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Symmetry analysis of the modulated icosahedral phase in AlCuFe

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Abstract. — The symmetry of the modulated icosahedral structure recently observed in Al_{63.5}Cu_{24}Fe_{12.5} is analyzed. The 12D superspace group associated with the structure is described by a pair of 6D icosahedral superspace groups, which can be identified as (P5\bar{3}m, P5\bar{3}m). Within the frame of a generalized Landau theory, the irreducible representation associated with the order parameter describing the distortion is determined. The possible form of the modulation is strongly symmetry restricted, so that some modulation parameters introduced in previous literature can be a priori set to zero. Ambiguities on the description of the modulated distortion when done in 6D superspace are stressed. It is demonstrated that the internal component of the modulation vectors, being undetermined by experiment, can be chosen along the corresponding 5-fold directions in the internal subspace; but, in contrast to previous assumptions, their modulus is not predetermined, and should be fitted to the diffraction intensity data once a model without deformations of the atomic hypersurfaces is chosen for the modulation.

1. Introduction.

AlCuFe alloys around the composition Al_{63.5}Cu_{24}Fe_{12.5} exhibit a modulated icosahedral phase as an intermediate state between a high-temperature icosahedral phase and a rhombohedral one that becomes stable below 675 °C [1-4]. The diffraction diagram of this modulated structure is characterized by an icosahedral quasilattice of main reflections similar to that observed in the normal icosahedral phase, and sets of twelve first order-satellites centered at main reflections and lying along the six 5-fold directions in the diffraction pattern. Synchrotron X-ray diffraction studies of this modulated phase have been recently reported [5, 6]. In reference [6] a quantitative analysis of integrated intensities of main and satellite reflections is presented. In these studies, experiments have been interpreted in the frame of superspace formalism; the distortion is described by a modulation of the periodic array of atomic hypersurfaces or occupation domains (AOD) in superspace. The results seem to indicate that the modulation can be essentially described as of phason type with the displacement of the AOD directed along the 5-fold axes in internal subspace [6]. Up to now, however, no systematic analysis of the
symmetry restrictions limiting the possible form of the modulation has been reported. Also, the non-uniqueness of the superspace description of the modulated phase and the resulting freedom in the way how the modulated distortion can be described have not been discussed. In the present work, a symmetry analysis of the modulated icosahedral phase of AlCuFe is presented based on the reported symmetry of its diffraction diagram. The 1D superspace group of the structure is determined. A generalized Landau theory is also introduced and the symmetry of the modulation is described in terms of a single irreducible representation of the icosahedral superspace group F53m. The possible forms of the modulation when described in 6D superspace and the arbitrariness in some features of this description are then discussed. Finally, and limiting the analysis to modulations with rigid displacements of the AOD, we determine a general expression for the modulation when restricted by the symmetry previously established. Its comparison with those used in previous works shows that some modulation features in the latter are forced by symmetry, but some others have no justification and have limited unnecessarily the space of possible distortions to be explored. On the other hand, some other variable parameters in the modulation, which should be fixed by symmetry, were considered free in [5, 6], and the diffraction intensity analysis in [6] led to values in accordance with the symmetry restriction proposed here.

2. Superspace group of a modulated icosahedral structure.

2.1 General Considerations. — The discrete set of diffraction vectors of a modulated quasicrystalline structure can be uniquely indexed in the form:

\[
\mathbf{H} = \sum_{i} h_i \mathbf{k}_i + \sum_{j} m_j \mathbf{q}_j = \mathbf{H}_k + \mathbf{H}_q
\]

where \( \{\mathbf{k}_i\} \) represents a rationally independent basis of wavevectors associated with the quasilattice of « main » reflections, while \( \{\mathbf{q}_j\} \) is a set of rational independent wavevectors present in the modulation. In fact, equation (1) can be taken as a definition of this type of structures.

Besides the expected weak intensity of those reflections with some \( m_j \neq 0 \) (satellite reflections) compared with the main reflections (all \( m_j = 0 \)), the essential feature distinguishing a modulated quasicrystalline structure from a pure quasicrystal is the fact that the rank of the quasilattice defined by (1), \( n + r \), must be greater than the minimum compatible with the point-group symmetry of the diffraction diagram, as the sets of satellite and main reflections remain disconnected by the point-symmetry operations. Hence, the set of main reflections forms a (sub)quasilattice which is invariant for the diffraction point-group symmetry. The vectors \( \mathbf{q} \) can then be chosen so that, for any rotational symmetry operation \( R \) (in real space) and any (real space) diffraction vector \( \mathbf{H} = \mathbf{H}_k + \mathbf{H}_q \), the transformed vector \( \mathbf{H}' = R \mathbf{H} = \mathbf{H}'_k + \mathbf{H}'_q \) satisfies:

\[
\mathbf{H}'_k = R \mathbf{H}_k \\
\mathbf{H}'_q = R \mathbf{H}_q.
\]

According to the general formalism of quasiperiodic structures the dimension of the superspace for a structure having a diffraction quasilattice as (1) is equal to the rank of the quasilattice, \( n + r \) in this case. A rotational symmetry operation in the superspace, \( R \), is given by a \( (n + r) \times (n + r) \) integer matrix representing the rotational transformation \( R \) of any diffraction vector (1) in terms of the corresponding linear transformation of its \( (n + r) \) integer components \( (h_i, m_j) \) in the chosen indexation basis [7]. From (2), these
matrices $R_s$ are reducible having a block diagonal form for the chosen basis \{\mathbf{k}_i, \mathbf{q}_j\}:

$$R_s(R) = \begin{pmatrix} R^i & 0 \\ 0 & R^q \end{pmatrix}. \quad (3)$$

Let us represent an operation of the superspace group by \{\mathbf{R} | \mathbf{t}, \mathbf{v}\}, where \(\mathbf{t} = (t_1, \ldots, t_n)\) and \(\mathbf{v} = (v_1, \ldots, v_n)\) indicate the translational components of the operation in direct superspace within the subspaces $V_k$ and $V_q$ associated with the $h_i$ and $m_j$ reciprocal indices, respectively. Then, the symmetry property associated with \{\mathbf{R} | \mathbf{t}, \mathbf{v}\} can be defined in terms of the condition that the structure factor of the real 3D structure should satisfy for any diffraction vector $\mathbf{H}$ of the form (1) [8, 9]:

$$F(\mathbf{RH}) = F(\mathbf{H}) \exp \left\{ -i 2 \pi \left( \sum h_i t_i + \sum m_j v_j \right) \right\}. \quad (4)$$

If we take into account (3), the product law of the group then satisfies:

$$\{R_2 | t_2, v_2\} \{R_1 | t_1, v_1\} = \{R_2 R_1 | R^i(R_2) t_1 + t_2, R^q(R_2) v_1 + v_2\} \quad (5)$$

and, therefore, the structure of any possible superspace group is such that its elements can be described by pairs of space groups operations \{\mathbf{R}^i | \mathbf{t}\}, \{\mathbf{R}^q | \mathbf{v}\} defined in the subspaces $V_k$ and $V_q$, the rotational operations in each subspace being correlated by equation (3).

### 2.2 ICOSAHEDRAL QUASICRYSTAL WITH ICOSAHEDRAL MODULATION.

In the particular case of the alloy Al$_{63.5}$Cu$_{24}$Fe$_{12.5}$, the icosahedral point-group symmetry $\overline{5}$m is maintained in the diffraction diagram of the modulated phase. The set of six vectors $\mathbf{k}$, can be chosen to lie along the six 5-fold axes, while the choice of the six modulation wavevectors $\mathbf{q}_j$ can be done so that their directions are the same as those for the vectors $\mathbf{k}$, of equal numerical index. In the following, this choice will be assumed. In this way, the matrix representations in the 6D subspaces $V_k$ and $V_q$ of any rotational operation $R$ belonging to the superspace point group symmetry coincide:

$$R^i(R) = R^q(R). \quad (6)$$

Thus, if we assume a centrosymmetry structure for AlCuFe, any possible superspace group of the modulated structure can be described by a pair, $(G_k, G_q)$, of icosahedral 6D space groups, both with point-group symmetry $\overline{5}$m. The main reflections in the modulated phase satisfy extinction rules corresponding to an F lattice (in direct space) with no additional extinction condition [5, 6], so that $G_k$ can be restricted to be F$\overline{5}$m, which is also the 6D superspace group of the non-modulated icosahedral phase of the same alloy [10]. According to [11] there are five 6D non-equivalent icosahedral superspace groups. Therefore, the number of possible 12D superspace groups for the modulated phase is in principle five, depending on $G_q$ being $\text{P}5\overline{3}m$, $\text{P}5\overline{3}q$, $\text{I}5\overline{3}m$, $\text{F}5\overline{3}m$ or $\text{F}5\overline{3}q$ ($\text{P}^*5\overline{3}m$, $\text{P}^*5\overline{3}q$, $\text{F}^*5\overline{3}m$, $\text{I}^*5\overline{3}m$ or $\text{I}^*5\overline{3}q$ in the notation of [11]). The last four possibilities for $G_q$ would imply extinction conditions for the satellite reflections: those due to the lattice centering I or F and/or those resulting from the glide planes $q$. I or F centering extinctions in the satellites can be discarded, as for the chosen indexation basis \{\mathbf{q}_j\} first order satellites with \(\{m_j\} = (\pm 1, 0, 0, 0, 0, 0)\) and symmetry related ones have been observed. This leaves only the possibility for $G_q$ being $\text{P}5\overline{3}m$ or $\text{P}5\overline{3}q$. If $G_q$ is $\text{P}5\overline{3}q$, it would imply the presence in the superspace group of glide planes, perpendicular to the binary axes (see Fig. 1), of the form \{\sigma | 0, 0, 0, 0, 0 ; 1/2, 1/2, 1/2, \}.
From equation (4), it is then easy to derive that first order satellites would be extinct on the planes of the diffraction diagram that are left invariant by these mirror plane operations \( \sigma \). Hence, for instance, reflections of the type \((\pm n, 0, 0, 0, 0, 0; \pm 1, 0, 0, 0, 0, 0)\) would be forbidden. Analogously, around the main reflection \((1, 1, 0, 0, 0, 0; 0, 0, 0, 0, 0, 0)\) only the four first order satellites \((1, 1, 0, 0, 0, 0; 0, 0, 0, 0, 0, \pm 1, 0)\) would be non-zero. Neither these, nor any other type of systematic extinction rule have been observed in AlCuFe [5, 6]. Therefore, we can conclude that the superspace group of the modulated structure in AlCuFe must be given by \((G, G') = (F53m, P53m)\).

3. A Landau approach.

Possible restrictions on the symmetry of modulated icosahedral structures can also be analyzed using Landau-type arguments. Let us assume that the modulated structure is the result of a distortion of an ordinary icosahedral structure, and this distortion can be understood as the result of a distortion of the 6D structure whose 3D section along «parallel» space represents the real quasicrystalline structure in superspace formalism. As is well known, in this superspace description the diffraction diagram in real space can be considered a projection of the 6D diffraction diagram and, therefore, the modulation wavevectors \(\{q_i\}\) can be taken as the parallel component of one or more modulation wavevectors present in the 6D distortion. If we assume, in the spirit of ordinary Landau argument, that this 6D distortion transforms according to an irreducible representation of the superspace group \(G = F53m\), the 12 vectors \(\{q_i, -q_i\}\) should then be identified with the components in parallel space of the 6D...
wavevectors belonging to the irreducible star of an irreducible representation. Nevertheless, the one-to-one relation between the diffraction vectors in 6D and the ones in parallel space, which is a fundamental point of the superspace formalism in ordinary quasicrystals, is no longer valid for satellite reflections. In other words, the modulation wave vectors in superspace could be such that several of them project on the same vector in parallel space, i.e. the representation star in superspace is not fully determined by the set of real space wave vectors \( \{ q_i \} \). This undetermination in the choice of the distortion representation can be easily understood if we consider that although, by construction, there is a one-to-one correspondence between the 6D icosahedral periodic structure and its section in parallel space, the same is not true once the 6D structure is distorted and has lost its periodicity: different distorted structures in 6D can give place to the same section in parallel space.

We have, therefore, some arbitrariness on the 6D description of modulated icosahedral structures. In the case of AlCuFe, if we identify the 12 vectors \( q_i \) as projections of superspace wave vectors \( \{ q, q_i \} \) with its internal components \( q_i \) having no symmetry restriction, the star of the representation of the 6D distortion would have 120 vectors, since for a fixed \( q \), there would be 10 different star wave vectors, \( \{ q, q_i(n) \} \) \( n = 1, \ldots, 10 \), obtained by the rotational operations that keep \( q \) invariant but transform the internal part. The structure factor of the real-space structure, \( F(H) \), for any diffraction vector, \( H \), indexed in the form (1), is then given by the superposition of those non-zero structure factors of the 6D structure with wavevectors having the same 3D parallel component \( H \):

\[
F(H) = \sum_{\{ n_j \}} F_s(H, H_t(\{ n_j \}))
\]

where \( F_s(H, H_t) \) is the structure factor of the 6D structure for the superspace reciprocal vector \( (H, H_t) \) with \( H_t \) being its internal component and

\[
H_t(\{ n_j \}) = \sum_{i=1}^{5} h_i k_{ii} + \sum_{j=1}^{5} m_j q_{ij}(n_j)
\]

where \( k_{ii} \) is the internal component of the vector \( k_i \) in the superspace construction. The sum in (7) extends to all possible sets of integers \( \{ n_1, n_2, n_3, n_4, n_5, n_6 \} \), with \( n_j = 1, \ldots, 10 \), that produce in (8) distinct vectors \( H_t \). Hence, for first order satellites the number of superspace structure factors superposing is 10, while for a satellite with \( \{ m_j \} = \{ 1, 1, 1, 1, 1 \} \) the superposition involves \( 10^6 \) terms! This clearly shows the lack of a unique relation between the 3D modulated structure and the 6D one.

There is, however, an obvious simple choice of \( q_{ij} \) which formally allows us to keep the one-to-one relation between the structure factors of the real and the 6D construction: if we consider \( q_{ij} \) along the five-fold axis in internal space so that is kept invariant by the same superspace rotational operations as \( q \), then there is a unique 6D wavevector associated with each \( q \), the number of branches of the star of the representation is reduced to 12, and the sum in (7) has a single term. Then, the local isomorphism among different sections of the 6D superspace construction along parallel subspace is also kept. This is the choice of modulation wavevectors that has been assumed in previous analyses of this phase [5, 6], and our analysis shall also pursue under this choice. However, it is important to have in mind that, although the simplest, this choice is one of the many possible ones, and therefore, the 6D «image» of the modulated structure depends to a great extent on our wish.

We therefore fix, the star of the representation of \( \text{F}_{53}^3 \text{m} \) associated with the modulated distortion by choosing the internal parts of the 6D modulation wavevectors so that they lie along the 5-fold axes in superspace, and the number of star branches reduces then to 12. Note
that within this choice the modulus of \( q_{h} \) still remains undetermined; the following symmetry arguments, however, do not depend on its particular value. Let us call \( D(\tau) \) the 12p-dimensional irreducible representation associated with the distortion, \( p \) being the dimension of the corresponding «small» representation \( \tau \). If \( Q_{e j}(e = 1, \ldots, 12; j = 1, \ldots, p) \) are the amplitudes in the representation basis of the 12p-dimensional frozen distortion, by definition, any superspace group operation \( \{R|t\} \) belonging to the superspace group \( F_{53m} \) transforms the distortion to a new one with modulation amplitudes \( Q'_{e j} \) that satisfy:

\[
Q'_{e j} = \sum_{j} D(\tau, \{R|t\})_{\eta e j} Q_{ej}
\]

(9)

where \( D(\tau, \{R|t\})_{\eta e j} \) stands for the coefficients of the matrix associated with \( \{R|t\} \) by representation \( D(\tau) \). Following the usual group-theory formalism [12], the form of these matrices can be derived from an irreducible «weighted» representation \( \tau \) of the invariance point-group, \( P_{ql} \), of one of the wavevectors in the representation star. As in the present case the star wavevectors do not lie on the Brillouin zone boundaries, the weighted representations reduce to ordinary ones and \( P_{ql} = 5 \, m \). The four possible inequivalent irreducible representations of this group are listed in table I. Thus, there are four possible irreducible representations for the symmetry of the distortion or «order parameter», depending on which of the four possible irreducible representations of \( 5 \, m \) is involved in the modulation.

Table I. — Characters of the irreducible representations of the point group \( 5 \, m \).

\begin{align*}
\tau_{1} & & 1 & & 1 & & 1 & & 1 \\
\tau_{2} & & 1 & & 1 & & 1 & & 1 \\
\tau_{3} & & 2 & & \tau - 1 & & - \tau & & 0 \\
\tau_{4} & & 2 & & - \tau & & \tau - 1 & & 0 \\
\end{align*}

Following [13], a superspace symmetry operation of the modulated structure, \( \{R|t, v\} \) represents a \( F_{53m} \) operation \( \{R|t\} \), followed by a phase shift \( 2 \pi m_{\eta} \, v \) of the resulting modulation amplitudes \( Q'_{e j} \), with \( m_{\eta} \, v = \Sigma m_{\eta} \, v, \) \( \{m_{\eta}\} \) being the indexation integers of the wavevector \( q_{\eta} \). That is, the invariance equation associated with a superspace symmetry operation \( \{R|t, v\} \) is:

\[
Q_{e j} = \exp(i \, 2 \pi m_{\eta} \, v) \sum_{j} D(\tau, \{R|t\})_{\eta e j} Q_{ej}.
\]

(10)

Equation (10) can be used in a systematic way to determine all the possible superspace groups that can result for a given irreducible representation. This requires first to construct the representation matrices \( D(\tau, \{R|t\}) \), and then, derive and enumerate all subspaces in the representation space that fulfill equation (10) for distinct sets of operations \( \{R|t, v\} \). This is a lengthy but straightforward process. In our case we are only interested in possible symmetry groups having \( 53m \) as its points group, since this is the diffraction symmetry observed. For the bidimensional representations in table I, \( \tau_{3} \) and \( \tau_{4} \), equation (10) cannot be simultaneously satisfied for all operations in the group \( 53m \). Therefore, these two representations can be discarded as possible symmetries of the distortion. On the other hand, \( \tau_{1} \) and \( \tau_{2} \) produce,
respectively, distortions with superspace groups \((\text{F}5\overline{3}m, \text{P}5\overline{3}m)\) and \((\text{F}5\overline{3}m, \text{P}5\overline{3}q)\) if the 6 independent complex modulation amplitudes have all the same modulus \([14]\). Hence, from the five possible superspace groups enumerated in the preceding section, only the first two can be realized by a distortion that complies with Landau rules and transforms, therefore, according to an irreducible representation of the symmetry group of the non-distorted phase. Comparing with the superspace group assigned to the modulated structure in the preceding section, \(\tau_1\) can then be identified as the irreducible representation associated with the distortion.

4. Symmetry restrictions on the modulation.

4.1 General Phonon and Phason Distortions. — Once identified the superspace group of the modulated structure and the corresponding symmetry of the modulation in terms of an irreducible representation, it is important to derive the resulting restrictions on the modulation functions. The wave vectors of the distorting modes in the 6D superspace can be written as \(\mathbf{q}_i = (\mathbf{q}_i, \mathbf{q}_i)\), \(i = 1, \ldots, 6\) (the star of the representation also includes their opposites), with \(\mathbf{q}_i\) being the observed real-space independent modulation wave vectors along the five-fold axes, and \(\mathbf{q}_i\) being their unknown internal component along the corresponding five-fold axes in internal space (henceforth we will indicate vectors in superspace with the symbol \(\hat{\cdot}\)). According to recent structural analyses [10], we will assume that the AOD of the non-modulated «parent» icosaedral AlCuFe quasicrystal are parallel to internal space. In the following, we enumerate the different AOD within one unit cell of the non-distorted quasicrystal with the label \(\mu\), and use \(\mathbf{r}_\mu\) to represent their centers, while \(\mathbf{r}_1\) is a generic position vector within an AOD, with respect to the corresponding AOD center.

A general modulation of the periodic structure in superspace, with wave vector \(\hat{\mathbf{q}}\), can have two very different components:

1) Deformations of the AOD along parallel space:

\[
\mathbf{u}_\mu(\hat{\mathbf{l}} | \mathbf{r}_1) = \mathbf{u}_\mu(\mathbf{r}_1) \exp[\imath \hat{\mathbf{q}} \cdot (\hat{\mathbf{l}} + \hat{\mathbf{r}}_\mu)]
\]

(11)

which in general can be not only cell dependent (\(\hat{\mathbf{l}}\)), but also position dependent within each AOD (\(\hat{\mathbf{r}}_\mu\)). If the displacement fields is \(\mathbf{r}_1\) independent, it represents modulated «rigid» translations of the AOD along the parallel space.

2) Deformations of the AOD in internal space, described by the displacement in internal space of the AOD contour limits that depend in general on the (unitary) direction \(\mathbf{n}_1\) in internal space:

\[
\mathbf{u}_{\mu\ell}(\hat{\mathbf{l}} | \mathbf{n}_1) = \mathbf{u}_{\mu\ell}(\mathbf{n}_1) \exp[\imath \hat{\mathbf{q}} \cdot (\hat{\mathbf{l}} + \hat{\mathbf{r}}_\mu)]
\]

(12)

If the contour displacements are \(\mathbf{n}_1\) independent, the displacement field represents modulated «rigid» translations of the AOD along the internal space.

Following rather extended jargon, these two kinds of distortions can be called phonon and phason-type, respectively. From the viewpoint of symmetry they belong to invariant subspaces; hence, they can be considered separately when enumerating possible symmetry modes. In fact, they represent very different physical distorting mechanisms. On the one hand, the first type describes atomic displacements in the quasicrystal that can be continuously set to zero by reducing the global amplitude of the distortion. On the other hand, the phason-type distortions describe discontinuous jumps of atoms, and the decrease of their global amplitude, instead, reduces continuously the density in real space of such atomic jumps, but not their magnitude. However, both types of distortions, separately or coexisting, can in principle give place to a diffraction diagram as the one observed.
4.2 AMBIGUITIES ON THE SUPERSPACE DESCRIPTION. — As already discussed in the preceding section, the breaking of the periodicity in superspace breaks also the one-to-one correspondence between superspace and real space structures. Some of the ambiguities were already eliminated by choosing arbitrarily the \( q_k \) components along the 5-fold axes in internal space. There exist, however, additional ones coming from the fact that only the section corresponding to real space is relevant. In the case of phonon-type distortions, for example, the general expression (11) can be simplified without lost of generality. Indeed, the only AOD displacements in (11) that are relevant are those corresponding to the section representing real space. For a given AOD \( r_i \) that crosses this section, the crossing point will occur at an AOD internal point given by \( r_i = -I_i - r_i \). Therefore, two distortions of the type (11) are physically equivalent if \( u_{\mu} (\hat{I} - I_i - r_i) \) are the same in both distortions for all AOD \( (\mu, \hat{I}) \) crossing the real space section. As a consequence, if we consider a general « rigid » phonon-type plane wave with wave vector \( \hat{q} \):

\[
u_{\mu} (\hat{I} - I_i - r_i) = u_{\mu} \exp [i \hat{q} \cdot (\hat{I} + \hat{r})] \quad (13)
\]

it will be equivalent to a non-rigid distortion wave with wave vector \( \hat{q} + \hat{k} \) having the form:

\[
u_{\mu} (\hat{I} + \hat{k}) = u_{\mu} \exp [i \hat{k} \cdot \hat{r}_i \cdot \exp [i (\hat{q} + \hat{k}) \cdot (\hat{I} + \hat{r})]] \quad (14)
\]

where \( \hat{k} = (0, k_1) \) is an arbitrary wavevector along the internal space. Figure 2 depicts an example of such type of equivalence: it shows two different superspace distortions representing the same modulated Fibonacci chain. Inversely, any general phonon-type distortion of the form (11) is equivalent to a sum of rigid plane wave distortions of type (13) with wavevectors differing only on their internal component. As we are assuming, following Landau theory, that the distortion should correspond to a single irreducible representation, only a single plane wave per \( \hat{q} \) should be present. Therefore, we can consider as the most general phonon-type modulation a rigid distortion of the form:

\[
u_{\mu} (\hat{I}) = \sum_{\hat{q}} u_{\mu} (\hat{q}) \exp [i \hat{q} \cdot (\hat{I} + \hat{r})] \quad (15)
\]

where the sum extends to the 12 branches of the representation star and \( u_{\mu} (-\hat{q}) = u_{n}^{*} (\hat{q}) \). The parallel components of the vectors \( \hat{q} \) are determined by the modulation wavevectors used in the indexation of the diffraction diagram ; the amplitude of their internal components along the five-folds axes in internal subspace, however, cannot be deduced from the geometry of the diffraction quasilattice and its value can only be derived from the analysis of the diffraction intensities. Alternatively, we could fix the internal components of the modulation wavevectors \( \hat{q} \) to an arbitrary value, but then, in order to consider any possible distortion, modulations of the AOD of type (14) would have to be allowed, complicating the picture.

In the case of phason-type distortions, an equivalence so simple as the one shown for phonon-type modulations does not exist. It is clear, however, that there are also infinitely equivalent superspace distortions, since the only physical relevance of any modulation along internal space of a AOD is its effect on its possible crossing of the real space section as the result of the distortion, or inversely the disappearance of this crossing if it existed in the non-distorted AOD. Therefore, it is plausible that a reduction of phason-type modulations to those with rigid AOD does not mean any important restriction. In the following we will restrict our
Fig. 2. — Two different superspace representations of the same phonon-type modulation in a Fibonacci chain. The dot lines represent the positions of the AOD in the ideal non-distorted Fibonacci chain. (a) Modulation with rigid AOD and wave vector along one of the unit cell lattice vectors. (b) Modulation with non-rigid AOD and wave vector along the parallel space (horizontal).

consideration to this type of phason-type modulations, i.e.:

\[
    u_{i\mu}(\hat{\mathbf{i}}) = \sum_{\hat{\mathbf{q}}, \hat{\mathbf{r}_\mu}} u_{i\mu}(\hat{\mathbf{q}}) \exp[i\hat{\mathbf{q}} \cdot (\hat{\mathbf{i}} + \hat{\mathbf{r}_\mu})]
\]

As in phonon-type modulations, only the component of \(\hat{\mathbf{q}}\) along parallel space is determined by
the diffraction quasilattice, while its internal component, together with the (complex) amplitudes \( u_{\mu}(\mathbf{q}) \) will influence the diffraction intensities. It should be stressed that, once limited the possible phason-type distortions to « rigid » ones as given by (16), an arbitrary choice of the internal component of the vectors \( \mathbf{q} \) as has been done in previous analyses of this icosahedral modulated phase is not justified. In fact, the intensities in the diffraction diagram of a modulation of the type (16) depend rather strongly on the actual value of the internal component of \( \mathbf{q} \). However, the rotational symmetry of the diffraction diagram and the hypothesis that the distortion conforms according to an irreducible representation of the icosahedral group imply that the modulus of this component should be the same for all modulation wave vectors. Note also that \( u_{\mu}(-\mathbf{q}) = u_{\mu}^*(\mathbf{q}) \).

4.3 SYMMETRY ADAPTED MODULATION. — We now analyze the symmetry restrictions on the general distortions (15) and (16) in order to have the observed symmetry (\( \overline{5} \tilde{3} m \), \( \overline{P} \tilde{3} m \)). General expressions known for normal modulated structures [8, 15] can be straightforwardly generalized. Let us call \( \hat{u}_{\mu}(\mathbf{q}) = (u_{\mu}(\mathbf{q}), u_{\mu}(\mathbf{q})) \) the superspace vector formed by the parallel and internal complex amplitudes in (15) and (16) for a given AOD \( \mu \). If \( \{R|t, v\} \) is a symmetry operation in the sense discussed in sections 1 and 2, that transforms AOD \( \mu \) into another one \( v \), then their distortion amplitudes should satisfy:

\[
\hat{u}_{\mu}(\mathbf{q}) = R^k \hat{u}_{\mu}(\mathbf{R^k q}) \exp[-i 2 \pi m \cdot v] \quad (17)
\]

where \( R^k \) is the matrix in equation (3). As introduced in section 2, \( m \) is the 6D «vector» given by the indexation integers of the vector \( \mathbf{q} \) in the basis used in (1). For the 12D superspace group mentioned, the «internal» translation \( v \) for all operations can be chosen to be zero. In addition, all the AOD in the non-distorted icosahedral phase of AlCufe are situated at fully symmetric points. Hence, condition (17) reduces to an invariance equation:

\[
\hat{u}_{\mu}(\mathbf{q}) = R^k \hat{u}_{\mu}(\mathbf{R^k q}) \quad (18)
\]

for all AOD in the unit cell and all rotational operations in the icosahedral point group \( \overline{5} \tilde{3} m \). Condition (18) is very restrictive; when considered for the operation \( C_3 \) that keeps invariant the vector \( \mathbf{q} \), implies that the vectors \( \hat{u}_{\mu}(\mathbf{q}) \) should be within the 2D \( C_3 \)-invariant subspace, i.e., the distortion should be «pseudo-longitudinal», the components \( u_{\mu}(\mathbf{q}) \) and \( u_{\mu}(\mathbf{q}) \) being directed along the same directions as the components of \( \mathbf{q} \) in parallel and internal space, respectively. When applied to the operations \( C_3 \) or \( C_2 \), condition (18) means that the moduli and phases of the amplitudes should be equal for all vectors \( \mathbf{q} \) in the 12-branch representation wave vector star. Condition (18) for the inversion implies that this common phase should be \( \pi/2 \) for all amplitude components. Consequently, the most general rigid distortion satisfying the symmetry observed in the diffraction diagram can be expressed as:

\[
\hat{u}_{\mu}(\mathbf{t}) = \sum \hat{U}_{\mu}(\mathbf{q}) \sin (\mathbf{q} \cdot (\mathbf{t} + \hat{\mathbf{r}}_{\mu}))) \quad (19)
\]

where the sum is now reduced to the six vectors \( \mathbf{q} \) used in the indexation and \( \hat{U}_{\mu}(\mathbf{q}) = (U_{\mu}(\mathbf{q}), U_{\mu}(\mathbf{q})) \) are real vectors in superspace with their internal and parallel components along the direction of the corresponding \( \mathbf{q} \) component in both subspaces, and, equal moduli for all vectors \( \mathbf{q} \) : \( |U_{\mu}(\mathbf{q})| = U_{\mu}, |U_{\mu}(\mathbf{q})| = U_{\mu} \), but, in general, depending on the AOD. The fact that sine functions appear is not significant. Indeed, we could change the
expression into cosine functions by means of a phase shift, which would be equivalent to a change of origin in superspace so that the vector \( \mathbf{v}_0 \) for the inversion would be \((1/2, 1/2, 1/2, 1/2, 1/2)\). We could even choose a more general translation of the origin in internal space so that the argument of each sine function in (19) also includes a different initial phase. These arbitrary phases that are set to zero in (19) represent the 6 new phason degrees of freedom in the modulated icosahedral phase. The diffraction pattern does not depend on their values. What is significant in (19) and comes from the symmetry condition is the fact that these initial phases for a given \( \mathbf{q} \) are the same for all AOD in the unit cell and all components of the vectorial amplitudes. However, the modulations of different AOD in the unit cell can have different amplitudes; in this case, their restriction in [5, 6] to a common value reducing the distortion to « acoustic » modulations is not symmetry grounded, although it may be physically sound for a first simple trial functions. Also note the necessary presence of the center of the AOD, \( \mathbf{i}_\mu \), in expression (19).

5. Conclusions.

The symmetry of the modulated icosahedral phase detected in alloys AlCuFe has been determined and expressed in terms of the 12D superspace group \((F\bar{5}3m, \bar{P}53m)\). The modulation has been interpreted in terms of a symmetry irreducible distortion, in the spirit of Landau theory, and the relevant irreducible representation can be identified as \( \tau_1 \). The ambiguities on the superspace description of the modulation have been discussed showing that the modulus of the internal components of the modulation wave vectors cannot be fixed a priori and requires a quantitative analysis of the diffraction intensities. The symmetry restrictions on the distortion imply that the modulations should be pseudo-longitudinal, in the sense that the parallel and internal components of the AOD displacements should be parallel to the wave vector component in each subspace. The diffraction quantitative analysis performed in [6] did not consider this restriction, but its final adjusted modulation is in accordance with it, confirming the symmetry proposed in the present work. Note, however, that in [6] the modulus of the internal component of the modulation wave vectors was fixed arbitrarily, while according to the arguments above, this value should also have been refined.

References


