superstructure. The phase transition from the normal phase to the superstructure occurs by a phason jump. [S0031-9007(97)03300-0]

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Quasicrystals show diffraction spots with noncrystallographic symmetry. The diffraction patterns are indexable with n vectors ($n \geq 5$) and n "Miller indices." They are described as crystals in n-dimensional space as are the modulated structures and their diffraction intensities can be calculated accurately by using such n-dimensional crystals [1]. In particular, quasicrystals with decagonal and icosahedral diffraction symmetries (decagonal and icosahedral quasicrystals) are described as five-dimensional (5D) and six-dimensional (6D) crystals. There exist several quasicrystals with different lattice constants, some of which can be considered as the superstructure of the others.

Since a superstructure in quasicrystals has been discovered in icosahedral Al-Pd-Mn [2], several other superstructures have been found in icosahedral and decagonal quasicrystals [3–6]. For the icosahedral case, their 6D models have been proposed [7,8]. On the other hand, there is no 5D model for the decagonal case. The first superstructure in a decagonal phase was found in decagonal Al-Ni-Co (d-Al-Ni-Co) quasicrystals [5]. This has a unit cell volume 5 times larger than that of the normal phase [9]. We proposed a model for this superstructure [10] based on high resolution transmission electron microscopy (HRTEM) images, where the clusters are arranged at the vertices of a Penrose pattern with edges of about 20 Å (3D model). This model is based on the facts that 20 Å clusters in the normal phase of d-Al-Ni-Co are located at the vertices of the pentagonal Penrose pattern, while those of the superstructure phase are on the vertices of the rhombic Penrose pattern with the same edge length and the latter pattern is a superstructure of the former [9–12]. In order to confirm the validity of the model, however, it is necessary to calculate the diffraction intensities including the satellite reflections. This requires a 5D model, which has not been proposed yet. So far, only the average structure has been analyzed based on single crystal x-ray data [13]. In this Letter, we show a corresponding 5D model of such a superstructure and discuss the phase transition between the normal and superstructure phases.

As is well known the unit cell of the superstructure is different from that of the normal phase and the external component of the unit vectors of the lattice is rotated by $\pi/10$ from the corresponding one for the normal phase [5] and the lattice constant a is larger by the factor $2\cos\pi/10 = 1.902\,11$. Since $a_0 = 2.745$ Å, $c_0 = 4.081$ Å for the normal phase (or average structure) [13], a and c are 5.221 and 4.081 Å. (We use the coordinate system used in a previous paper [12].) The unit vectors of the decagonal lattice are given by $\mathbf{d}_j = (2a/\sqrt{5})[(c_j - 1)\mathbf{a}_1 + s_j\mathbf{a}_2 + (c_{2j} - 1)\mathbf{a}_3 + s_{2j}\mathbf{a}_4]$ $(j = 1, 2, 3, 4)$, $\mathbf{d}_5 = c\mathbf{a}_5$ and their reciprocal vectors are $\mathbf{d}_j^* = (a^*/\sqrt{5})[c_j\mathbf{a}_1 + s_j\mathbf{a}_2 + c_{2j}\mathbf{a}_3 + s_{2j}\mathbf{a}_4]$ $(j = 1, 2, 3, 4)$, $\mathbf{d}_5^* = c^*\mathbf{a}_5$, where $a^* = 1/a$ and $c^* = 1/c$ are the lattice constants of the reciprocal lattice. The vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_5$ are the unit vectors in the external space while $\mathbf{a}_3$ and $\mathbf{a}_4$ represent those of the internal space. There exist planes including the c^* axis on which reflections are extinct in both phases. They are at the same positions in both the superstructure and normal phases. The former gives a reflection condition $h_5 = 2n$ for $h_1h_2h_2h_1h_5$ while for the latter $h_5 = 2n$ for $h_1h_2\bar{h}_2\bar{h}_1h_5$, because of the rotation of the unit vectors mentioned above. The reflection conditions lead to the space group $P10_5/mcm(10^71mm)$ for the superstructure and $P10_5/mmc(10^71mm)$ for the normal phase. (These two are inequivalent [14].) Here we use a new symbol which is the combination of symbols in the external and internal space similar to a superspace group symbol for modulated structures [15] in order to show the action of the symmetry operators in the external and internal spaces. For example, the tenfold rotation $10_5(10^7)$ indicates that the tenfold screw axis in the external space is combined with a $7\pi/5$ rotation in the internal space, while $m(1)$ shows the mirror plane normal to the c axis, with the identity operation in the internal space.

In cluster models, we consider occupation domains which generate cluster centers [16,17]. Since the cluster centers form the Penrose pattern [9], they are generated by

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four pentagons. In order to define the pentagons, we introduce five vectors $\mathbf{e}_j = (2a/\sqrt{5})(c_{2j}\mathbf{a}_3 + s_{2j}\mathbf{a}_4)$ $(j = 1, 2, \ldots, 5)$. Then the Penrose pattern with an edge length of 20 Å is given by four pentagons with corner vectors $\pm\tau^{-3}\mathbf{e}_j$ (small pentagons) and $\mp\tau^{-2}\mathbf{e}_j$ (large pentagons) at $\pm(1, 1, 1, 1, 1.25)/5$ and $\pm(2, 2, 2, 2, 1.25)/5$, because $\tau^3 2a/\sqrt{5} \simeq 20$ Å.

The atom positions around a cluster center can be obtained from the occupation domain for the center by shifting it by the interatomic distance along the external space [16]. Such positions have a lower site symmetry than the center. All atom positions around the center proposed by us [10] can be obtained from the occupation domains around 20 points in the 5D unit cell of the superstructure, which are equivalent to $\pm(i, i, i, i, 5z)_0/5$ $(i = 1, 2)$ in the normal phase. Since their site symmetry is $mm(1m)$ with order 4 and the point group of the structure is $10/mmm(10^7 1mm)$ (order 40), there are ten equivalent positions [related by $10_5(10^7)$]. Thus the number of independent sites is two. The two independent occupation domains located at $-(1, -2, 0, 2, 1.25)/5$ and $-(-2, 2, 1, 0, 1.25)/5$ are shown in Fig. 1. The coordinates of the normal phase x_{0i} $(i = 1, 2, \ldots, 5)$ are related with those of the superstructure by $x_{0i} = \sum_{j=1}^{5} S_{ij} x_j$ with the transformation matrix

$$S = \begin{bmatrix} 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ 1 & 1 & 2 & 1 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}. \qquad (1)$$

Therefore, their corresponding coordinates in the normal phase are $-(1, -4, 1, 1, 5z)_0/5$ and $-(-3, 2, 2, 2, 5z)_0/5$, which are translationally equivalent to $-(1, 1, 1, 1, 5z)_0/5$ and $-(2, 2, 2, 2, 5z)_0/5$ in the normal phase but inequivalent to them in the superstructure phase since in the latter, the occupation domains at $-(1, 1 \pm 5, 1, 1, 5z)_0/5$, $(-(2 \pm 5, 2, 2, 2, 5z)_0/5)$ and $-(1, 1, 1, 1, 5z)_0/5$, $(-(2, 2, 2, 2, 5z)_0/5)$ are the same in shape but different in orientation by a multiple of $2\pi/5$. It should be noted that the shape of the occupation domain is quite different from that of the Penrose pattern and has only a mirror plane $m(m)$ represented by m in Fig. 1. [The mirror plane normal to the c axis $m(1)$ does not give any restraint for the occupation domain.]

Each independent occupation domain consists of pentagons, most of which are overlapped with neighboring pentagons and has an irregular shape with the symmetry of $m(m)$. The large and small pentagons mentioned above are seen in Fig. 1(a). Triangles, trapezoids, pentagons, and hexagons with a concave part are obtained from small or large pentagons by removing the overlapped parts. Several outside pentagons are partially cut off in order to avoid unreasonably short interatomic distances. The resulting 5D model is quite different from 5D structures of known decagonal quasicrystals, where each large occupation domain has pentagonal symmetry $5m(5^2 m)$ [13,17,18]. It is however remarkable that the number of independent occupation domains is two and that the other domains are related to them by symmetry operations.

The atom arrangement in 3D space is obtained from a 5D model by taking a 3D section [19,20]. Figure 2 shows the view of the superstructure projected along the c axis (tenfold axis) given by the occupation domains in Fig. 1. It is clear from Fig. 2 that the structure consists of the clusters observed by HRTEM images [9] and the cluster centers of the decagonal clusters with the radius of 20 Å construct the (rhombic) Penrose pattern. In the

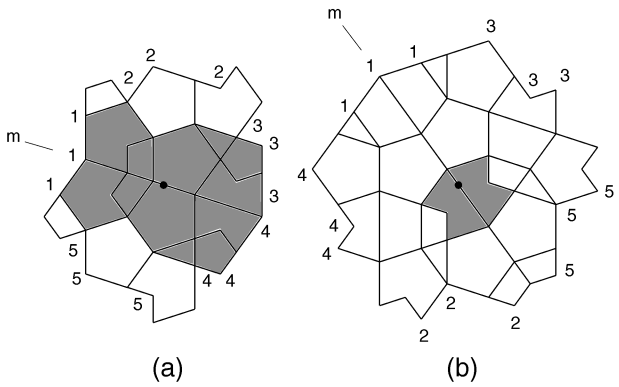

FIG. 1. Two independent large occupation domains D' and C' of the superstructure of d-Al-Ni-Co. The coordinates of dots near the domain centers are (a) $-(1, -2, 0, 2, 1.25)/5$ and (b) $-(-2, 2, 1, 0, 1.25)/5$. The shaded parts are occupied by transition metal and the other parts by Al. For the numbers, see text.

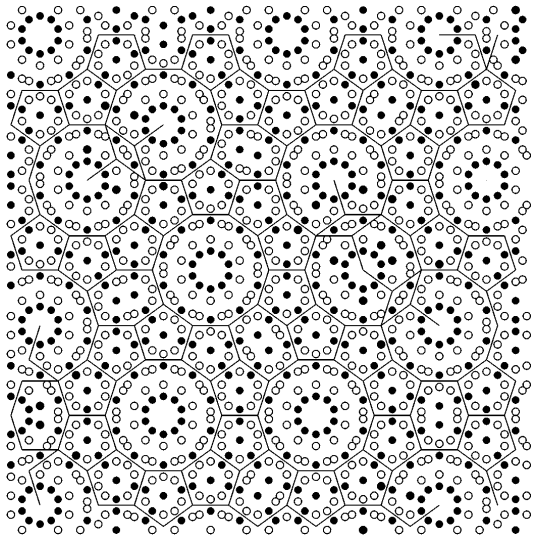

FIG. 2. Projection of the model given by Fig. 1 along the tenfold axis. Solid and open circles represent transition metal and Al atoms. The decagonal clusters are on the vertices of the (rhombic) Penrose pattern.

present model, the distribution of transition metal (TM) and Al atoms is slightly different from that of the previous model [10]. A perfect chemical ordering is considered in the former, while in the latter, many sites are statistically occupied by TM and Al atoms. Such chemical ordering is obtained if the shaded parts in Fig. 1 are occupied by TM and the other ones by Al.

In order to confirm the validity of the present model, we have to analyze the structure in detail with diffraction intensities including satellite reflections but this is out of the scope of this Letter. Instead, we show the diffraction pattern from the model, in order to demonstrate that it gives an essentially correct superstructure. (For the structure factor calculations, see [1].) Figure 3 represents an x-ray diffraction pattern of the model structure. It is noted that the structure shows an intensity distribution similar to that of the corresponding electron diffraction pattern of the superstructure. In particular, the appearance of the satellite reflections and their intensity distribution can be explained by the model. (Compare Fig. 3 with the electron diffraction pattern by Edagawa *et al.* [5].) Since the present 5D model is based on the previous 3D model, it explains HRTEM images [10]. When the two occupation domains in Fig. 1 are placed on the mirror plane $m(1)$ normal to the c axis ($z = -1/4$), the 5D model gives the space group mentioned above and explains the observed extinction rules.

As shown by Yamamoto [18], the model of the normal phase with the same cluster on the vertices of the pentagonal Penrose pattern is given by the occupation domains in Fig. 4. These are located at $-(i, i, i, i, 1.25)_0/5$ ($i = 1, 2$) in the unit cell of the normal phase. According to an x-ray analysis [13], the domain D at $-(1, 1, 1, 1, 1.25)_0/5$ is mainly occupied by TM and C at $-(2, 2, 2, 2, 1.25)_0/5$ by Al. If the central atoms of the five pentagons around each cluster and ten atoms in a decagon are TM atoms as in our previous model [10], the shaded part in C and ten decagons in D are occupied by TM. [See Fig. 6(a) in [10].] In this phase, there are five sites in the unit cell of the superstructure, which are translationally equivalent to it, since the unit cell of the superstructure is 5 times larger than that of the normal phase. This means that the occupation domains on these sites are the same in size and in orientation. On the other hand, these sites are related by fivefold rotation in the superstructure. Thus if the occupation domains have fivefold symmetry as in the normal phase, these are translationally equivalent. As is clear from this fact, the superstructure is caused from the breakdown of the translational symmetry, which comes from the loss of the pentagonal symmetry of the occupation domains. The difference in their size and shape generates different arrangements of the clusters. The point densities of both phases are however only a little different since the sum of the areas of two occupation domains is nearly equal. The point density is 0.0737 $Å^{-3}$ for the present model, 0.0731 and 0.0724 $Å^{-3}$, respectively, for the previous model of the normal phase [1] and for the model by Burkov [17]. These point densities are reasonable from the value of crystal approximants ($\simeq$0.073) [21].

Recently, it was clarified that a slight change in the shape and size of occupation domains changes the cluster arrangement of d-Al-Cu-Co drastically. This leads from the Burkov model with an intercluster distance of 12 Å to the model of the normal phase with the cluster distance of 20 Å mentioned above, changing the cluster size [17,18]. This structural change occurs by small jumps of atom positions similar to the phason jump. We also call it a phason jump, although such an atom flip is due neither to the linear phason nor to the random phason. It is also possible to explain the phase transition from the normal

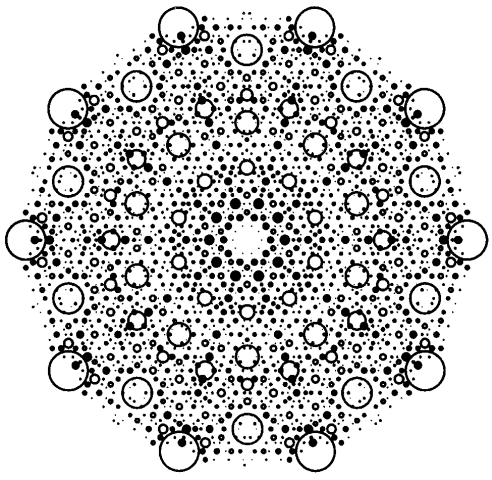

FIG. 3. Diffraction pattern of the superstructure of d-Al-Ni-Co. The radius of each reflection is proportional to the absolute value of the structure factor. Open and solid circles represent the main and satellite reflections.

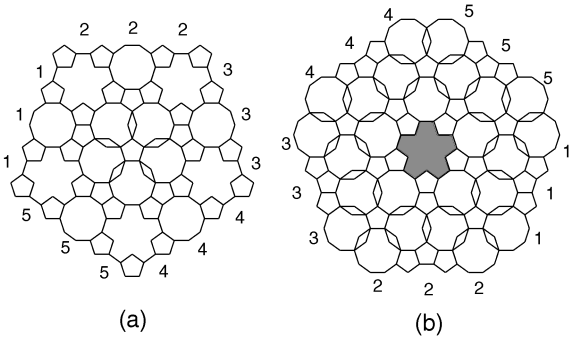

FIG. 4. The two independent large occupation domains D and C of the normal structure of d-Al-Ni-Co at (a) $-(1, 1, 1, 1, 1.25)_0/5$ and (b) $-(2, 2, 2, 2, 1.25)_0/5$. In this model, the 20 Å clusters are the same as those in Fig. 2 but they are on the vertices of the pentagonal Penrose pattern in contrast to Fig. 2. The shaded part generates central atoms in five pentagons around each cluster center. See Fig. 6(a) in [10].

phase to the superstructure phase with such a phason jump. When the 5D structure is projected onto the internal space, each occupation domain is surrounded by five occupation domains sharing their outer edges (contact condition). In the normal phase the occupation domain D [Fig. 4(a)] at $\mathbf{x}_1 = -(1, 1, 1, 1, 1.25)_0/5$ is surrounded by domain C [Fig. 4(b)] at $\mathbf{x}_2 = -(-3, 2, 2, -3, 1.25)_0/5$ and the other four positions equivalent to it by a fivefold rotation axis at $\mathbf{x}_1$ and the external component of $\mathbf{x}_2 - \mathbf{x}_1$ gives the interatomic distance $2\tau^{-2}a_0/\sqrt{5} \simeq 0.97$ Å . When these occupation domains are projected onto the internal space, the domains D and C share the outer edges denoted by 1 in Fig. 4. Thus the change of the occupation domain boundaries of central and surrounding domains keeping the contact condition unchanged leads to the phason jump of atoms. According to the x-ray analysis, the occupation domain D is mainly occupied by TM and domain C, by only Al [13]. This suggests that there exists some chemical disordering.

Similarly, in the superstructure there are five occupation domains C' in the contact condition surrounding the domain D' [Fig. 1(a)] when the 5D model is projected onto the internal space. They are obtained from Fig. 1(b) by rotating about an angle which is a multiple of $2\pi/5$ and translating to contact edges with the same numbers. Noting that the difference of the point densities of both phases is small, the domain D' in Fig. 1(a) is obtained from those in Fig. 4 by cutting several small parts from D and adding to domains C in the contact condition or vice versa. The domain in Fig. 1(b) is also obtained by a similar change of occupation domains. Therefore, the atom positions of the superstructure are deduced from those of the normal phase by a small phason jump. In a real structure, replacement of atoms may also be necessary in addition to the phason jump, in order to obtain the chemically ordered 20 Å clusters in a structure with different cluster arrangement. This implies that the migration (diffusion) of atoms may be necessary for such a phase transition [22]. It is, however, remarkable that the atom positions of the superstructure with a quite different cluster arrangement can be obtained by a small phason jump and the migration of atoms is only necessary to form chemically ordered clusters.

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