

Continuous Rotation from Cubic to Icosahedral Order*

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(Received 23 June 1986; accepted 5 January 1987)

Abstract

Al-Mn alloys display the competition of condensed matter phases with periodic cubic and non-periodic icosahedral order respectively. Both types of order are connected by a single continuous rotation $M(\beta)$ in the hypercubic lattice of 6-space projected to 3-space. The rotation $M(\beta)$ results from Schur's lemma [Schur (1905). *Sitzungsber. Preuss. Akad. Wiss.* pp. 406–432] applied to the cubic and icosahedral point groups. For $0 \leq \beta < \pi$ it preserves tetrahedral symmetry. For $\beta^c = 0^\circ$ one finds cubic symmetry, for $\beta^i = 13 \cdot 28^\circ$ icosahedral symmetry. Implications for the Al-Mn structure are presented.

Introduction

The experimental observation by Schechtman, Blech, Gratias & Cahn (1984) of a phase in Al-Mn with diffraction patterns of icosahedral point symmetry has stimulated many experimental and theoretical investigations [see Mackay & Kramer (1985)]. A quasilattice with two rhombohedral cells associated with the icosahedral group was constructed by Kramer & Neri (1984) before the experimental observation and now serves as a possible model for the icosahedral phase. The system Al-Mn has a cubic phase which can be converted by appropriate phase transitions to the icosahedral one (Urban, Moser & Kronmüller, 1985). The similarity between the cubic and icosahedral phases has been noted by several authors. Pauling (1985) proposed a structure for the new phase based on multiple twinning of cubic crystals. Guyot & Audier (1985) and Audier & Guyot (1986) in detailed models of the cubic and icosahedral phases pointed out the striking correspondence of the two phases. Elser & Henley (1985) described quasicrystal structures as the limit of periodic structures and discussed these and similar phases. In the present article it is shown that a detailed analysis of the crystallographic and non-crystallographic point groups leads to a continuous rotation which preserves tetrahedral symmetry and connects cubic with icosahedral symmetry and order.

1. Point subgroups of the hyperoctahedral group in the Euclidean space E^6

Consider the hypercubic lattice in E^6 . Its point symmetry group is the hyperoctahedral group $\Omega(6)$, described by Coxeter & Moser (1965). The elements of $\Omega(6)$ are all $6!$ permutations of the symmetric group $S(6)$ along with 2^6 reflections of the six orthonormal basis vectors. We denote elements f of $\Omega(6)$ by

$$f: \begin{cases} i \rightarrow f(i), & i = 1, \dots, 6, \text{ a permutation from } S(6) \\ \varepsilon_i(f) = \pm 1, & i = 1, \dots, 6, \end{cases} \quad (1)$$

which may be condensed into the two-row symbol

$$f = \begin{vmatrix} 1 & \dots & 6 \\ \varepsilon_1 f(1) & \dots & \varepsilon_6 f(6) \end{vmatrix}. \quad (2)$$

We shall indicate any $\varepsilon_i = -1$ by $-f(i) \rightarrow \bar{f}(i)$. To f there corresponds a 6×6 matrix representation $\tilde{D}^6(f)$, with elements

$$\tilde{D}_{ij}^6(f) = \varepsilon_i(f) \delta_{i, f(j)}, \quad i, j = 1, \dots, 6. \quad (3)$$

Now we define the orthogonal 6×6 matrix by

$$m^c: m^c = \frac{1}{2} \begin{vmatrix} 0 & 1 & 1 & 0 & 1 & \bar{1} \\ 1 & 0 & 1 & \bar{1} & 0 & 1 \\ 1 & 1 & 0 & 1 & \bar{1} & 0 \\ 0 & \bar{1} & 1 & 0 & \bar{1} & \bar{1} \\ 1 & 0 & \bar{1} & \bar{1} & 0 & \bar{1} \\ \bar{1} & 1 & 0 & \bar{1} & \bar{1} & 0 \end{vmatrix}, \quad (m^c)^T = (m^c)^{-1}. \quad (4)$$

The six column vectors of m^c form six orthogonal unit vectors which could serve as a basis of the hypercubic lattice in E^6 . The selection of the first three or last three rows of m^c determines a projection of these vectors from E^6 to two three-dimensional orthogonal spaces E_1^3 and E_2^3 respectively. In E_1^3 , the projected six basis vectors become

$$m_1^c = \frac{1}{2} \begin{vmatrix} 0 & 1 & 1 & 0 & 1 & \bar{1} \\ 1 & 0 & 1 & \bar{1} & 0 & 1 \\ 1 & 1 & 0 & 1 & \bar{1} & 0 \end{vmatrix}. \quad (5)$$

These six vectors, together with their images under inversion, are the three basis vectors of the face-

* Work supported by the Deutsche Forschungsgemeinschaft.

Table 1. Generators g of cubic and icosahedral groups

The index denotes the order of the generator. $\tilde{D}^6(g)$ denotes the embedding and representation in E^6 and β the Schur rotation angle. The transformed representation $D^6(g) = m(\beta)\tilde{D}^6(g)[m(\beta)]^{-1}$ splits into irreducible representations $D_1^3(g)$ and $D_2^3(g)$ in E_1^3 and E_2^3 respectively. We use $\Phi = (1 + \sqrt{5})/2$.

g	$D^6(g)$	β	$D_1^3(g)$	$D_2^3(g)$
g_2	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & \bar{5} & \bar{3} & 1 & \bar{2} & \bar{6} \end{vmatrix}$	$0 \leq \beta < \pi$	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}$	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}$
g_3	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 1 & 5 & 6 & 4 \end{vmatrix}$	$0 \leq \beta < \pi$	$\begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}$	$\begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}$
g_4	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ \bar{5} & 1 & 6 & 2 & \bar{4} & \bar{3} \end{vmatrix}$	$\beta = 0$	$\begin{vmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}$
h_2	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 3 & \bar{5} & \bar{4} & \bar{6} \end{vmatrix}$	$\beta = 0$	$\begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}$
g_5	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 4 & 2 & \bar{5} & \bar{6} & 3 \end{vmatrix}$	$\beta = 13 \cdot 28^\circ$	$\begin{vmatrix} \Phi^{-1/2} & \Phi/2 & -\frac{1}{2} \\ -\Phi/2 & \frac{1}{2} & \Phi^{-1/2} \\ \frac{1}{2} & \Phi^{-1/2} & \Phi/2 \end{vmatrix}$	$\begin{vmatrix} -\Phi/2 & -\Phi^{-1/2} & -\frac{1}{2} \\ \Phi^{-1/2} & \frac{1}{2} & -\Phi/2 \\ \frac{1}{2} & -\Phi/2 & -\Phi^{-1/2} \end{vmatrix}$
i_2	$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ \bar{1} & \bar{2} & \bar{3} & \bar{4} & \bar{5} & \bar{6} \end{vmatrix}$	$0 \leq \beta < \pi$	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}$	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}$

centred cubic lattice (Henry & Lonsdale, 1969), along with their images under the full cubic group $O_h \sim m\bar{3}m$. The left application of elements g from O_h to m_1^c generates permutations and reflections of the six column vectors which may be expressed by right application to m_1^c of a 6×6 matrix $\tilde{D}^6(g)$. It is verified that a similar result, with the same matrix $\tilde{D}^6(g)$, applies to m_2^c , so that we get the combined result

$$D^6(g)m^c = m^c\tilde{D}^6(g), \quad D^6(g) := m^c\tilde{D}^6(g)(m^c)^{-1}. \quad (6)$$

The 3×3 blocks $D_1^3(g)$ and $D_2^3(g)$ of $D^6(g)$ and the two-row symbol (1) for $\tilde{D}^6(g)$ are given in Table 1 for the generators g_k of order k of the cubic groups. In passing we note that this six-dimensional representation of the full cubic group could be obtained from the non-trivial one-dimensional representation of the subgroup D_{2h} by induction (Haase, Kramer, Kramer & Lalvani, 1987).

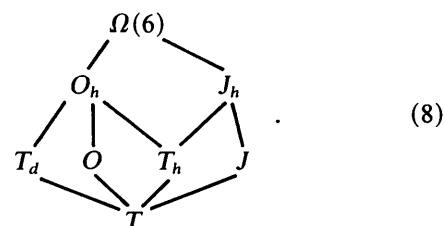
From (6) and Table 1 we establish the following results: The generators g and hence the cubic groups are embedded into the hyperoctahedral group through $\tilde{D}^6(g)$. The 6×6 representation $\tilde{D}^6(g)$ is explicitly reduced by the matrix m^c in the block-diagonal form

$$m^c\tilde{D}^6(g)(m^c)^{-1} = D^6(g) = D_1^3(g) + D_2^3(g). \quad (7)$$

The representations D_1^3 and D_2^3 are irreducible and are related in Table 2 to standard notation as given by Lax (1974).

Consider now the embedding of the icosahedral group J into $\Omega(6)$ proposed by Kramer & Neri (1984).

This embedding may be modified for the present setting of the generators g_2 and g_3 with the new generator g_5 given in Table 1. The group-subgroup diagram for the present purpose then becomes



2. The representation of the tetrahedral group T and the Schur rotation from cubic to icosahedral point symmetry

Consider the tetrahedral subgroup $T \sim 23$ of $\Omega(6)$. The reduced form $D^6 \downarrow T$ of its representation from Tables 1 and 2 becomes

$$D^6 \downarrow T = \begin{vmatrix} \Gamma_4 & 0 \\ 0 & \Gamma_4 \end{vmatrix}, \quad (9)$$

where the irreducible representation Γ_4 appears twice in identical form. Schur (1905) in his celebrated lemma considered a matrix M which commutes with all matrices of a group representation D . He showed that if D is irreducible then the matrix M must be a multiple of the identity.

We look now for 6×6 matrices M fulfilling

$$MD^6(g) = D^6(g)M \quad \text{for all } g \in T. \quad (10)$$

Table 2. Generators and irreducible representations D_1^3 and D_2^3 of cubic icosahedral groups G in the notation of Lax (1974)

G	Order	Generators	D_1^3	D_2^3
$T, 23$	12	g_2, g_3	Γ_4	Γ_4
$O, 432$	24	g_2, g_3, g_4	Γ_4	Γ_5
$T_h, m\bar{3}$	24	g_2, g_3, i_2	Γ_4^-	Γ_4^-
$T_d, \bar{4}3m$	48	g_2, g_3, h_2	Γ_5	Γ_4
$O_h, m\bar{3}m$	48	g_2, g_3, g_4, i_2	Γ_4^-	Γ_5^*
$J, 235$	60	g_2, g_3, g_5	$[31_4^+]$	$[31_4^+]$ †
$J_h, m\bar{3}\bar{5}$	120	g_2, g_3, g_5, i_2	$[31_4^+]$	$[31_4^+]$

* Notation for $O < O_h$.
 † Notation from Haase, Kramer, Kramer & Lalvani (1987).

We are interested only in orthogonal matrices M . Application of Schur's lemma to D^6 from (9) and use of the irreducibility of Γ_4 yields that M must correspond to an element of the orthogonal group $O(2, \mathbb{R})$ which in block form may be parametrized as

$$M = \begin{pmatrix} I_3 \cos \beta & \mp I_3 \sin \beta \\ I_3 \sin \beta & \pm I_3 \cos \beta \end{pmatrix}, \quad 0 \leq \beta < \pi \quad (11)$$

where I_3 denotes the 3×3 unit matrix. For present purposes it suffices to consider only the upper sign in (11) so that $M = M(\beta)$ describes an element of $SO(2, \mathbb{R})$ which we call a Schur rotation.

Since the Schur rotation $M(\beta)$ commutes with $D^6 \downarrow T$, we are free to rotate m^c according to

$$m^c \rightarrow m(\beta) = M(\beta)m^c. \quad (12)$$

An explicit computation of $m(\beta)$ yields

$$m(\beta) = \sqrt{\frac{1}{2}} \begin{pmatrix} 0 & c & s & 0 & c & \bar{s} \\ s & 0 & c & \bar{s} & 0 & c \\ c & s & 0 & c & \bar{s} & 0 \\ 0 & \bar{s} & c & 0 & \bar{s} & \bar{c} \\ c & 0 & \bar{s} & \bar{c} & 0 & \bar{s} \\ \bar{s} & c & 0 & \bar{s} & \bar{c} & 0 \end{pmatrix}, \quad (13)$$

where

$$\begin{aligned} c &= \cos \alpha, & s &= \sin \alpha, \\ \bar{c} &= -\cos \alpha, & \bar{s} &= -\sin \alpha, \\ \alpha &= (\pi/4) - \beta, & \cot 2\alpha &= \tan 2\beta. \end{aligned}$$

For the tetrahedral group, we have then found a continuous family of matrices $m(\beta)$ which reduce the representation $\bar{D}^6 \downarrow T$.

Consider now the other cubic groups O and T_d obtained by extension of T . In both cases the irreducible representations D_1^3 and D_2^3 are inequivalent (cf. Table 2) and Schur's lemma enforces $\beta = 0$, $m = M(0) = m^c$.

Next consider the icosahedral group J which has the tetrahedral group T as a subgroup. From Kramer & Neri (1984) we know that there exists a reduced form with

$$D^6 \downarrow J = \begin{pmatrix} D_1^3 & 0 \\ 0 & D_2^3 \end{pmatrix}, \quad (14)$$

where D_1^3 and D_2^3 are two inequivalent irreducible representations denoted in Kramer & Neri (1984) by i and ω and in Haase *et al.* (1987) by $[31_+^2]$ and $[31_-^2]$. If we choose the restrictions to T as $D_1^3 \downarrow T = \Gamma_4 = D_2^3 \downarrow T$, there should exist a Schur rotation $M(\beta^i)$ such that $D^6 \downarrow J$ takes the form (14). The angle β^i is found by inspection of $m(\beta)$ to be

$$\begin{aligned} \beta^i: \tan 2\beta^i &= \frac{1}{2}, & \beta^i &= 13 \cdot 2825^\circ \\ \tan 2\alpha^i &= 2, & \alpha^i &= 31 \cdot 7174^\circ. \end{aligned} \quad (15)$$

We have found then that, among the continuous family of reductions $\Omega(6) > T$ obtained by a Schur rotation, the reduction to cubic point symmetry $\Omega(6) > O, T_d$ occurs at $\beta = \beta^c = 0$ and the reduction to icosahedral point symmetry $\Omega(6) > J$ at $\beta = \beta^i = 13 \cdot 2825^\circ$. The six vectors associated with the face-centred cubic order are continuously transformed into the six vectors associated with icosahedral order and perpendicular to the faces of the regular dodecahedron.

3. First application to lattices and quasilattices in \mathbb{E}^3

In the general projection method described by Kramer & Neri (1984), the projections of hyperplanes from a periodic lattice in \mathbb{E}^n yield in \mathbb{E}^3 an n -grid whose sets of planes are orthogonal to the projections of the basis vectors from \mathbb{E}^n to \mathbb{E}^3 . A quasilattice is constructed from the n -grid by dualization. The edges of the quasilattice are formed from the projections of the basis vectors. This construction applies in particular to the projection from \mathbb{E}^6 to a quasilattice in \mathbb{E}^3 associated with the representation $[31_+^2]$ of the icosahedral group (Kramer & Neri, 1984; Kramer, 1985, 1986).

Consider now the hypercubic lattice in \mathbb{E}^6 and the projection of its six basis vectors to the space \mathbb{E}_1^3 obtained from $m(\beta)$ [(13)] as the three top lines. The six projected vectors define a hexagrid in \mathbb{E}_1^3 and a corresponding quasilattice for any β . We obtain:

(a) for $0 \leq \beta < \pi$, a continuous family of quasilattices compatible with tetrahedral point symmetry, and periodic for $\beta = 0, \beta = \pi/4, \beta = 3\pi/4$;

(b) for $\beta = \beta^c = 0$ cubic periodic lattices and in particular the face-centred cubic lattice with cubic point symmetry;

(c) for $\beta = \beta^i = 13 \cdot 2825^\circ$ a quasilattice which is non-periodic and is compatible with icosahedral point symmetry.

The symmetric 6×6 matrix formed by the scalar products of the six projected vectors in \mathbb{E}_1^3 is given in Table 3.

4. Concluding remarks

In the third part of this article attention was directed to the continuous rotation from the face-centred cubic lattice to the icosahedral quasilattice. The Schur rota-

Table 3. *Scalar products of the six projected vectors in E_1^3 appearing in the three top rows of $m(\beta)$, equation (13), multiplied by 2*

	1	2	3	4	5	6
1	1	cs	cs	$c^2 - s^2$	$-cs$	cs
2		1	cs	cs	$c^2 - s^2$	$-cs$
3			1	$-cs$	cs	$c^2 - s^2$
4				1	$-cs$	$-cs$
5					1	$-cs$
6						1

tion preserves the tetrahedral symmetry and hence three twofold and four threefold axes. This may be part of the answer to the question why Guyot & Audier (1985) and Audier & Guyot (1986) in their models find a smooth connection of the cubic and icosahedral structure along a threefold axis. Note that the vectors corresponding to columns 4, 5, 6 of $m(\beta)$ in E_1^3 are in a plane for $\beta = 0$ and span the thin rhombohedron for $\beta = 13.28^\circ$. Clearly a study of the diffraction pattern is required as a function of β .

The group-subgroup analysis given in the second part does not depend on the choice of the face-centred cubic lattice in E_1^3 . The same Schur rotation applies to other cubic lattices in E_1^3 and their parent lattices in E^6 . The Schur rotations could be considered in the Landau theory for the stability problems as analysed, for example, by Bak (1985). In this relation we note that Birman (1966) has proposed and applied group-subgroup techniques for second-order phase transitions. The scheme of equation (8) suggests the extension of this approach to higher point groups.

It was proposed by Kramer & Neri (1984) to select, among the many possible projections from spaces of

higher dimension, the ones compatible with a point-group symmetry. The present use of a Schur rotation shows that many symmetry elements may be preserved even when going from periodic to non-periodic order. It is tempting to think of other Schur rotations which might unify the understanding of the new phases of condensed matter and of their relation to known periodic phases.

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Acta Cryst. (1987). **A43**, 489-501

An Efficient General-Purpose Least-Squares Refinement Program for Macromolecular Structures

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(Received 16 July 1986; accepted 12 November 1986)

Abstract

A package of programs has been developed for efficient restrained least-squares refinement of macromolecular crystal structures. The package has been designed to be as flexible and general purpose as possible. The process of refinement is divided into basic units and an independent computer program

handles each task. Each functional unit communicates with other programs in the package by way of files of well defined format. To modify or replace any program, the user need only understand the function of that particular element. Stereochemical restraints are defined in a general way that can be applied to proteins, nucleic acids, prosthetic groups, solvent atoms and so on. Guide values for bond lengths and bond angles are specified in a straightforward direct manner. Designated groups of atoms can be held

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