Eur. Phys. J. B **7**, 85–89 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Cubic superspace symmetry and inflation rules in metastable MgAl alloy

L. Elcoro[a] and J.M. Perez-Mato

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain

Received: 25 June 1998 / Received in final form and Accepted: 23 September 1998

Abstract. The diffraction properties of a quenched Al-Mg alloy which has been recently termed as a "cubic quasicrystal" are quantitatively reanalyzed. It is shown that the phase can be interpreted within the superspace formalism as an *ordinary* incommensurately modulated structure. The cubic six-dimensional superspace group that describes its symmetry properties has been determined. The additional inflation symmetry features exhibited by the diffraction diagram can be summed up by its invariance for the inflation factor $(2+\sqrt{3})$, but this property has its origin in the specific value of the modulus of the modulation wave vectors, which is composition dependent. Other particular values of this modulus can give rise to similar scaling properties. Further experiments are required to ellucidate if the mentioned inflation symmetry is a fortuitous situation in a composition dependent wave vector, or has indeed the physical significance which would allow to describe the system as a "cubic quasicrystal".

PACS. 61.44.Fw Incommensurate crystals – 61.44.-n Semi-periodic solids – 61 Structure of solids and liquids; crystallography

1 Introduction

A new metastable phase with very peculiar features has been reported in the Al-Mg system [1]. At 61 at% Al, the diffraction pattern of rapidly solidified samples apparently exhibits quasicrystalline properties and cubic rotational symmetry at the same time. The ratios among the moduli of parallel diffraction vectors take such values as $\sqrt{3}$, $\sqrt{3}+1$ or $(\sqrt{3}+1)/2$, that remind the inflation parameters $\sqrt{5}+2$ and $(\sqrt{5}-1)/2$ of icosahedral and decagonal diffraction patterns, respectively, but, on the other hand, the symmetry of the electron diffraction pattern corresponds to a conventional cubic point group. This has led to the identification of this structure as a "cubic quasicrystal" with some kind of "new organisation of the condensed matter" [1]. In the present paper, the experimental diffraction results for this alloy are revised and reinterpreted in a quantitative manner. It is shown that the structure can be described as a cubic incommensurate modulated structure with a well defined superspace group symmetry [2], the incommensurate modulation being three-dimensional. The inflation invariant features of the diffraction diagram can be traced back to the peculiar value taken by the modulus of the modulation wave vectors.

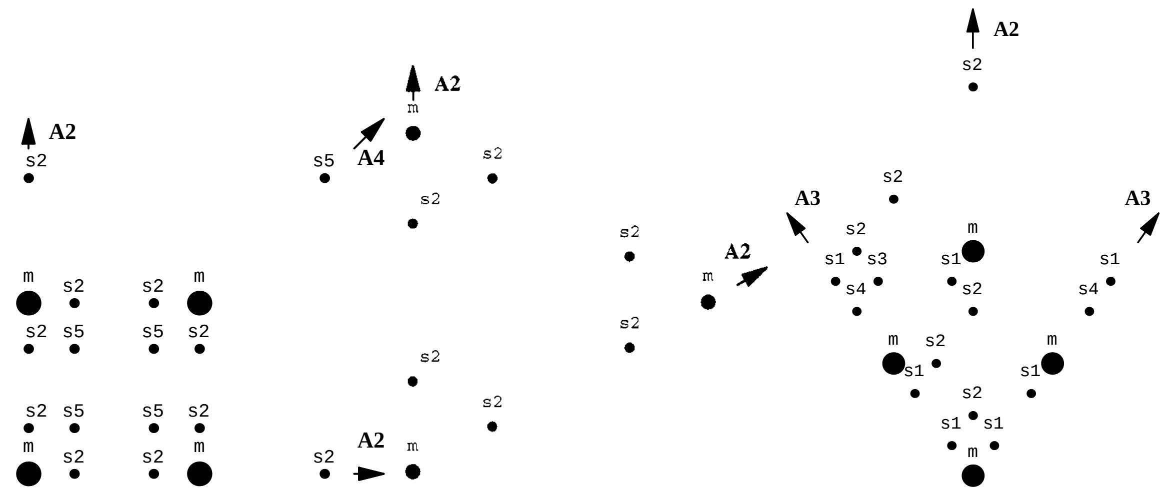
[a] e-mail: wmpelcel@lg.ehu.es

2 Indexation of the diffraction pattern and superspace symmetry

Figure 1 reproduces Figure 6 of reference [1] where a scheme of the Bragg peaks observed for this peculiar quenched state of $Al_{61}Mn_{39}$ was depicted. The diagrams correspond to planes perpendicular to 4-fold, 3-fold and 2-fold axes, the point group of the diffraction pattern being $m\bar{3}m$. As usual in incommensurate modulated structures, all Bragg reflections in the observed diffraction diagram can be indexed with a basis of n (>3) rationally independent vectors, n being the so-called rank of the structure. The main reflections define a periodic average structure and the remaining ones are the satellite reflections that indicate the existence of a structural modulation. In the case depicted in Figure 1, the main reflections form a bcc reciprocal latice, *i.e.* the shortest diffraction vectors are parallel to the 3-fold axes. Hence, we can choose for their indexation $(\sum_{i=1}^{3} h_i\mathbf{a}_i^*)$ an orthonormal cubic basis parallel to the 4-fold axes:

$$\mathbf{a}_1^* = a^*(1,0,0),\quad \mathbf{a}_2^* = a^*(0,1,0),\quad \mathbf{a}_3^* = a^*(0,0,1) \quad (1)$$

with the indices h_1, h_2, h_3 satisfying the extinction rule that yields a bcc lattice (h_1, h_2, h_3 all even or all odd). The scale parameter a^* is 1.460 nm^{-1}, so that the fcc cubic unit cell parameter of the average structure in direct space is $a = 0.685$ nm.



(a) (b) (c)

Fig. 1. Scheme of three sections perpendicular to a, (a) 4-fold axis, (b) 3-fold axis and (c) 2-fold axis, of the reciprocal quasilattice defined by equations (1), (2) and (3). m labels indicate main reflections (big spots) and s labels satellite reflections (small spots). In this last case, a second label shows the order of the satellite, according to our indexation model. A_2, A_3 and A_4 arrows indicate 2-, 3- and 4-fold axes, respectively.

Three additional vectors $\mathbf{q}_i$ are necessary to index the remaining (satellite) reflections and they can be chosen parallel to the previously defined $\mathbf{a}_i^*$ with values:

$$\mathbf{q}_i = (2 - \sqrt{3})\mathbf{a}_i^* \qquad i = 1, 2, 3. \tag{2}$$

Therefore, 6 indices $(h_1, h_2, h_3, m_1, m_2, m_3)$ are necessary for the indexation of all diffraction vectors $\mathbf{H}$:

$$\mathbf{H} = \sum_{i=1}^{3} (h_i \mathbf{a}_i^* + m_i \mathbf{q}_i). \tag{3}$$

In Figure 1, main reflections and satellites are distinguished by means of the labels m and s, respectively. For satellites, a second label indicates the order of the satellite, which is defined in this case as their sequential order in an arrangement from lower to higher values of the modulus of the satellite "part" of the diffraction vector (*i.e.* $|\sum_{i=1}^{3} m_i \mathbf{q}_i|$).

According to the diffraction photographs and schemes shown in reference [1], the whole quasilattice of Bragg reflections apparently exhibits a centering extinction rule ($h_1 + h_2$, $h_2 + h_3$, $h_1 + h_3$, $m_1 + m_2$, $m_2 + m_3$, $m_1 + m_3$ even), from which the one on main reflections, mentioned above, is a particular case.

Main reflections suffer an additional systematic extinction described by the absence of reflections of type (h_1 h_2 0, 0 0 0) with $h_1 + h_2 = 4n + 2$, and (cubic) symmetry-related ones, while satellite reflections seem to have also a similar one: around each non-extinct main reflection of type (h_1 h_2 0, 0 0 0) with $h_1 + h_2 = 4n$, the associated satellite reflections of type (h_1 h_2 0, m_1 m_2 0) are not present when $m_1 + m_2 = 4n + 2$.

These are the only set of consistent systematic extinctions that can be observed. Some low-order satellites which according to the rules above should be non-extinct were, however, not depicted in the graphical schemes of Figure 6 in reference [1]. But, indeed, if some of the photographs of the same reference are carefully studied, these additional satellites can be actually seen in the experimental diffraction pattern, confirming the validity of the above description. Figure 2 shows a more complete section perpendicular to a 2-fold axis of the reciprocal quasilattice. The spots represent all reflections of type (3), except systematic extinctions, including all satellite reflections up to 9th order. The similarity of this figure and the corresponding diffraction photograph shown in [1] is noticeable.

It is worth mentioning at this point that $2 - \sqrt{3} \approx 0.268$, the scale of the modulation wave vectors, is relatively close to 1/4. If it were exactly 1/4, the structure would be periodic with a cell parameter about 2.740 nm, which is rather close to the cell parameter of the β phase, the stable phase (of $Fd\bar{3}m$ symmetry) in this composition range [3]. From the extinction rules associated to the main reflections, the symmetry of the average structure can also be identified as $Fd\bar{3}m$.

The superspace symmetry of the incommensurate structure as a whole can also be derived from the observed diffraction pattern. The point group symmetry being $m\bar{3}m$, for each operation R of such group and each reflection $\mathbf{H}$ of the reciprocal quasilattice, there is another vector $\mathbf{H}'$ in the quasilattice which satisfies $\mathbf{H}' = R\mathbf{H}$. According to the general formalism of superspace symmetry, a rotational symmetry operation in superspace, $R_s(R)$, is then given by a 6×6 integer matrix representing the rotational transformation R of any diffraction vector

(3) in terms of the corresponding linear transformation of its 6 integer components (h_i, m_i) in the chosen indexation basis [4]. Symmetry operations do not mix the "main" and "satellite" parts of the reflections, *i.e.* the matrices R_s are reducible, having a block diagonal form for the chosen basis $\{\mathbf{a}_i^*,\ \mathbf{q}_i\}$:

$$R_s(R) = \begin{pmatrix} R^{\mathbf{a}}(R) & 0 \\ 0 & R^{\mathbf{q}}(R) \end{pmatrix}. \tag{4}$$

This corresponds to a superspace group with pure incommensurate modulated wave vectors [5]. A generic operation of the superspace group can be represented by $\{R|\mathbf{t},\boldsymbol{\nu}\}$, where $\mathbf{t} \equiv (t_1,t_2,t_3)$ and $\nu \equiv (\nu_1,\nu_2,\nu_3)$ indicate the translational components of the operation in direct superspace within the subspaces $V_{\mathbf{a}}$ and $V_{\mathbf{q}}$ associated with the h_i and m_i reciprocal indices, respectively. Notice that $V_{\mathbf{q}}$ is the so-called internal space, while $V_{\mathbf{a}}$ is not real space, but the one spanned by the superspace lattice translations which are not fully contained in internal space. The product law of the group is then given by:

$$\{R_2|\mathbf{t}_2,\boldsymbol{\nu}_2\}\{R_1|\mathbf{t}_1,\boldsymbol{\nu}_1\} = \{R_2R_1|R^a(R_2)\mathbf{t}_1 + \mathbf{t}_2, R^q(R_2)\boldsymbol{\nu}_1 + \boldsymbol{\nu}_2\}. \tag{5}$$

In our case, for the indexation basis chosen $R^a(R) = R^q(R) = R$. Therefore, the structure of any possible superspace group is such that its elements can be described by pairs of space group operations $\{R|\mathbf{t}\}$, $\{R|\boldsymbol{\nu}\}$ defined in the subspaces $V_{\mathbf{a}}$ and $V_{\mathbf{q}}$ [6]. Hence, any possible superspace group of the modulated structure under discussion can be described by a pair $(G_{\mathbf{a}}, G_{\mathbf{q}})$ of conventional 3-dimensional cubic space groups with point group $m\bar{3}m$, with their operations forming pairs in the sense of equations (4, 5).

The existence of a superspace symmetry operation $\{R|\mathbf{t},\boldsymbol{\nu}\}$ should be reflected in the symmetry properties of the structure factor of the real 3D structure, which must fulfill for any diffraction vector $\mathbf{H}$ indexed according to (3):

$$F(\tilde{R}\mathbf{H}) = F(\mathbf{H}) \exp\left\{-i2\pi\left(\sum_{i=1}^{3} h_i t_i + \sum_{i=1}^{3} m_i \nu_i\right)\right\}. \tag{6}$$

The extinction rules resulting from (6), as in conventional crystallography, help to determine the symmetry of the system. According to (6), $G_{\mathbf{a}}$ is to be identified with the space group of the average structure $Fd\bar{3}m$, while $G_{\mathbf{q}}$, is also F centered cubic group. The extinction rule observed for satellites is only compatible with the existence also in $G_{\mathbf{q}}$ of a glide plane d, so that the corresponding superspace operation is $\{m_z|1/4\ 1/4\ 0, 1/4\ 1/4\ 0\}$. Indeed, according to equation (6), such operation is to cause extinction for reflections ($h_1\ h_2\ 0$, $m_1\ m_2\ 0$) with $h_1 + h_2 + m_1 + m_2 = 4n + 2$. The observed extinctions for satellites around non-extinct main reflections ($h_1 + h_2 = 4n$), mentioned above, fit into this rule. The corresponding space group can then only be $Fd\bar{3}m$ or $Fd\bar{3}c$. The extinction rule which would result from a plane c is not observed. From all these considerations, the superspace group of the modulated structure can in principle be labelled as $P(Fd\bar{3}m,\ Fd\bar{3}m)$, where the label P indicates the primitive character of the modulated wave vectors. If a different set of modulation vectors (2) were chosen to index the satellite reflections, the superspace group would be $P(Fd\bar{3}m,\ Fm\bar{3}m)$, so both superspace groups are equivalent.

3 Inflation symmetry

The so-called inflation symmetry is a characteristic feature of the quasilattice of Bragg reflections from a quasicrystal. Once a vector basis for its indexation has been chosen, an alternative basis of diffraction vectors can be found with vectors parallel to the original ones and an irrational number as scale factor. For example, in icosahedral quasicrystals with a primitive quasilattice, two sets of 6 vectors pointing to vertices of two concentric icosahedra can index the same reciprocal quasilattice, and the ratio between the moduli of the vectors of both basis is $(2+\sqrt{5})$ [4]. This means that if we multiply each vector of the reciprocal quasilattice by that factor, the new vectors belong to the initial quasilattice and, conversely, all vectors in the first quasilattice are in the new one. Hence, the relation between both quasilattices is one to one and one talks of inflation symmetry, with inflation parameter $(2+\sqrt{5})$. Obviously, there will also be another basis which differs from the first one by a scale factor $(2+\sqrt{5})^2$ and so on. Conversely, a deflated basis with the factor $(2+\sqrt{5})^{-1} = (2-\sqrt{5})$ can also be defined.

This type of purely geometrical inflation symmetry properties in reciprocal space of the (non-weighted) diffraction points exists in all quasicrystals. In the case of experimental quasicrystalline systems, the usual non-crystallographic rotational symmetry implies geometrical constrains on the diffraction vectors which are at the origin of the observed inflation features. The presence of similar features in a diffraction diagram of conventional cubic symmetry, as reported in reference [1] for the quenched $Al_{61}Mg_{39}$ alloy is, therefore, rather peculiar.

Let us first quantitatively demonstrate that we are indeed in the presence of a genuine inflation symmetry. For this purpose, it is sufficient to check that inflation symmetry exists along one of the directions corresponding to a primitive unit cell vector of the main reflections, say $\mathbf{k}_1 = a^*(\bar{1},\ 1,\ 1)$, since, in this case,the point symmetry of the diagram forces the same inflation symmetry in two other equivalent directions parallel to, say $(1,\ \bar{1},\ 1)$ and $(1,\ 1,\ \bar{1})$. As any diffraction vector can be expressed as the sum of three quasilattice vectors along these three directions, then all reciprocal quasilattice directions will have such symmetry. Along the direction $(\bar{1},\ 1,\ 1)$, the Bragg reflections can be indexed using primitive basis vectors in the form:

$$\mathbf{H} = h_1\mathbf{k}_1 + m_1\mathbf{p}_1 = (h_1 + (2-\sqrt{3})m_1)\mathbf{k}_1 \tag{7}$$

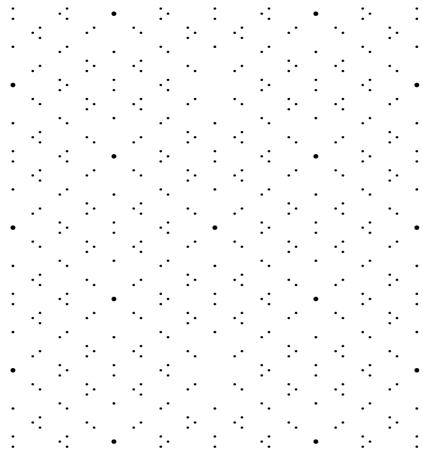


Fig. 2. Section of the reciprocal quasilattice perpendicular to a 2-fold axis according to our indexation model. Satellite reflections have been included up to 9th order.

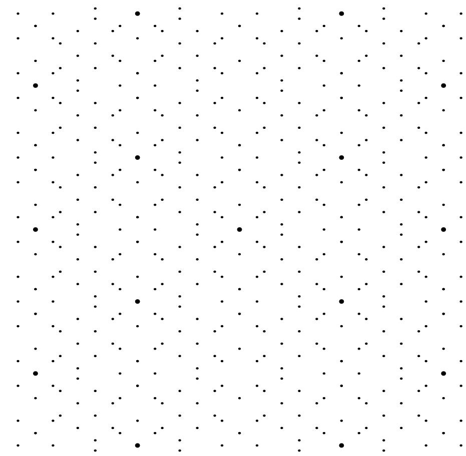


Fig. 4. The same section of Figures 2 and 3, with modulation parameter $\sqrt{2}-1$.

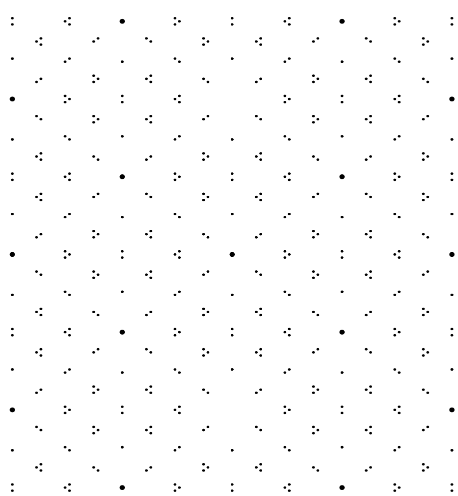


Fig. 3. The same section of Figure 2, with a slightly different modulation parameter 0.26.

where $\mathbf{p}_1 = (2-\sqrt{3})\mathbf{k}_1 = |\mathbf{q}_1|(\bar{1}, 1, 1)$. It can be easily shown that this 1D sublattice has indeed inflation symmetry with inflation parameter $\alpha = (2+\sqrt{3})$. Any vector of the quasilattice (7) multiplied by this factor is also an integer linear combination of $\mathbf{k}_1$ and $\mathbf{p}_1$: $\mathbf{H}' = \alpha\mathbf{H} = h_1'\mathbf{k}_1 + m_1'\mathbf{p}_1$, with $h_1' = 4h_1 + m_1$ and $m_1' = -h_1$. Conversely, for each $\mathbf{H}$ in the reciprocal quasilattice it is possible to find another vector $\mathbf{H}''$ in the same quasilattice so that $\mathbf{H} = \alpha\mathbf{H}''$. It can be demonstrated that all possible inflation parameters of the reciprocal quasilattice are powers of this parameter α, the negative powers being in fact deflation parameters.

It is important to note that all the superspace extinction rules discussed in the previous section are invariant for this scale transformation, ensuring that the above determined superspace group is well defined and independent of the choice among the multiple set of equivalent scale-transformed indexation bases.

A quasilattice of points as given in (2, 3) is *dense* in real space and inflation symmetry does not consider, in principle, the intensity of the Bragg reciprocal points. One could say, then, that any quasilattice is inflation symmetric for any arbitrary factor up to any chosen accuracy level. However, in practice, only a scarce *discrete* set of Bragg spots are visible. Within this practical context, the important property of the actual inflation factor $(2+\sqrt{3})$ is that the inflated quasilattice is *exactly* indexed in the old basis using relatively small indices. This implies that the scaling features of the quasilattice are likely to be observable within the limited set of observed quasilattice points. This is shown, for instance, in Figure 2, where only satellite reflections up to a certain order are depicted. The inflation symmetry resulting from the peculiar value of the moduli of $\mathbf{q}_i$ is first remarkable by the fact that Bragg spots are distributed rather regularly in reciprocal space. In contrast, if the incommensurate parameter relating $\mathbf{a}_i^*$ and $\mathbf{q}_i$ takes an arbitrary value, the rather uniform distribution of satellite spots is lost, and some kind of accumulation regions are visible where observable Bragg reflections concentrate. This is shown for instance in Figure 3, where the same section of Bragg reflections as in Figure 2 is shown for a "normal" incommensurate modulation parameter $|\mathbf{q}_i|/|\mathbf{a}_i^*| \approx 0.26$ (a change of less than 5%).

In quasicrystals with non-crystallographic point-group, inflation symmetry is a consequence of the particular geometry forced on the quasilattice by the non-crystallographic point-group symmetry. In the present case, however, inflation properties appear as a result of the special value of $(2-\sqrt{3})$ taken by the modulation parameter $|\mathbf{q}_i|/|\mathbf{a}_i^*|$, this value being not forced by the point group symmetry of the system. In fact, this is not the only possible value of $|\mathbf{q}_i|/|\mathbf{a}_i^*|$, which can give rise to inflation symmetry features on the diagram. For instance, ratios $\sqrt{2}$ and $\sqrt{5}-2$ would cause similar scaling properties with inflation parameter $\sqrt{2}+1$ and $\sqrt{5}+2$, respectively (see Fig. 4). The first one is quite far from the actual experimental value, the second one, however, is also close to 1/4, and may be relevant for similar alloys with other compositions.

The main question which the experiments reported so far have not ellucidated is whether this peculiar value of the modulation vectors, observed at a particular composition, is a pure fortuitous situation in a modulated system where the value of the modulation parameter is composition dependent, or indeed it has some physical significance, in the sense that this particular modulation parameter somehow "locks-in" for some finite range of alloy composition. Indeed, when the value of the modulation parameter is $2-\sqrt{3}$ the aspect of the diffraction pattern drastically changes, but it could merely be a geometrical property realised at some accidental point of the phase diagram because of the continuous variation of the modulation parameter as a function of composition. In fact, according to reference [1] the observed scaling features were anticipated and searched for a specific composition from a simple extrapolation of the composition dependence of the modulation vector.

4 Conclusions

The metastable phase $Al_{61}Mg_{39}$ obtained by Donnadieu *et al.* [1] by rapid solidification can be interpreted as an incommensurately modulated structure with crystallographic cubic average structure. Its diffraction pattern can be indexed by means of 6 basis vectors, three of them generate the reciprocal lattice of the average structure, while three modulation vectors must be added to index the satellite reflections. The modulation parameter relating both vector sets is, within experimental resolution, $2-\sqrt{3}$. The superspace group of the incommensurate structure is $P(Fd\bar{3}m,\, Fd\bar{3}m)$, so that the average structure is $Fd\bar{3}m$, the same as for the stable phase at that composition. Due to the specific value taken by the modulation parameter the reciprocal quasilattice possesses inflation symmetry, but is an open question if it is physically significant or a fortuitous situation for a modulation parameter which is composition dependent. The peculiar value of the observed modulation parameter is not unique for producing scaling features; other particular values could give rise to similar inflation symmetry properties of the diffraction diagram.

References

1. P. Donnadieu, H.L. Su, A. Proult, M. Harmelin, G. Effenberg, F. Aldinger, J. Phys. I France **6**, 1153 (1996).
2. T. Janssen, A. Janner, A. Looijenga-Vos, P.M. de Wolff, *International Tables for Crystallography*, edited by A.J.C. Wilson (Kluwer Academic Publishers, 1992), Vol. C, p. 797.
3. S. Samson, Acta Cryst. **24**B, 1004 (1968).
4. T. Janssen, Phys. Rep. **55**, (1988).
5. T. Janssen, A. Janner, Adv. Phys. **36**, 519 (1987).
6. J.M. Perez-Mato, L. Elcoro, J. Phys. I France **4**, 1341 (1994).