

refinement for low-symmetry SSG P_{111}^{P4ncc} with harmonic displacive modulations and with 44 positional parameters was performed. It yielded an R factor of 0.054. Results of all these refinements are collected in Table 4. For the last two refinements corresponding atomic positional coordinates in the superstructure are not exactly related by the inversion centre (the discrepancy exceeds a few standard deviations). However, taking into account the number of structural parameters and the minor differences in R values obtained by different models, it can be concluded that the SSG description of the TaTe₄ structure at room temperature with $P_{111}^{P4/ncc}$ as well as the corresponding centrosymmetric SG $P4/ncc$, represent very good approximations.

5. Conclusions

It is shown that the room-temperature TaTe₄ superstructure ($2a \times 2a \times 3c$) can be described as a commensurately modulated basic structure ($2a \times 2a \times c$) with $\mathbf{q} = (00\frac{2}{3})$. The SSG $P_{111}^{P4/ncc}$ describes not only the structural symmetry and relations between coordinates of groups of atoms but also predicts extinction rules which are, together with additional conditions on reflections, in agreement with experiment. The origin of these additional limitations is also explained.

Analysis of different 'real' sections through the supercrystal gives a more general insight into the problem of centro- or noncentrosymmetry of the room-temperature TaTe₄ modulated structure. The refinements show that the choice of SG $P4/ncc$ (Bronsema *et al.*, 1987) is justified on basis of a reduced number of parameters needed for the structure description. It is also shown that this reduction

does not, at least significantly, increase the discrepancy factor R .

We acknowledge useful discussions with Dr W. A. Paciorek and Dr J. Kusz as well as their help in modifying the refinement program. The Executive Secretary of the International Union of Crystallography is thanked for providing X-ray data and Mrs B. Koziol and Mrs. Z. Škraba for their technical assistance.

References

- BJERKELUND, E. & KJEKSHUS, A. (1964). *J. Less Common Met.* **7**, 231–234.
- BRONSEMA, K. D., VAN SMAALEN, S., DE BOER, J. L., WIEGERS, G. A., JELLINEK, F. & MAHY, J. (1987). *Acta Cryst.* **B43**, 305–313.
- CORBETT, J. M., HILTZ, L. G., BOSWELL, F. W., BENNET, J. C. & PRODAN, A. (1988). *Ultramicroscopy*, **26**, 43–50.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DAMM, B. & JANNER, A. (1986). *Acta Cryst.* **B42**, 69–77.
- JANSSEN, T. & JANNER, A. (1987). *Adv. Phys.* **36**, 519–624.
- MAHY, J., VAN LANDYUT, J. & AMELINCKX, S. (1987). *Phys. Status Solidi A*, **102**, 609–618.
- PACIOREK, W. A. & ŁUKASZEWICZ, K. (1987). *Fizyka i Chemia Ciężkich Metali*, Vol. 2, *Wybrane Zagadnienia*, edited by J. Z. DAMM & J. KLAMUT, pp. 9–40. Warsaw: Ossolineum.
- PACIOREK, W. A. & USZYŃSKI, I. (1987). *J. Appl. Cryst.* **20**, 57–59.
- PÉREZ-MATO, J. M., MADARIAGA, G., ZUÑIGA, F. J. & GARCÍA ARRIBAS, A. (1987). *Acta Cryst.* **A43**, 216–226.
- SAHU, D. & WALKER, M. B. (1985). *Phys. Rev. B*, **32**, 1643–1648.
- SMAALEN, S. VAN (1985). PhD Thesis, Univ. of Groningen, The Netherlands.
- SMAALEN, S. VAN (1987). *Acta Cryst.* **A43**, 202–207.
- SMAALEN, S. VAN, BRONSEMA, K. D. & MAHY, J. (1986). *Acta Cryst.* **B42**, 43–50.
- WALKER, M. B. (1985). *Can. J. Phys.* **63**, 46–49.
- WOLFF, P. M. DE (1984). *Acta Cryst.* **A40**, 34–42.
- WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* **A37**, 625–636.
- YAMAMOTO, A. (1982). *Acta Cryst.* **B38**, 1446–1451, 1451–1456.
- YAMAMOTO, A. & NAKAZAWA, H. (1982). *Acta Cryst.* **A38**, 79–86.

Acta Cryst. (1989). **B45**, 534–542

Five-Dimensional Patterson Analysis of the Decagonal Phase of the System Al–Mn

BY WALTER STEURER

Institut für Kristallographie und Mineralogie der Universität, Theresienstrasse 41, D-8000 München 2, Federal Republic of Germany

(Received 10 November 1988; accepted 3 July 1989)

Abstract

A complete single-crystal X-ray data set with 1807 unique reflections has been measured for the metastable decagonal phase of the system Al–Mn with the composition Al₇₈₍₂₎Mn₂₂₍₂₎. A Patterson analysis describing the quasicrystal in five-dimensional space has been carried out in which full lattice periodicity

is restored and a structure model suggested. The quasicrystal has superspace group $P10_5/mmc$ and is built up by six non-equidistant slightly puckered layers two of which are in the asymmetric unit. To a first approximation each layer can be represented by a different decorated partial Penrose pattern. With the aid of higher-dimensional Patterson analysis, the local isomorphism class was determined. Displacive

disorder is present perpendicular rather than parallel to the aperiodic layers.

Introduction

The discovery of the first decagonal phase in the system Al-Mn (Bendersky, 1985) and subsequent observations of decagonal phases in many other binary and ternary alloys (*cf.* Steurer & Mayer, 1989) have led to numerous attempts to elucidate the structures of these two-dimensional quasicrystals. Because of the lower symmetry and the layer structure, the structure solution is much more difficult than for the icosahedral phases. Indeed, for some icosahedral phases structure refinements have been carried out successfully in a semi-quantitative way (Elswijk, de Hosson, van Smaalen & de Boer, 1988) whereas, owing to the lack of appropriate single crystals, nothing comparable has been possible for the decagonal phases. Therefore, besides the fundamental theoretical studies of the characteristics of two- and three-dimensional quasicrystals (Jarić, 1986; Levine & Steinhardt, 1986; Socolar & Steinhardt, 1986), electron diffraction and spectroscopical investigations have quantitatively determined only partial aspects of the two-dimensional quasicrystalline structures.

All diffraction studies on the decagonal phase of Al-Mn except that of Steurer & Mayer (1989) have been performed using selected-area and convergent-beam electron diffraction (Bendersky, 1985) or, in some rare cases, X-ray powder diffraction (Koopmans, Schurer, van der Woude & Bronsveld, 1987). With these techniques the point symmetry and the metrics of decagonal Al-Mn have been obtained. It was shown by Ho (1986) that though the metrics of the reciprocal lattices of the icosahedral and decagonal phases are closely related to each other their real structures differ by more than small atomic shifts. These relationships are also discussed by Fung, Yang, Zhou, Zhao, Zhan & Shen (1986). They demonstrate that the symmetry of decagonal Al-Mn can be obtained by introducing into icosahedral Al-Mn a set of reflection planes normal to the existing ones which intersect in a fivefold axis. These additional mirror planes prohibit a closer structural relationship between these quasicrystalline phases.

The local order of decagonal Al-Mn has been studied by EXAFS, NMR and Mössbauer techniques. Bridges, Boyce, Dimino & Giessen (1987) found from their EXAFS measurements that the average number of Al atoms surrounding a central Mn atom is eight for the decagonal phase, smaller than the ten observed for the icosahedral phase. On this basis, they are of the opinion that the two phases have very different structures. EXAFS investigations by Schurer, van Netten & Niesen (1988) suggested 9

± 1 nearest-neighbour Al atoms and a different structural interpretation. They assume a high similarity of both structures with the same icosahedral basic elements (Mackay icosahedra, for example).

Mössbauer-effect studies (Koopmans, Schurer, van der Woude & Bronsveld, 1987) show that the local iron environment in decagonal Al-(Mn,Fe) is similar but less asymmetric than in the icosahedral phase and that the (Fe,Mn) atoms have Al next-nearest neighbours only.

A comparative discussion of the different periodicities along the tenfold axis of the decagonal quasicrystals of different composition, and of the possible relations to the respective crystalline phases, has been undertaken by Li & Kuo (1988) and He, Wu & Kuo (1989). They demonstrate that the translational periods are always multiples of a 4 Å basic double layer. Examples with one-, two-, three- and fourfold superperiods are presented and compared with the lattice parameters of the crystalline phases. In the case of the system Al-Mn the tenfold axis corresponds to the *b* axis of Al₁₁Mn₄.

A detailed discussion of the possible structures of decagonal Al-Mn and decagonal Al-Fe has been given by Ishihara & Yamamoto (1988) and Yamamoto & Ishihara (1988). They interpret the electron diffraction patterns with models consisting of four kinds of layers which represent partial Penrose patterns. Projecting the crystal structure down the tenfold axis the complete Penrose pattern is obtained again.

The fundamental problem with all the structure investigations up to now is that all discussions deal only with the best way of decorating a quasilattice with atoms and do not consider how to select the right quasilattice. Hence, the original Penrose tiling has always been chosen as a model for the quasilattice in a completely arbitrary manner. As mentioned by Steinhardt (1987), an infinite number of different general Penrose quasilattices exist which belong to different local isomorphism classes and give, if selected for a decoration with atoms, different quasicrystal structures with, however, only slightly different diffraction patterns. This has to be taken into account to perform a correct structure analysis, and if the decoration method is used the correct quasilattice has to be determined first. However, as pointed out by Jarić (1986) it would not be possible generally to separate the problem of the determination of the local isomorphism class from that of the decoration of the quasilattice by atoms.

This is a strong argument for higher-dimensional structure analysis (*cf.* Janssen, 1986*a,b*). In this approach, the aperiodic structure is embedded in an appropriate higher-dimensional space \mathbb{R}_r , so that full lattice periodicity is obtained. Then the real quasicrystal structure results as a section of the

n -dimensional supercrystal with three-dimensional physical space. The main problem with this description is to obtain the correct analytical expression for the atoms of such a supercrystal as this might involve rather complicated hypersurfaces (Bak, 1986).

A good start for a structure analysis of decagonal Al-Mn, therefore, is to study the n -dimensional Fourier transform of the X-ray diffraction pattern. In other words this necessitates carrying out a higher-dimensional Patterson analysis, without the need for a structural model, and learning something about the distribution and the shape of the n -dimensional atoms in the n -dimensional unit cell. The type of quasicrystalline arrangement of the atoms in the layers, *i.e.* the local isomorphism class *and* the decoration of the quasilattice then result automatically from the section of the supercrystal structure with physical space. The present work represents the first step of such a study.

Symmetry and metrics

A detailed analysis of the X-ray diffraction patterns of the decagonal phase in the system Al-Mn (Steurer & Mayer, 1989) shows that the point symmetry of the reciprocal lattice is $10/mmm$ (D_{10h}). All reciprocal lattice vectors of each quasiperiodic reciprocal lattice layer can be represented by linear combinations of five basis vectors pointing to the corners of a regular pentagon $\mathbf{a}_i^* = a_i^*(\cos 2\pi i/5, \sin 2\pi i/5, 0)$ with $i = 0, \dots, 4$. The vector components refer to a Cartesian coordinate system with unit vectors $\mathbf{v}_1, \mathbf{v}_2$ and \mathbf{v}_3 . Four of the five vectors are rationally independent. This is the same basis-vector set as used for the description of the hypothetical diffraction pattern of the Penrose tiling (*cf.* Janssen, 1986*a,b*). Perpendicular to the plane formed by this basis-vector set and parallel to the tenfold axis a further reciprocal basis vector $\mathbf{a}_5^* = a_5^*(0, 0, 1)$ is required. The set \mathbf{M}^* of all reciprocal vectors $\mathbf{H}_E = \sum_{i=1}^5 h_i \mathbf{a}_i^*$ remains invariant under the action of the symmetry operators of the group D_{10h} . For the tenfold rotation α , the reflection plane β and the inversion center γ , the matrix representations are given by

$$\Gamma(\alpha) = \begin{pmatrix} 0 & 0 & 0 & \bar{1} & 0 \\ 1 & 1 & 1 & 1 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \Gamma(\beta) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(\gamma) = \begin{pmatrix} \bar{1} & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 0 & \bar{1} \end{pmatrix}$$

Now we follow the scheme given by Janssen (1986*b*) to derive the basis for embedding our quasilattice of rank five in the five-dimensional space \mathbb{R}_5 . It would not be correct to take the decagonal lattice derived for the two-dimensional Penrose tiling and simply add a fifth basis vector [as was done by Yamamoto & Ishihara (1988)]. The characters of the representation of D_{10} $\chi(\varepsilon, \alpha, \alpha^2, \alpha^3, \alpha^4, \alpha^5, \beta, \alpha\beta) = \chi(5, 2, 0, 2, 0, -3, 1, 1)$ correspond to the sum of the characters of the irreducible representations $\Gamma_5 + \Gamma_1 + \Gamma_7$ [*cf.* Tables 1 and 2 of Janssen (1986*b*)]. Using these decompositions our matrix representation $\Gamma(\alpha)$, for example can be written in the form

$$\Gamma(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 & 0 & 0 \\ \sin\alpha & \cos\alpha & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \cos 3\alpha & -\sin 3\alpha \\ 0 & 0 & 0 & \sin 3\alpha & \cos 3\alpha \end{pmatrix}$$

$$= \begin{pmatrix} \Gamma_E(\alpha) & 0 \\ 0 & \Gamma_I(\alpha) \end{pmatrix}$$

The five-dimensional configurational space \mathbf{V} can be decomposed in this way into two orthogonal subspaces: the three-dimensional physical (external, parallel) space \mathbf{V}_E and the two-dimensional complement (internal, perpendicular) space \mathbf{V}_I . From the matrix representation we find that a 36° rotation in the physical space is accompanied by a 108° rotation in the internal space (coupling factor 3). For the two-dimensional Penrose quasilattice embedded in the \mathbb{R}_4 (Janssen, 1986*b*) there is a coupling factor of 2.

A basis for the representation of the lattice Σ^* in the five-dimensional configuration space \mathbf{V} which is projected parallel to \mathbf{V}_I onto \mathbf{M}^* and is invariant under the action of the group D_{10h} can then be written as $\mathbf{d}_i^* = (\mathbf{a}_i^*, 0, c\mathbf{a}_{3i}^*)$ with $i = 1, \dots, 4$ and $\mathbf{d}_5^* = (0, \mathbf{a}_5^*, 0)$ (short \mathbf{D} basis). The parameter c can be chosen arbitrarily without any consequence for the physical space. If we refer the vectors \mathbf{a}_i^* to a five-dimensional orthogonal coordinate system with unit vectors $\mathbf{v}_i, \mathbf{v}_i^*$ with $\mathbf{v}_i \cdot \mathbf{v}_i^* = \delta_{ij}$ (short \mathbf{V} basis) then we obtain the expression $\mathbf{d}_i^* = a_i^*(\cos 2\pi i/5, \sin 2\pi i/5, 0, c\cos 6\pi i/5, c\sin 6\pi i/5)$ with $i = 1, \dots, 4$ and $\mathbf{d}_5^* = a_5^*(0, 1, 0)$. It should be kept in mind that the vectors $\mathbf{v}_i, \mathbf{v}_i^*$ with $i = 1, 2, 3$ belong \mathbf{V}_E and those with $i = 4, 5$ to \mathbf{V}_I . The reciprocal-lattice vector on the \mathbf{D} basis has the form $\mathbf{H} = \sum_{i=1}^5 h_i \mathbf{d}_i^*$.

The basis of the direct five-dimensional lattice Σ is easily constructed by using the relationships $\mathbf{d}_i^* = a_i^* \sum_{j=1}^5 U_{ji} \mathbf{v}_j^*$ and $\mathbf{d}_i = 1/a_i^* \sum_{j=1}^5 u_{ij} \mathbf{v}_j$ with $(U_{ji}) = [(u_{ij})^{-1}]^T$ and we obtain $\mathbf{d}_i = 2/(5a_i^*)(\cos 2\pi i/5 - 1, \sin 2\pi i/5, 0, c\cos 6\pi i/5 - 1, c\sin 6\pi i/5)$ with $i = 1, \dots, 4$, $\mathbf{d}_5 = 1/a_5^*(0, 0, 1, 0, 0)$ and $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$. The metric

tensor \mathbf{g} of the lattices Σ^* and Σ for the simple case $c = 1$ is given by

$$\mathbf{g} = \begin{pmatrix} A & C & C & C & 0 \\ C & A & C & C & 0 \\ C & C & A & C & 0 \\ C & C & C & A & 0 \\ 0 & 0 & 0 & 0 & B \end{pmatrix}$$

with $A = \mathbf{d}_i^* \cdot \mathbf{d}_i^* = 2a_i^{*2}$, $B = \mathbf{d}_5^* \cdot \mathbf{d}_5^* = a_5^{*2}$ and $C = \mathbf{d}_i^* \cdot \mathbf{d}_{j \neq i}^* = -1/2a_i^{*2} = d_i^* d_j^* \cos 104.5^\circ$ for the reciprocal lattice Σ^* and $A = \mathbf{d}_i \cdot \mathbf{d}_i = 4/(5a_i^{*2})$, $B = \mathbf{d}_5 \cdot \mathbf{d}_5 = 1/a_5^{*2}$ and $C = \mathbf{d}_i \cdot \mathbf{d}_{j \neq i} = 2/(5a_i^{*2}) = d_i d_j \cos 60^\circ$ for the direct lattice Σ . Inserting the experimental values $a_i^* = 0.2556(1) \text{ \AA}^{-1}$, $i = 1, \dots, 4$ and $a_5^* = 0.08065(5) \text{ \AA}^{-1}$ (Steurer & Mayer, 1989) we obtain $d_i^* = 2^{1/2} a_i^* = 0.3615(1) \text{ \AA}^{-1}$, $i = 1, 4$ and $d_5^* = 0.08065(5) \text{ \AA}^{-1}$ and $d_i = 2/(5^{1/2} a_i^*) = 3.499(1) \text{ \AA}$, $i = 1, 4$ and $d_5 = 12.400(7) \text{ \AA}$.

Since it is impossible to determine a_i^* in a unique way we always have the possibility of taking multiples of πa_i^* or a_i^*/τ instead. But this has no influence on the absolute distances between the peaks in a Patterson diagram.

Experimental

The preparation of crystals of the sample was described by Steurer & Mayer (1989). The crystal was mounted on top of a glass capillary with the tenfold axis approximately parallel to the capillary. Because of the pseudoicosahedral symmetry, the search for metrics was not successful. Therefore the crystal was first aligned by X-ray film methods and the metrics then easily found. The lattice parameters were refined from a set of 25 reflections.

Data collection: Enraf-Nonius CAD-4 four-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator. In a first run all reflections in the asymmetric unit within $0 \leq \theta \leq 30^\circ$ and $-3 \leq h_i \leq 3$ ($i = 1, 4$), $0 \leq h_5 \leq 17$ were collected with a constant scan time of 4 min per reflection. Of the 1807 reflections measured 332 had intensities $I > 2\sigma(I)$ and were measured again with the symmetrically equivalent reflections in all decants.

The full set of 5189 reflections was averaged with an internal R factor $R_i = 0.052$ yielding 1807 independent reflections. The standard deviations were calculated from the averaging of at least ten intensities in each case.

Systematic absences: $0000h_5$ and $h_1 h_1 00 h_5$ with $h_5 = 2n + 1$ indicating a tenfold screw axis 10_5 parallel $[00001]$ and a glide plane $\{11000\}$ with a glide component of $\frac{1}{2}$ along $[00001]$; the absences were consistent with five-dimensional space groups $P10_5/mmc$ or $P10_5mc$. With convergent-beam electron diffraction, a reflection plane perpendicular to the tenfold axis was found (Bendersky, 1985) ruling $P10_5mc$ out.

Higher-dimensional Patterson functions (PF's)

The principles

The higher-dimensional PF has been used successfully in the analysis of incommensurately modulated structures (Steurer, 1987; Steurer & Jagodzinski, 1988) and can be applied to the analysis of quasicrystalline structures in an analogous manner (Cahn, Gratias & Mozer, 1988). Geometrically, the Patterson function is defined as the map of all possible weighted vectors between the atoms of a crystal structure. In the case of an incommensurately modulated structure embedded in \mathbb{R}_{3+d} space the atoms are continuous in the internal space. Consequently, the $(3+d)$ -PF is continuous in this space too.

If we apply this approach to structures that are quasicrystalline in one, two or three dimensions then the n -dimensional atoms can be represented by spheres as usual in physical space and by lines, pentagons or triacontahedrons, respectively, in orthogonal subspace. The n -dimensional PF represents the weighted-vector diagram between such n -dimensional atoms.

What can we learn from such a higher-dimensional PF? First, we obtain information about the occupation of the equipoints in the unit cell and can compare it with mathematical models (two- or three-dimensional Penrose quasilattices, for example). It can be easily recognized whether or not only the vertices of a quasilattice are decorated since in that case additional sites in the n -dimensional unit cell would be occupied or the atoms would be enlarged parallel to the internal space V_I . Second, we get an idea about the amount of displacive disorder in both the external and the internal spaces by studying the half-widths of the Patterson maxima in both spaces. Third, at least in some special cases, the local isomorphism class can be determined because the size, shape and distribution of the n -dimensional atoms in the n -dimensional unit cell depend on the local isomorphism class.

In contrast, the conventional three-dimensional PF allows a better visualization of the real crystal structure but the identical information content is much more difficult to interpret and to characterize. A combination of sections of both types of PF's will give the most transparent structure information (*cf.* Cahn, Gratias & Mozer, 1988) showing the correspondence between n -dimensional and real structure directly.

Symmetry and metrics in Patterson space

The five-dimensional PF can be calculated with the formula $P(\mathbf{U}) = \sum_{\mathbf{H}} I(\mathbf{H}) \cos(2\pi \mathbf{H} \cdot \mathbf{U})$. \mathbf{U} is the five-dimensional vector $\mathbf{U} = \sum_{i=1}^5 u_i \mathbf{d}_i$ and \mathbf{H} the five-dimensional reciprocal-lattice vector $\mathbf{H} = \sum_{i=1}^5 h_i \mathbf{d}_i^*$.

The vector lattice obtained (**D** basis) is inherently centrosymmetric and has the supersymmetry $P10/mmm$. Transforming the indices using the relation $h_i^v = \sum_{j=1}^5 U_{ij} h_j$ we switch to the **V** basis and the diffraction vector becomes $\mathbf{H} = \mathbf{H}_E + \mathbf{H}_I = \sum_{i=1}^5 h_i^v \mathbf{v}_i^*$. The metric tensor \mathbf{g} of the resulting vector lattice (**V** basis) is simply

$$\mathbf{g} = \begin{pmatrix} A & 0 & 0 & 0 & 0 \\ 0 & A & 0 & 0 & 0 \\ 0 & 0 & A & 0 & 0 \\ 0 & 0 & 0 & A & 0 \\ 0 & 0 & 0 & 0 & B \end{pmatrix}$$

with $A = \mathbf{v}_1^* \cdot \mathbf{v}_1^* / (a_1^{*2}) = 1/a_1^{*2}$ and $B = \mathbf{v}_5^* \cdot \mathbf{v}_5^* / (a_5^{*2}) = 1/a_5^{*2}$. On the reciprocal **V** basis we find $A = a_1^{*2} \mathbf{v}_1^* \cdot \mathbf{v}_1^* = a_1^{*2}$ and $B = a_5^{*2} \mathbf{v}_5^* \cdot \mathbf{v}_5^* = a_5^{*2}$. The basis-vector lengths on the orthogonal direct **V** basis correspond to $1/a_1^* = 3.912 \text{ \AA}$, $i = 1, \dots, 4$ and $1/a_5^* = 12.400 \text{ \AA}$.

Results and discussion

Patterson functions in \mathbb{R}_4 and \mathbb{R}_5 space have been calculated in two-dimensional sections as well on the **D** and **V** bases. The choice of the **V** basis allows a simple calculation of sections through physical space as well as sections combining arbitrary directions of the external and the internal space. Fig. 1 shows sections through the four-dimensional Fourier function (4-FF) and four-dimensional Patterson function (4-PF) of a hypothetical two-dimensional quasicrystal structure and the 4-PF of the projected structure of decagonal Al-Mn calculated from the $(h_1 h_2 h_3 h_4 0)$ reflections only. Since the projected structure of decagonal Al-Mn has C_{10v} symmetry, a comparison has been made using the only quasilattice exhibiting exactly this symmetry, the exceptionally singular Penrose quasilattice (Jaric, 1986), which is decorated with atoms on the vertices. The structure factors for this quasilattice have been calculated by the formula derived by Janssen (1986a) and denoted as equation (16) by him. Additionally, an artificial overall atomic scattering factor (that for Al) and an overall isotropic temperature factor ($B = 1.4 \text{ \AA}^2$) have been applied for both spaces. The reflection indices have been limited to $\sin \theta / \lambda = 0.7 \text{ \AA}^{-1}$ for the components \mathbf{H}_E . The infinite number of theoretically possible

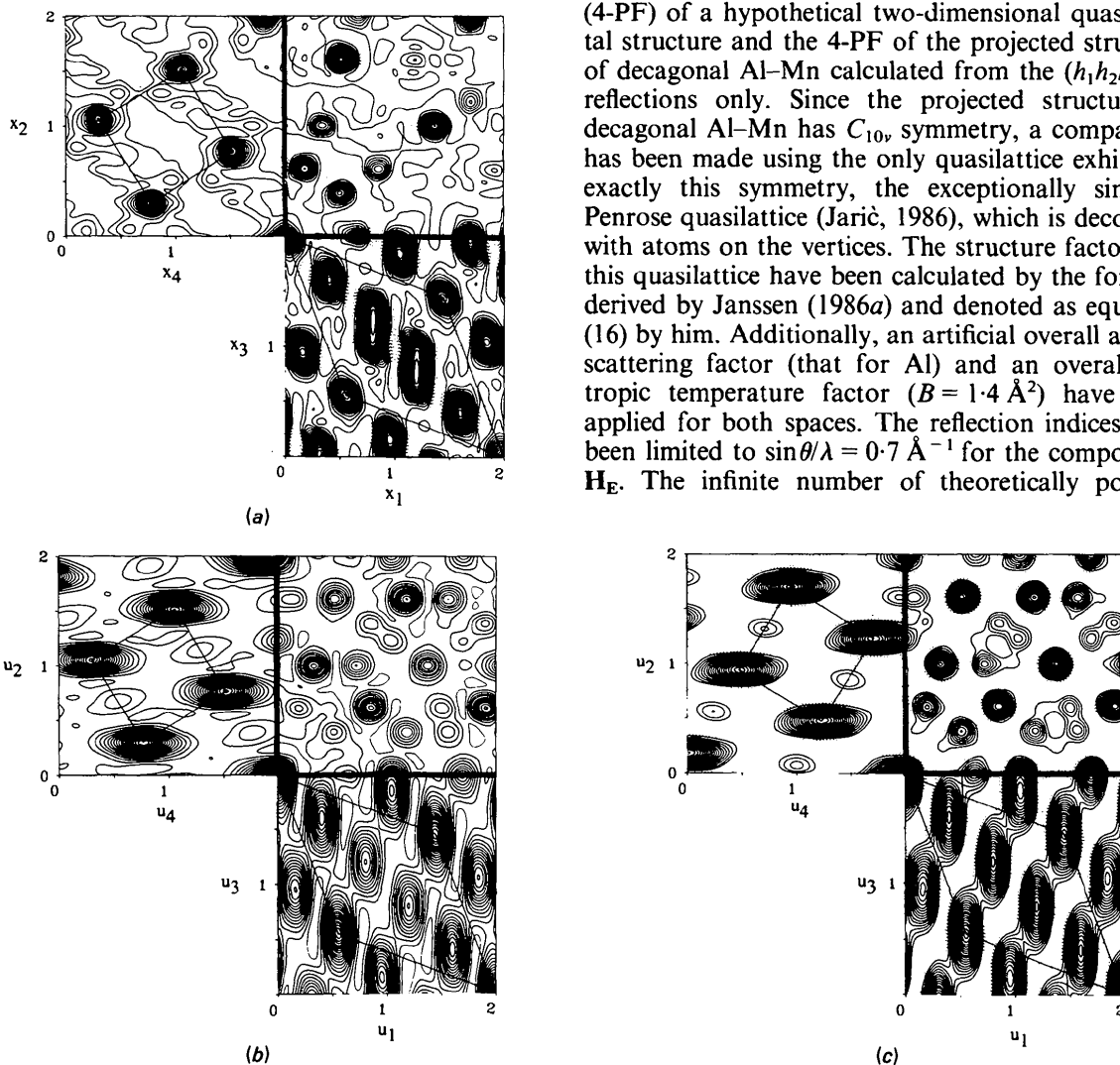


Fig. 1. **V** basis sections of (a) the four-dimensional FF of a hypothetical two-dimensional quasicrystal with an exceptionally singular Penrose quasilattice, (b) the four-dimensional PF thereof and (c) the four-dimensional PF of the projected structure of decagonal Al-Mn obtained from a calculation using $(h_1 h_2 h_3 h_4 0)$ reflections only. In all cases the (1100) section and the (1010) section orthogonal to it as well as (0101) are plotted. This combination illustrates the correspondence of the Patterson peaks in physical and four-dimensional space.

reflections within this region has been limited by the condition $|\mathbf{H}_I| \leq |\mathbf{H}_E^{\max}|$. The section of the 4-FF given in Fig. 1(a) clearly shows the positions of the five pentagonal atoms on the body diagonal of the four-dimensional unit cell at $p(\frac{1}{5}\frac{1}{5}\frac{1}{5}\frac{1}{5})$ with $p = 0, \dots, 4$ illustrated in Fig. 3 of Janssen (1986b).

What then is the meaning of the components of the atomic scattering factor and the temperature factor parallel to \mathbf{V}_I ? The smearing of the five-dimensional atoms corresponds to a kind of periodic disorder, the phason strain (Socolar, Lubensky & Steinhardt, 1986). Practically, it results in the appearance of some additional atoms in physical space but with lower probability the farther away from the center the four-dimensional atom intersects the real space. Another possible interpretation is that these larger atoms correspond to a special decoration of the basic quasilattice.

A comparison of the PF of the Penrose tiling with that of the decagonal phase (Fig. 1) shows that all peaks of both Patterson diagrams coincide although their heights naturally are different. The widths of the maxima in the physical space \mathbf{V}_E are similar indicating a normal temperature factor for the atoms of the decagonal phase. This means that the atoms show no large shifts from their mean positions. Consequently, there cannot be much displacive disorder (relaxation effects) in the layers. The widths of the Patterson peaks parallel to \mathbf{V}_I are, however, even larger than those simulated with the temperature factor for the model structure. This means that additional sites are occupied compared with the Penrose quasilattice. If this elongation of the atoms parallel to \mathbf{V}_I is present in all unit cells of the five-dimensional 'real' quasicrystal and is not the result of space and time averaging over the whole

crystal then it corresponds to an ordered decoration of the fat and thin rhombi of the basic quasilattice. If it results from an averaging of five-dimensional atoms statistically fluctuating parallel to \mathbf{V}_I around their mean positions then statistical substitutional disorder exists in the quasicrystal. Without a quantitative analysis of the diffuse scattering we cannot distinguish between these different cases.

Fig. 2 demonstrates that this elongation of the atoms parallel to \mathbf{V}_I in comparison to \mathbf{V}_E is not due to a strongly asymmetric distribution of Fourier coefficients (reflection intensities) in the internal and external spaces leading to series-termination effects as is the case, for example, for the six-dimensional PF's of icosahedral Al-Mn-Si shown in Cahn, Gratias & Mozer (1988).

The layer structure

For the study of the layer structure different sections on the \mathbf{V} basis have been calculated. Fig. 3 shows characteristic Patterson diagrams. They can be referred to a layer structure as demonstrated schematically in Fig. 5(b). The distances between the layers are not uniform as assumed recently (Yamamoto & Ishihara, 1988) and the layers are split indicating a slight roughening (about $\pm 0.1 \text{ \AA}$). Additionally, as can best be seen from the the layers of Patterson peaks with $u_3 = 0$ and $\frac{1}{2}$ some maxima are elongated normal to the layers. This suggests displacive disorder in this direction whereas the layers themselves appear to be well ordered considering the atomic positions only. Such a puckering of the layers can be expected as a relaxation effect since the lattice points (vertices) of a quasilattice have, unlike the three-dimensional translation lattices, different local

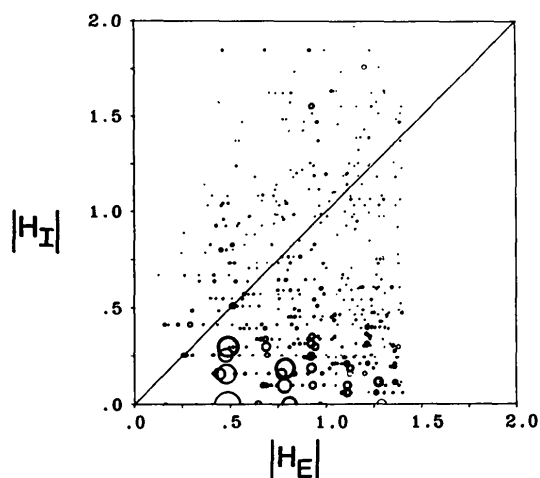


Fig. 2. Plot of the external component $|\mathbf{H}_E|$ of the diffraction vector versus the internal component $|\mathbf{H}_I|$ for all $|F| > 3\sigma(F)$. The radii of the circles are proportional to the $|F|^2$'s.

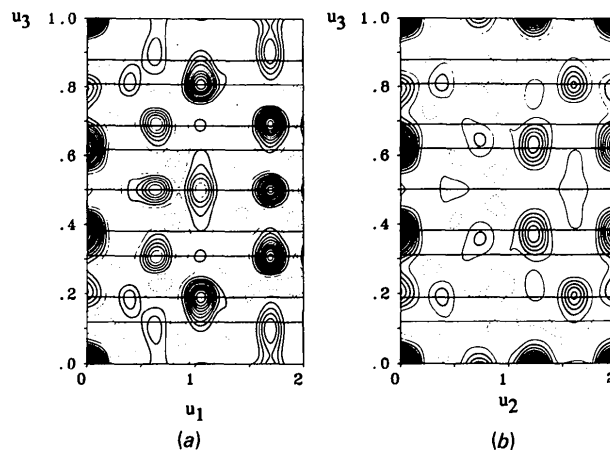


Fig. 3. Sections of the five-dimensional PF (\mathbf{V} basis) of decagonal Al-Mn. The (10100) plane is shown in (a) and the (01100) plane in (b). In both cases the tenfold axis is plotted vertically. Both sections lie fully in the external space \mathbf{V}_E . Their dimensions correspond to $12.4 \times 7.82 \text{ \AA}^2$.

coordinations. Kumar, Sahoo & Athithan (1986) in their model of the decagonal Al-Mn structure found significantly different volumes of the Voronoi cells occupied by Al which would lead to a relaxation of the lattice. This can occur in a more-or-less ordered way.

From the absent three-dimensional Patterson peak $(0\ 0\ \frac{1}{2})$ we learn that the layers must lack tenfold rotational symmetry and an inversion center. Otherwise the action of the 10_5 screw axis would generate atoms sitting one above the other giving rise to such a peak. Therefore the layer symmetry is $5m$ only.

To be sure that no other Patterson peaks exist between the layers shown in Fig. 3 we had to plot the three-dimensional PF to infinity for u_1 and u_2 . A better way to represent the same information is in a

single section of the periodic five-dimensional PF (Fig. 5a). There are no other Patterson maxima in the five-dimensional unit cell of the vector space apart from those given in this section at $(-2p/5\ 0\ 0\ -2p/5\ 0)$ with $p=0,\dots,4$. This corresponds to equidistantly spaced peaks on the body diagonal $[11011]$ of the four-dimensional subcell on the \mathbf{D} basis with the coordinates $\mathbf{u}_p = (p/5\ p/5\ u_5\ p/5\ p/5)$, $p=0,\dots,4$. These are the same equipoint positions which are occupied in the four-dimensional description of the general Penrose quasilattice. The n -dimensional atoms (occupation domains) of the different local isomorphism classes of Penrose patterns always occupy the same equipoint positions, and only differ in their size and shape [cf. Fig. 10 of Pavlovitch & Klèman (1987)]. What then is the

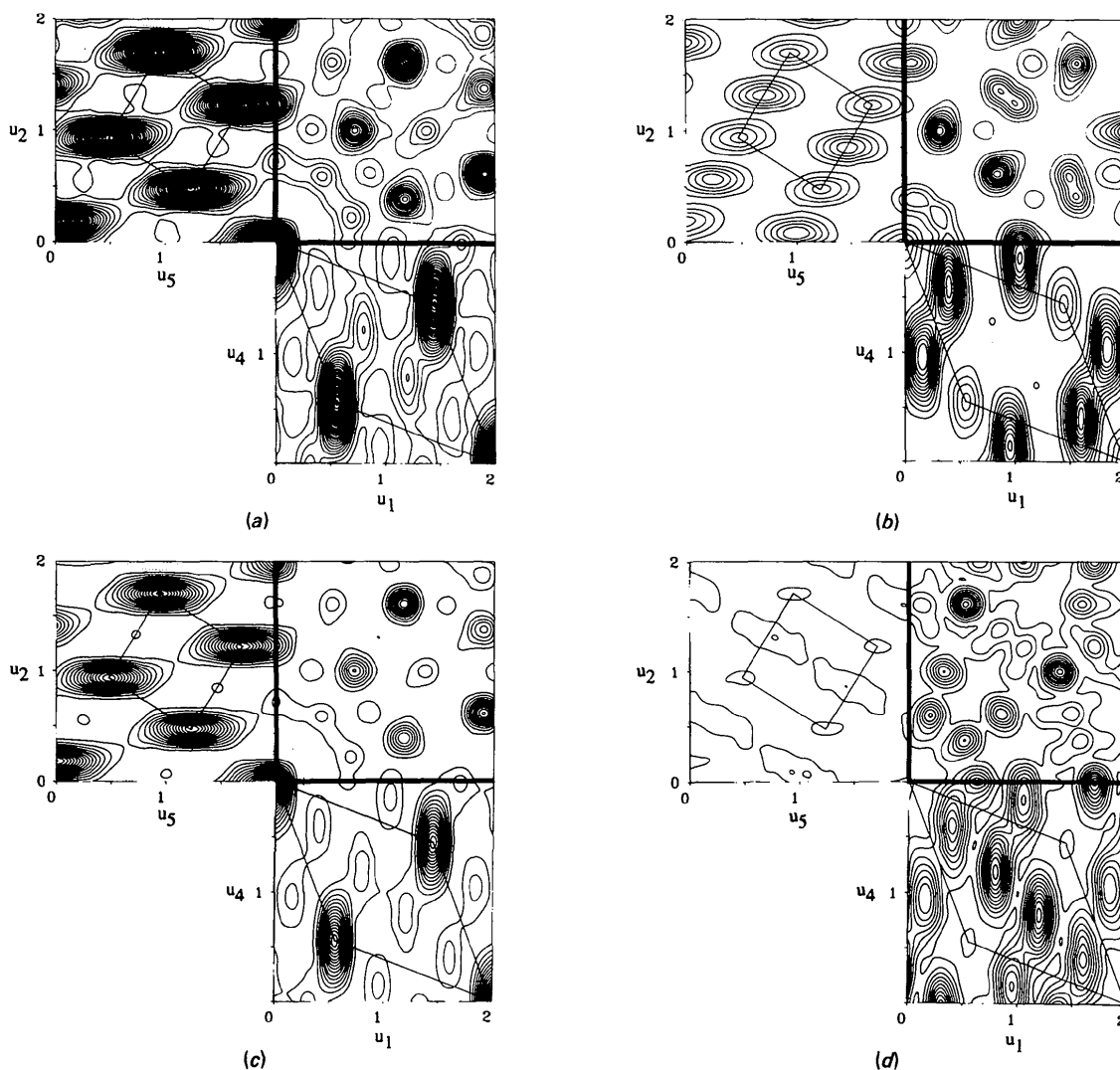


Fig. 4. Sections of the five-dimensional PF (\mathbf{V} basis) of decagonal Al-Mn for different values of u_3 corresponding to the layers shown in Fig. 3. In all cases the \mathbf{V}_E planes (11000) are plotted with the orthogonal (10010) and (01001) sections. (a) $u_3 = 0$, (b) $u_3 = 0.19$, (c) $u_3 = 0.38$, (d) $u_3 = \frac{1}{2}$.

action of the hyperscrew axis on a pentagonal atom on such a special site? If $\mathbf{x}_p = (p/5 \ p/5 \ x_5 \ p/5 \ p/5)$ denotes the five-dimensional positional vector of the atom p then a rotation of 36° acts like $\Gamma(\alpha)\mathbf{x}_p = (-p/5 \ -p/5 \ x_5 + \frac{1}{2} \ -p/5 \ -p/5)$. This corresponds to $(2p/5 \ 0 \ x_5 + \frac{1}{2} \ 2p/5 \ 0)$ on the V basis. The mirror plane $\Gamma(\beta)$ is parallel to the aperiodic layers and only changes x_5 to $\frac{1}{2} - x_5$ by its action on \mathbf{x}_p . The inversion center $\Gamma(\gamma)$ reverses the sign of \mathbf{x}_p .

The structure of the layers

Sections of the five-dimensional PF corresponding to the characteristic layer distances have been calculated (Fig. 4). All peaks are distributed equidistantly along the [11011] direction as is the case for all types of two-dimensional Penrose tilings. For each different layer the distance u_3 corresponds to a characteristic distribution of the heights of the Patterson maxima, indicating incomplete Penrose tilings. The action of the tenfold screw axis, visible in the section with $u_3 = \frac{1}{2}$, consists in interchanging the positions of the five-dimensional atoms on the [11011] axis.

From the analysis of the Patterson diagrams one is able to suggest a model for the five-dimensional unit cell as is shown in Fig. 5(b). It consists of two layers A and B both corresponding to partial Penrose patterns with plane symmetry $5m$. It is comparable in its principles with the model suggested by Yamamoto & Ishihara (1988) which, however, is not in agreement with our Patterson analysis. It is not

practically possible to extract from the shape of the peaks of the five-dimensional PF the correct size and shape of the five-dimensional atoms and to plot with this information the three-dimensional quasicrystal structure. This could only be done by a quantitative five-dimensional structure refinement. However, we can derive the local isomorphism class of the basic quasilattice considering the missing Patterson vectors $(0 \ 0 \ \frac{1}{2} \ 0 \ 0)$. From this it follows that the site with $p = 0$ is not occupied by an atom. On the other side, the only local isomorphism class of general Penrose patterns that is generated by four occupation domains in the four-dimensional unit cell is that with $\gamma = 0$ [in the terminology of Pavlovitch & Kléman (1987)], the one the original Penrose tiling belongs to. All others are generated by five atoms in the unit cell.

Summary

It has been shown by a five-dimensional Patterson analysis using X-ray single-crystal data that the quasicrystal structure of decagonal Al-Mn consists of six slightly puckered layers. Two of these belong to the asymmetric unit, the others are generated by the action of the tenfold screw axis and the reflection plane perpendicular to it. The structure projected along the screw axis has the two-dimensional point symmetry $10mm$ (C_{10v}), and shows a four-dimensional Patterson diagram similar to that of the exceptionally singular Penrose quasilattice which has the same symmetry. The distribution of atoms in the five-dimensional unit cell has been obtained from the five-dimensional PF and it was shown that the local isomorphism class of the original Penrose tiling is the only one possible. The layers, with plane symmetry $5m$, correspond to partial Penrose quasilattices. The exact shape of the five-dimensional atoms and corresponding therewith the correct structure of decagonal Al-Mn in physical space (the decoration of the basic Penrose quasilattice) can only be obtained by a subsequent five-dimensional structure refinement.

References

- BAK, P. (1986). *Phys. Rev. Lett.* **56**, 861–864.
 BENDERSKY, L. (1985). *Phys. Rev. Lett.* **55**, 1461–1463.
 BRIDGES, F., BOYCE, J. B., DIMINO, G. M. & GIessen, B. C. (1987). *Phys. Rev. B*, **36**, 8973–8978.
 CAHN, J. W., GRATIAS, D. & MOZER, B. (1988). *J. Phys. (Paris)*, **49**, 1225–1233.
 ELSWIJK, H. B., DE HOSSON, J. T. M., VAN SMAALEN, S. & DE BOER, J. L. (1988). *Phys. Rev. B*, **38**, 1681–1685.
 FUNG, K. K., YANG, C. Y., ZHOU, Y. Q., ZHAO, J. G., ZHAN, W. S. & SHEN, B. G. (1986). *Phys. Rev. Lett.* **56**, 2060–2063.
 HE, L. X., WU, Y. K. & KUO, K. H. (1989). *J. Mater. Sci.* Submitted.
 HO, T. L. (1986). *Phys. Rev. Lett.* **56**, 468–471.
 ISHIHARA, K. N. & YAMAMOTO, A. (1988). *Acta Cryst.* **A44**, 508–516.
 JANSSEN, T. (1986a). *J. Phys. (Paris) Colloq.* **3**, 85–94.

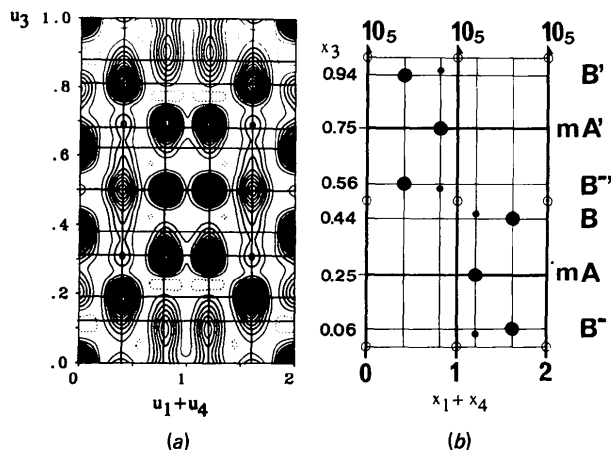


Fig. 5. (a) Five-dimensional PF of decagonal Al-Mn showing the section parallel to [10110]. The direction [10010] on the V basis corresponds to the direction [11110] on the D basis about which the structure elements of the Penrose tiling are centered. (b) A model for the characteristic section of the five-dimensional unit cell of decagonal Al-Mn derived from the five-dimensional PF. The large/small circles are responsible for the large/small Patterson peaks. The symmetry elements in this plane are marked (\circ inversion center, \uparrow 10_5 axis and m reflection plane). The layers are denoted by A and B. The action of the screw axis is marked by the superscripts ' and of the mirror by $-$.

- JANSSEN, T. (1986b). *Acta Cryst.* A42, 261–271.
 JARIĆ, M. V. (1986). *Phys. Rev. B*, 34, 4685–4698.
 KOOPMANS, A., SCHURER, P. J., VAN DER WOUDE, F. & BRONVELD, P. (1987). *Phys. Rev. B*, 35, 3005–3008.
 KUMAR, V., SAHOO, D. & ATHITHAN, G. (1986). *Phys. Rev. B*, 34, 6924–6932.
 LEVINE, D. & STEINHARDT, P. J. (1986). *Phys. Rev. B*, 34, 596–616.
 LI, X. Z. & KUO, K. H. (1988). *Philos. Mag. Lett.* 58, 167–171.
 PAVLOVITCH, A. & KLĚMAN, M. (1987). *J. Phys. A*, 20, 687–702.
 SCHURER, P. J., VAN NETTEN, T. J. & NIESEN, L. (1988). *J. Phys. (Paris)*, 49, 237–241.
 SOCOLAR, J. E., LUBENSKY, T. C. & STEINHARDT, P. J. (1986). *Phys. Rev. B*, 34, 3345–3359.
 SOCOLAR, J. E. S. & STEINHARDT, P. J. (1986). *Phys. Rev. B*, 34, 617–647.
 STEINHARDT, P. J. (1987). *Mater. Sci. Forum*, 22–24, 397–408.
 STEURER, W. (1987). *Acta Cryst.* A43, 36–42.
 STEURER, W. & JAGODZINSKI, H. (1988). *Acta Cryst.* B44, 344–351.
 STEURER, W. & MAYER, J. (1989). *Acta Cryst.* B45, 355–359.
 YAMAMOTO, A. & ISHIHARA, K. N. (1988). *Acta Cryst.* A44, 707–714.

Acta Cryst. (1989). B45, 542–549

Structure Refinements of Mg_2TiO_4 , MgTiO_3 and MgTi_2O_5 by Time-of-Flight Neutron Powder Diffraction

BY BARRY A. WECHSLER*

Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA

AND ROBERT B. VON DREELE†

LANSCE, MS H805, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

(Received 20 March 1989; accepted 30 June 1989)

Abstract

Rietveld refinements using time-of-flight neutron diffraction data are reported for two forms of Mg_2TiO_4 ($M_r = 160.51$), MgTiO_3 ($M_r = 120.20$) and two samples of MgTi_2O_5 ($M_r = 200.10$). The compounds were synthesized at 1673 K and subsequently annealed and quenched from other temperatures. All data were collected at room temperature on a 10 m powder diffractometer at a nominal scattering angle of $150^\circ 2\theta$. Mg_2TiO_4 annealed at 973 K has the spinel structure, space group $Fd\bar{3}m$, with $a = 8.4376$ (5) Å, $V = 600.71$ (11) Å³, $Z = 8$. Mg_2TiO_4 prepared at 773 K is tetragonal, space group $P4_122$, $a = 5.9748$ (5), $c = 8.414$ (7) Å, $V = 300.37$ (7) Å³, $Z = 4$. Final weighted-profile R values are 0.0376 and 0.0327 for the cubic and tetragonal spinels, respectively. In the cubic form, Mg and Ti are disordered in a single octahedral site to form a nearly perfect inverse spinel, although there may be considerable short-range order. The tetragonal structure is a slight distortion of the cubic one, with two inequivalent octahedral sites over which the Mg and Ti are highly, but completely, ordered. MgTiO_3 annealed at 1073 K has the ilmenite structure, space group $R\bar{3}$, $a = 5.05478$ (26), $c = 13.8992$ (7) Å, $V = 307.56$ (4) Å³, $Z = 6$. The final R_{wp} is 0.0257. Mg and Ti are completely ordered between two octahedral sites, and probably remain so at temperatures up to

at least 1673 K. MgTi_2O_5 has the pseudobrookite structure, space group $Bbmm$, $Z = 4$. A specimen quenched from 973 K has $a = 9.7289$ (9), $b = 10.0057$ (9), $c = 3.7416$ (3) Å, $V = 364.22$ (10) Å³. A second specimen, quenched from 1773 K, has $a = 9.7492$ (9), $b = 9.9896$ (10), $c = 3.7460$ (4) Å, $V = 364.82$ (10) Å³. Final R_{wp} are 0.0251 and 0.0230 for the 973 and 1773 K samples, respectively. The Mg–Ti distribution in both samples is disordered, with the 1773 K sample substantially more disordered. The lattice parameters of MgTi_2O_5 are sensitive to the degree of disorder. These results have been combined with thermochemical data obtained on the same specimens to derive an understanding of the effects of order–disorder on the phase-stability relations of these compounds.

Introduction

The magnesium titanates Mg_2TiO_4 , MgTiO_3 and MgTi_2O_5 are important as components in industrial ceramics and natural mineral systems. An understanding of the structural variations observed in these compounds and their effects on the stability relations in the system MgO-TiO_2 would be beneficial for estimating properties in more complex systems with related structures. The thermodynamics of these materials has recently been investigated by Wechsler & Navrotsky (1984). In order to characterize the structural state of samples used for thermochemical measurements, we have refined the structures of these compounds.

* Present address: Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, CA 90265, USA.

† Author to whom correspondence should be addressed.