Superstructure and Color Symmetry in Quasicrystals

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(Received 18 February 1997)

The first modulated structure found in decagonal Al-Ni-Fe quasicrystals [M. Saito, M. Tanaka, A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. **31**, L112 (1992)] is a superstructure in five-dimensional space with a unit cell volume identical to that in the superstructure of decagonal Al-Ni-Co. Peculiar systematic extinction rules observed in the diffraction patterns can be explained by a color symmetry group $P_{2c}\overline{1}02m'(5mm')$ in five-dimensional space. A five-dimensional model is proposed, which can explain the electron diffraction patterns of decagonal Al-Ni-Fe. [S0031-9007(97)03643-0]

Since the first decagonal quasicrystal was discovered in Al-Mn alloys [1], a number of different decagonal diffraction patterns have been observed in several alloys [2–7]. Decagonal quasicrystals can be classified into several types with the period along the tenfold axis, which are multiples of $\simeq 4$ Å. In addition, there exist several kinds of superstructures in five-dimensional (5D) space [7]. The first found superstructure in a decagonal Al-Ni-Co (d-Al-Ni-Co) quasicrystal [4] has a 4 Å period and a unit cell volume 5 times larger than that of the normal phase [8], and coincides with the superstructure discussed by us [9]. We proposed 3D and 5D models for this superstructure [8,10] based on high resolution transmission electron microscopy (HRTEM) images, where the clusters are arranged at the vertices of a Penrose pattern with an edge length of about 20 Å. There exist other peculiar diffraction patterns, which were first found in d-Al-Ni-Fe [5]. These patterns indicate an 8 Å period along the tenfold axis.

The diffraction pattern in a plane perpendicular to the tenfold axis shows completely different intensity distributions in even and odd layers. In the even layers, the diffraction pattern is similar to that of the normal phase, while it is quite different in the odd layers and cannot be indexed by the reciprocal unit vectors for the normal phase. The diffraction spots are therefore considered to be the satellite reflections due to some kind of modulations [5]. The origin of the modulations, however, has been unknown. Recently, it was shown that melt-quenched d-Al-Cu-Co quasicrystals also give similar diffraction patterns [11]. The symmetry of the average structure for these superstructures has been determined to be $P\overline{1}0m2(5mm)$ by convergent-beam electron diffraction [5,11], whereby we use a symbol similar to that for four-dimensional superspace groups in order to express the action of the symmetry operator in the external and internal space [12]. The first part is the symmetry operation in the external space and the second (in parentheses) the corresponding operation in the internal space. A characteristic feature of these structures is that they consist of 20 Å clusters with pentagonal symmetry with the same orientation. The present paper shows that they have a special superstructure with the same lattice as the d-Al-Ni-Co superstructure found first, if a cell doubling along the c axis is neglected. In order to explain the peculiar diffraction patterns mentioned above, we discuss so-called color symmetry in quasicrystals. This suggests that the superstructure is due to the chemical ordering in the central part of the 20 Å clusters.

As is well known, a decagonal quasicrystal can be described as a periodic structure in five-dimensional (5D) space, and the unit cell of the superstructure in d-Al-Ni-Co is different from that of the normal phase. The external component of the unit vectors of the lattice is rotated by $\pi/10$ against the corresponding one for the normal phase [4,8], and the lattice constant a is larger by the factor of $2\cos\pi/10 = 1.90211$. In addition, the lattice constant c along the tenfold axis is doubled in the superstructure. Since $a_0 \simeq 2.7$ Å and $c_0 \simeq 4.1$ Å for the normal phase (average structure) [13], a and c are about 5.2 Å and 8.2 Å, respectively. The unit vectors of the decagonal lattice are given by [14] $\mathbf{d}_j = (2a/\sqrt{5})[(c_j - 1)\mathbf{a}_1 + s_j\mathbf{a}_2 + (c_{2j} - 1)\mathbf{a}_3 + s_{2j}\mathbf{a}_4]$ ($j = 1, 2, 3, 4$), $\mathbf{d}_5 = c\mathbf{a}_5 = \mathbf{c}$, and their reciprocal vectors are $\mathbf{d}_j^* = (a^*/\sqrt{5})[c_j\mathbf{a}_1 + s_j\mathbf{a}_2 + c_{2j}\mathbf{a}_3 + s_{2j}\mathbf{a}_4]$ ($j = 1, 2, 3, 4$), $\mathbf{d}_5^* = c^*\mathbf{a}_5 = \mathbf{c}^*$, 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. The diffraction vector $\mathbf{h} = \sum_{i=1}^{5} h_i\mathbf{d}_i^*$ is represented by the Miller indices $h_1h_2h_3h_4h_5$. The unit vectors in the reciprocal space of the normal phase $\mathbf{d}_{0i}^*$ ($i \le 5$) are related with $\mathbf{d}_i^*$ by $\mathbf{d}_{0i}^* = \sum_{j=1}^{5} S_{ij}\mathbf{d}_j^*$, where the determinant of the transformation matrix S is 5 [4,9]. In the usual sense, reflections on the layer with h_5 odd are satellite reflections. In the present paper, however, only reflections which are not indexable with $\mathbf{d}_{0j}^*$ ($j = 1, 2, 3, 4$) are called satellite reflections independent of h_5. As shown in a previous paper, the main and satellite reflections are then classified by $\sum_{i=1}^{4} h_i$ [9]. If this is 0 (mod 5), it is a main reflection, otherwise, a satellite reflection.

As mentioned above, the average structure has a 4 Å period, and its symmetry is $P\overline{10}m2(5mm)$, which has no reflection condition. The superstructure with the 8 Å period is considered to have a point group isomorphic to that of the average structure $\overline{10}m2(5mm)$. If the rotation of the unit vectors is taken into account and no extinction rule exists, the possible space group of the superstructure is $P\overline{10}2m(5mm)$. [This is not equivalent to $P\overline{10}m2(5mm)$ [15].] There exists, however, a reflection condition $h_5 = 2n$ for $h_1h_2\overline{h}_2\overline{h}_1h_5$, implying the presence of the c-glide plane, though it is sometimes broken by weak diffuse streaks. In addition, the even layers show only main reflections. No space group is, however, consistent with such reflection conditions.

In order to explain such reflection conditions, we can use the color symmetry, which is usually used to describe the symmetry of magnetic materials [16]. In this case, so-called antisymmetry operators (ASOs) are introduced in addition to the (usual) symmetry operators (SOs). These are the combination of the SO and the spin inversion. They are known to be equivalent to a black and white or color group. In the color group, the ASO is the combination of the SO and a color change operation. In the present case, we consider two sites, which are related with some SO and occupied by transition metal (TM) and Al atoms. Such atoms are called color atoms. Then the change of colors corresponds to the spin flip in magnetic materials. On the other hand, corresponding to the nonmagnetic atoms, we consider colorless (gray) atoms.

For example, consider a case where one site is occupied by TM and the other by Al and their positions are related to each other by a SO. Then they are color atoms, which are represented by black and white colors. The color atom and its position in one site are obtained from those in the other by the ASO, while atoms with the same color are related by a SO. For colorless atoms, the ASO acts just as the SO, since the color change operation does not affect the colorless atoms. The SOs give the conventional reflection conditions, while the ASOs sometimes give peculiar reflection conditions, as shown below. We represent the ASO with a prime.

The zero-layer diffraction pattern in d-Al-Ni-Fe is similar to that of d-Al-Cu-Co or the normal phase of d-Al-Ni-Co and shows no satellite reflection, as mentioned above. This implies that the structure projected along the tenfold axis has a four-dimensional unit cell equal to that of the projected normal structure. We take a structure similar to a previous model for d-Al-Cu-Co [10], in which there is 20 Å cluster at each vertex of a Penrose pentagon pattern with an edge length of 20 Å. In d-Al-Cu-Co, there are four large occupation domains at $\pm(i, i, i, i, 5z')_0/5$ ($i = 1, 2, z' = 1/4$). (For the method deriving such a cluster model from a 5D model, refer to Ref. [17].)

In order to explain additional reflections, which are assumed to be the satellite reflections of the superstructure, we consider a case where the antisymmetric translation

gives rise to a doubled c axis. The color space group is $P_{2c}\overline{10}2m'(5mm')$. The prefix P_{2c} means that there exists an antisymmetric centering translation $\{E \,|\, \mathbf{c}/2\}'$, where a prime means an ASO [16]. This group is generated by $\{C_5 \,|\, 0\}$, $\{\sigma_z \,|\, \mathbf{c}/4\}$, $\{\sigma' \,|\, 0\}'$, $\{E \,|\, \mathbf{c}/2\}'$, and lattice translations of the 5D decagonal lattice. Then there exist 40 occupation domains in the unit cell, all of which are equivalent to $\pm(i, i, i, i, 5z')_0/5$ ($i = 1, 2$) in the normal phase. The coordinates of the normal phase are given by $x_{0i} = \sum_{j=1}^{5} S_{ij}x_j$.

Since the site symmetry of all such sites is either $mm'(1m')$ or $m'm'(1'm')$ with order 4 and the point group of the structure is $\overline{10}2m'(5mm')$ (order 20), there are five equivalent positions [related by $5(5^2)$]. Thus the number of independent sites is four. We take the independent occupation domains located at $\pm(0, 2, -1, 1, 5z)/5$ and $\pm(0, 4, -2, 2, 5z)/5$ with $z = 1/8$. Their corresponding coordinates in the normal phase are $\pm(1, 1, 1, 1, 5z')_0/5$ and $\pm(2, 2, 2, 2, 5z')_0/5$ ($z' = 1/4$). Consider their equivalent positions $\pm(-3, -1, 1, -2, 5z)/5$ and $\pm(-6, -2, 2, -4, 5z)/5$ related with $5(5^2)$. Their coordinates $\pm(-4, 1, -4, 1, 5z')_0/5$ and $\pm(-8, 2, -8, 2, 5z')_0/5$ in the normal phase are translationally equivalent to $\pm(1, 1, 1, 1, 5z')_0/5$ and $\pm(2, 2, 2, 2, 5z')_0/5$. This consideration can show that atom positions related by $5(5^2)$ in the superstructure are translationally equivalent to each other in the normal phase. This implies that if occupation domains of these sites have fivefold symmetry, they are translationally equivalent, and satellite reflections disappear.

The color space group $P_{2c}\overline{10}2m'(5mm')$ includes two mirror planes $m(1)$ normal to the c axis at $\mathbf{c}/8$, $5\mathbf{c}/8$, and two antisymmetric mirror planes $m'(1')$ at $3\mathbf{c}/8$, $7\mathbf{c}/8$ which are perpendicular to the internal space and the c axis. In the present case, all the occupation domains are either on the mirror plane or on the antisymmetric mirror plane.

The shape of the occupation domains is restricted by the site symmetry. In the present case, this allows low-symmetric occupation domains as in d-Al-Ni-Co [18]. However, the diffraction patterns imply that an additional restriction has to be imposed, since the even-layer diffraction patterns show no satellite reflections. This means that the average of two occupation domains related by $\{E \,|\, \mathbf{c}/2\}'$ has a fivefold symmetry. For this reason, we consider the occupation domains to be the same as those of d-Al-Cu-Co, which have fivefold symmetry [10]. The independent occupation domains are shown in Fig. 1.

Each independent occupation domain consists of decagons and pentagons, most of which are overlapped with neighboring decagons, and has a shape with the symmetry of $5m(5^2m)$. Small domains can be occupied by different atoms, so that their weight can generally be different. In order to obtain satellite reflections, the atom distribution (weight) in the domain has to destroy the fivefold symmetry. This is realized by color atoms because the $m'(m')$ relate one-half of the occupation
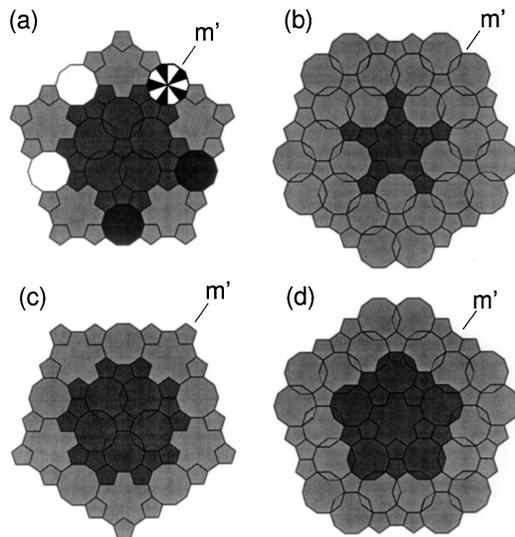
FIG. 1. Four independent large occupation domains of the superstructure of d-Al-Ni-Fe. Light and dark gray represent colorless Al and TM, atoms, respectively, while white and black stand for colored Al and TM, respectively. The domains A and D are at $\pm(0, 2, -1, 1, 5z)/5$, (a), (c), and B and C are at $\pm(0, 4, -2, 2, 5z)/5$, (b), (d), with $z = 1/8$. m' means an antisymmetric mirror plane.

FIG. 2. Projected structure of the two layers in the model given by Fig. 1 ($0 < z < 0.5$). Solid and open circles represent transition metal and Al atoms. The decagonal clusters are on the vertices of a Penrose pentagon pattern.

domain to the other half. In Fig. 1, light gray and dark gray represent colorless Al and TM atoms, respectively, while white and black stand for colored ones. It should be noted that the ASO sometimes inhibits the color atom. In the present case, the occupation domains at $3\mathbf{c}/8$ and $7\mathbf{c}/8$ [Figs. 1(c) and 1(d)] are on the antisymmetric mirror plane $m'(1')$. Therefore they have to be gray atoms. A possible atom distribution is shown in Fig. 1. In the present model, the domain A is partially occupied by color atoms. On the other hand, there is no color atom in domains B, C, and D. The color atoms in A' at $5\mathbf{c}/8$ are obtained from those in A by $\{E \mid \mathbf{c}/2\}'$, so that black and white are interchanged in A'.

The atom arrangement in 3D space is obtained from a 5D model by taking a 3D section [17]. Figure 2 shows the projection of the lower half (two layers) along the c axis (tenfold axis), which is given by the occupation domains in Fig. 1. The size of the cluster is $\simeq 20$ Å and the cluster centers are on the vertices of a Penrose pentagon pattern with the edge length of 20 Å. It is noted that there are two clusters (denoted by 1 and 2), without and with transition metals in the first neighbor positions. The upper two layers have a similar structure, but the cluster 1 is stacked on 2 and 2 on 1, since the first neighbor atoms are color atoms and these two structures are related by the antisymmetric centering translation $\{E \mid \mathbf{c}/2\}'$. Therefore it is clear that the total projection gives the same pentagonal clusters in the same orientation as seen in HRTEM images [11]. This ensures that the zero-layer diffraction patterns give no satellite reflections. One cluster column is shifted

relative to the other by $\mathbf{c}/2$. This shift gives the satellite reflections in the odd layers.

In order to demonstrate that this model gives an essentially correct superstructure, we calculate the diffraction patterns. (For the structure factor calculations, see [17].) Figure 3 represents x-ray diffraction patterns of the model structure. It is noted that Fig. 3(c) shows a characteristic diffraction pattern including satellite reflections observed in the corresponding electron diffraction pattern
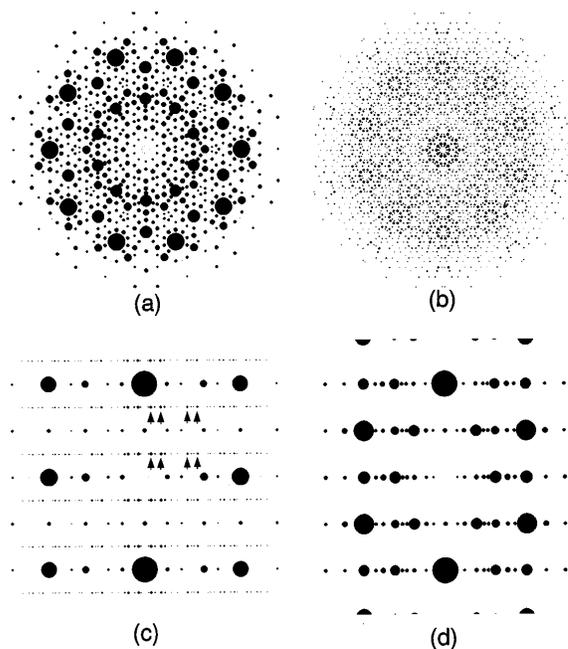
FIG. 3. Diffraction patterns of the superstructure of d-Al-Ni-Fe. (a) $h_1 h_2 h_3 h_4 0$ plane. (b) $h_1 h_2 h_3 h_4 1$ plane. (c) $h_1 h_2 h_2 h_1 h_5$ plane. (d) $h_1 h_2 \overline{h}_2 \overline{h}_1 h_5$ plane. The radius is proportional to the square root of the structure factor.

of d-Al-Ni-Fe. The strong reflections in the odd layers indicated by arrows were considered to be satellite reflections due to some kind of modulations [5]. However, they seem to be satellite reflections of the superstructure. Such satellite reflections have also been observed in melt-quenched d-Al-Co, d-Al-Co-Ni, and d-Al-Cu-Co [11,19], indicating that they have a similar superstructure. In particular it has been shown recently that a precession photograph of the first layer of d-Al$_{72}$Co$_{16}$Ni$_{12}$ shows a pattern similar to Fig. 3(b), supporting the present model [20].

The structure factor of the quasicrystals is given by the summation of the structure factor for each occupation domain $\exp(2\pi i \sum_{i=1}^{5} h_i x_i)F'(\mathbf{h})$. For convenience, we classify the contribution of the color atoms to the structure factor into two parts: the contribution from the colorless part $F(\mathbf{h})$ and that from the color part $\Delta F(\mathbf{h})$, as for the nonmagnetic scattering and magnetic scattering in magnetic materials. Then the former is the contribution of the occupation domains with a weight, which is the average between two parts related by $\{E \,|\, \mathbf{c}/2\}'$, while the latter is the difference of the two. The former is transformed by the ASO as in the gray atoms, while the latter changes its sign. The occupation domains for the colorless components have fivefold symmetry, including the weight. This gives no satellite reflections. On the other hand, the contribution of $F(\mathbf{h})$ and $\Delta F(\mathbf{h})$ from two occupation domains related with $\{E \,|\, \mathbf{c}/2\}'$ cancels out when h_5 is an odd and even number, respectively, since $F(\mathbf{h})$ of the former pair has the same value and $\Delta F(\mathbf{h})$ of the the latter has an opposite sign. Thus the colorless parts contribute only to diffraction intensities on the even layers, and the colored parts, to odd layers. This explains why the even layers show no satellite reflections. The systematic extinction of the odd layers in Fig. 3(d) is due to the existence of the glide plane $\{\sigma' \,|\, \mathbf{c}/2\}$, which is generated by the two antisymmetric operators $\{\sigma' \,|\, 0\}'$ and $\{E \,|\, \mathbf{c}/2\}'$. It is noted that there are only main reflections on the $h_1 h_2 \overline{h}_2 \overline{h}_1 h_5$ plane. Satellite reflections on the odd layers are extinct due to the glide plane. Thus the peculiar diffraction patterns in d-Al-Ni-Fe can be explained by the model with the color group $P_{2c}\overline{10}2m'(5mm')$. The above discussion clarifies that the color symmetry comes from the chemical ordering of Al and TM but the physical origin of such an ordering is left for future works.

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