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## Structure Refinement of Orthorhombic MnAl<sub>3</sub>

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### Abstract

Structure refinements on a crystal of composition Mn<sub>3</sub>Al<sub>10</sub> were performed in space groups *Pnma* and *Pn2<sub>1</sub>a* (standard setting *Pna2<sub>1</sub>*). The space group *Pnma* was found to be correct.

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### Comment

The approximate chemical composition and lattice parameters of orthorhombic MnAl<sub>3</sub> were first reported by Hofmann (1938). The phase was found to be stable in the temperature range 1123–1263 K (Taylor, 1960) and to crystallize in space group *Pnma* with 36 Mn and 124 Al atoms per unit cell (Taylor, 1961). A structure model with 156 atoms per unit cell (space group *Pnma*) was proposed by Li, Shi & Kuo (1992), and refined from single-crystal X-ray data by Kang, Malaman, Venturini & Dubois (1992), using a crystal of composition Al<sub>61.3</sub>Cu<sub>7.4</sub>Fe<sub>11.1</sub>Cr<sub>17.2</sub>Si<sub>3</sub>, and by Hiraga, Kaneko, Matsuo & Hashimoto (1993), using a crystal of composition Mn<sub>3.3</sub>Al<sub>9.7</sub> (found in an ingot prepared by arc melting). Recently, the structure of MnAl<sub>3</sub> was redetermined by Shi, Li, Ma & Kuo (1994) from X-ray diffraction data on a single crystal (found in an ingot prepared by arc melting and annealed at 1223 K for 72 h), and was described with the non-centrosymmetric space group *Pn2<sub>1</sub>a* (standard setting *Pna2<sub>1</sub>*). At the same time an independent X-ray study of that compound was performed in our laboratories.

Well developed single crystals with orthorhombic symmetry were isolated from a binary alloy containing small amounts of lithium. Structure refinements were performed in centrosymmetric *Pnma* and non-centrosymmetric *Pn2<sub>1</sub>a* based on both isotropic and anisotropic displacement amplitudes. For *Pnma*, the results of the anisotropic refinement are summarized in Table 1. For *Pn2<sub>1</sub>a*, the anisotropic refinement did not converge, therefore only the results of the isotropic refinements are compared in Table 2. Clearly, the

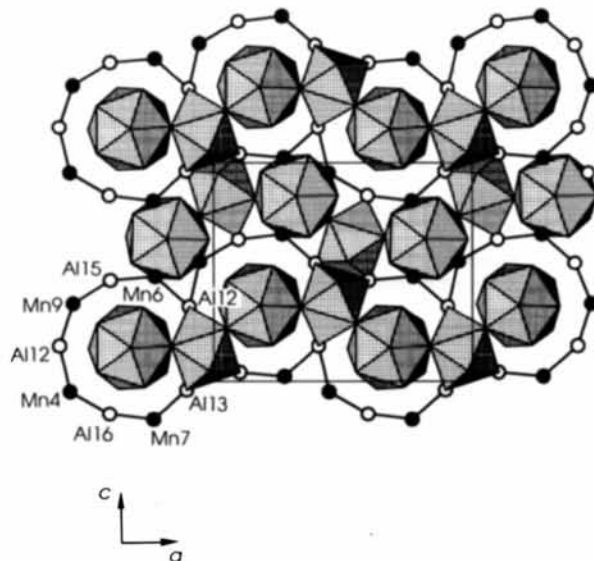


Fig. 1. Structural projection of orthorhombic MnAl<sub>3</sub> along [010], showing the coordination polyhedra of Mn(2) (icosahedra) and Mn(9) (nine-coordinate).

refinement in  $Pn2_1a$  (161 parameters) did not give significantly better results than that in  $Pnma$  (95 parameters). All atom sites in  $Pn2_1a$  (not reproduced here) were within  $3\sigma$  from those in  $Pnma$ , except Al(6), Al(8) and Al(10) which were within  $6\sigma$ . The sites having mixed Mn/Al occupancy are the same as those described by Hiraga *et al.* (1993), except for Al(1) which was found to be fully occupied by Al in our study. Our refined overall composition,  $Mn_{3.01(6)}Al_{9.99(6)}$ , is more Al rich than the compositions stated by Hofmann (1938) ( $Mn_3Al_9$ ) and refined by Hiraga *et al.* (1993) ( $Mn_{3.3}Al_{9.7}$ , without standard deviations), and Shi *et al.* (1994) ( $Mn_{10.9}Al_{28.1}$ , without standard deviations), but slightly less rich in Al than that proposed by Taylor (1961) ( $Mn_3Al_{10.3}$ ).

## Experimental

Single crystals were found in a sample of nominal composition  $Li_{10}Mn_{40}Al_{50}$  which was prepared from the elements Al (99.99%), Li and Mn (99%) by arc melting under an Ar atmosphere. The ingot was annealed at 473 K for 350 h in an evacuated silica tube and quenched in water.

### Crystal data

$Mn_{3.01(6)}Al_{9.99(6)}$   
 $M_r = 434.83$   
 Orthorhombic  
 $Pnma$   
 $a = 14.883(3) \text{ \AA}$   
 $b = 12.447(4) \text{ \AA}$   
 $c = 12.560(3) \text{ \AA}$   
 $V = 2327(1) \text{ \AA}^3$   
 $Z = 12$   
 $D_x = 3.724 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 8.5\text{--}19^\circ$   
 $\mu = 5.842 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Needle  
 $0.049 \times 0.013 \times 0.009 \text{ mm}$   
 Silver

### Data collection

CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: analytical  
 $T_{\min} = 0.0227$ ,  $T_{\max} = 0.0575$   
 4412 measured reflections  
 1142 independent reflections  
 462 observed reflections  
 $[F > 3\sigma(F)]$

$R_{\text{int}} = 0.18$   
 $\theta_{\max} = 20^\circ$   
 $h = 0 \rightarrow 11$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 14$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 2.7, 2.2%

### Refinement

Refinement on  $F$   
 $R = 0.045$   
 $wR = 0.025$   
 $S = 1.316$   
 462 reflections  
 175 parameters  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\max} = 0.0007$   
 $\Delta\rho_{\max} = 2.70 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -3.51 \text{ e \AA}^{-3}$

Extinction correction: Zachariasen (1968)  
 Extinction coefficient:  $g = 0.005$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|        | Occupancy | x | y          | z          | $U_{\text{eq}}/U_{\text{iso}}^\dagger$ |            |
|--------|-----------|---|------------|------------|--|------------|
| Mn(1)  | 8(d)      | a | 0.1281 (3) | 0.0628 (7) | 0.1592 (8)                             | 0.009 (2)† |
| Mn(2)  | 8(d)      | 1 | 0.1798 (4) | 0.5575 (5) | 0.3466 (7)                             | 0.009 (1)  |
| Mn(3)  | 8(d)      | b | 0.3167 (6) | 0.061 (1)  | 0.4607 (8)                             | 0.008 (3)† |
| Mn(4)  | 4(c)      | 1 | 0.052 (1)  | 1/4        | 0.453 (1)                              | 0.013 (4)  |
| Mn(5)  | 4(c)      | c | 0.058 (1)  | 1/4        | 0.242 (1)                              | 0.005 (5)† |
| Mn(6)  | 4(c)      | 1 | 0.2249 (8) | 1/4        | 0.5236 (7)                             | 0.006 (4)  |
| Mn(7)  | 4(c)      | 1 | 0.2348 (7) | 1/4        | 0.1749 (9)                             | 0.008 (4)  |
| Mn(8)  | 4(c)      | d | 0.3343 (6) | 1/4        | 0.346 (1)                              | 0.006 (3)† |
| Mn(9)  | 4(c)      | 1 | 0.5417 (6) | 1/4        | 0.647 (1)                              | 0.007 (3)  |
| Al(1)  | 8(d)      | 1 | 0.0162 (5) | 0.066 (1)  | 0.350 (1)                              | 0.005 (2)  |
| Al(2)  | 8(d)      | 1 | 0.051 (1)  | 0.626 (1)  | 0.460 (1)                              | 0.005 (2)  |
| Al(3)  | 8(d)      | 1 | 0.050 (1)  | 0.622 (1)  | 0.240 (1)                              | 0.019 (4)  |
| Al(4)  | 8(d)      | 1 | 0.1299 (6) | 0.065 (1)  | 0.535 (1)                              | 0.011 (3)  |
| Al(5)  | 8(d)      | 1 | 0.180 (1)  | 0.1475 (7) | 0.350 (1)                              | 0.012 (3)  |
| Al(6)  | 8(d)      | 1 | 0.2264 (9) | 0.6221 (9) | 0.162 (1)                              | 0.010 (4)  |
| Al(7)  | 8(d)      | 1 | 0.265 (1)  | 0.124 (1)  | 0.026 (1)                              | 0.013 (5)  |
| Al(8)  | 8(d)      | 1 | 0.3097 (7) | 0.066 (1)  | 0.2298 (8)                             | 0.010 (3)  |
| Al(9)  | 8(d)      | 1 | 0.3371 (7) | 0.6224 (7) | 0.337 (1)                              | 0.018 (4)  |
| Al(10) | 8(d)      | 1 | 0.4587 (7) | 0.1081 (9) | 0.349 (1)                              | 0.012 (4)  |
| Al(11) | 8(d)      | 1 | 0.5193 (8) | 0.079 (1)  | 0.549 (1)                              | 0.013 (4)  |
| Al(12) | 4(c)      | 1 | 0.094 (1)  | 1/4        | 0.659 (1)                              | 0.006 (5)  |
| Al(13) | 4(c)      | 1 | 0.105 (1)  | 1/4        | 0.039 (2)                              | 0.026 (7)  |
| Al(14) | 4(c)      | 1 | 0.318 (1)  | 1/4        | 0.845 (2)                              | 0.011 (4)  |
| Al(15) | 4(c)      | 1 | 0.399 (1)  | 1/4        | 0.540 (1)                              | 0.011 (6)  |
| Al(16) | 4(c)      | 1 | 0.403 (1)  | 1/4        | 0.148 (2)                              | 0.016 (5)  |

Occupancies: (a) Mn 0.50 (3), Al 0.50 (3); (b) Mn 0.40 (3), Al 0.60 (3); (c) Mn 0.53 (5), Al 0.47 (5); (d) Mn 0.64 (4), Al 0.36 (4).

Table 2. Comparison of refinements with isotropic atomic displacement parameters for  $MnAl_3$

|   | $Pnma$     | $Pn2_1a$  |
|---|------------|-----------|
| Independent reflections                                       | 1142       | 1142      |
| Observed reflections  | 462        | 462       |
| $[ F_{\text{rel}}  > 3\sigma( F_{\text{rel}} )]$              |            |           |
| Refined parameters  | 95         | 161       |
| Displacement parameters                                       | Isotropic  | Isotropic |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$ ( $\text{e \AA}^{-3}$ ) | 3.26/−4.56 | 5.1/−5.34 |
| $R$   | 0.058      | 0.046     |
| $wR$ [ $w = 1/\sigma^2( F_{\text{rel}} )$ ]                   | 0.033      | 0.027     |
| $S$   | 1.535      | 1.371     |

Structure solution was performed using *SIR92* (Altomare *et al.*, 1994) in space group  $Pn2_1a$ . Least-squares refinement was based on  $|F|$  values in space groups  $Pn2_1a$  and  $Pnma$ , varying scale factor, atomic positional, anisotropic or isotropic displacement, and site-occupancy parameters. Sites with mixed Mn/Al occupancy were set isotropic in the final refinement. Programs used for the data reduction and structure refinement are from *Xtal3.2* (Hall, Flack & Stewart, 1992). Only results of the refinement in space group  $Pnma$  based on anisotropic displacement amplitudes are deposited. The atomic coordinates in Table 1 are standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Lists of structure factors, anisotropic displacement parameters and bond distances have been deposited with the IUCr (Reference: DU1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Silicatonibate de Potassium, K<sub>3</sub>Nb<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>

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#### Abstract

Single crystals of tripotassium niobium oxide silicate, K<sub>3</sub>Nb<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>, have been obtained by slow cooling from a melt. This compound crystallizes in the hexagonal system with space group  $P\bar{6}2c$ . The framework, built up from Si<sub>2</sub>O<sub>7</sub> ditetrahedra and a group of three corner-linked NbO<sub>6</sub> octahedra, is isotopic with that of Ba<sub>3</sub>Nb<sub>6</sub>O<sub>12</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>. The filling of tunnels by K<sup>+</sup> (or Ba<sup>2+</sup>) cations determines the space group to be  $P\bar{6}2c$  (or  $P\bar{6}2m$ ).

#### Commentaire

Les composés K<sub>3</sub>M<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> avec M = Nb ou Ta ont été synthétisés et leurs structures cristallines affinées à partir des diffractogrammes de poudres (Choisnet, Nguyen, Groult & Raveau, 1976) par isotypie avec la structure de Ba<sub>1,5</sub>Nb<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> (Shannon & Katz, 1970). L'obtention de monocristaux de K<sub>3</sub>Nb<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> nous a permis de déterminer avec précision sa structure cristalline.

Chaque cation présente une coordination oxygénée classique compte tenu de sa taille: quatre pour Si<sup>IV</sup> ( $r_i = 0,26 \text{ \AA}$ ), six pour Nb<sup>V</sup> ( $r_i = 0,64 \text{ \AA}$ ) et 12 pour K<sup>I</sup> ( $r_i = 1,64 \text{ \AA}$ ) (Shannon, 1976). La structure est constituée d'un arrangement de tétraèdres SiO<sub>4</sub> et d'octaèdres NbO<sub>6</sub> qui ne partagent que des sommets

pour former un squelette structural tout à fait comparable à celui de Ba<sub>3</sub>Nb<sub>6</sub>O<sub>12</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (Shannon & Katz, 1970).

Bien qu'elle soit tridimensionnelle, cette structure se décrit commodément par une succession de plans (001). Une section équatoriale carrée de chacun des octaèdres NbO<sub>6</sub> est confondue avec le plan *ab* ainsi que la face triangulaire équilatérale de chaque tétraèdre SiO<sub>4</sub>; il en résulte donc un agencement planaire de ces polyèdres (Fig. 1). Les octaèdres NbO<sub>6</sub> constituent des blocs Nb<sub>3</sub>O<sub>15</sub> liés entre eux par des tétraèdres SiO<sub>4</sub> qui sont en disposition hexagonale et pointent alternativement un sommet au-dessus et en dessous du plan *ab*.

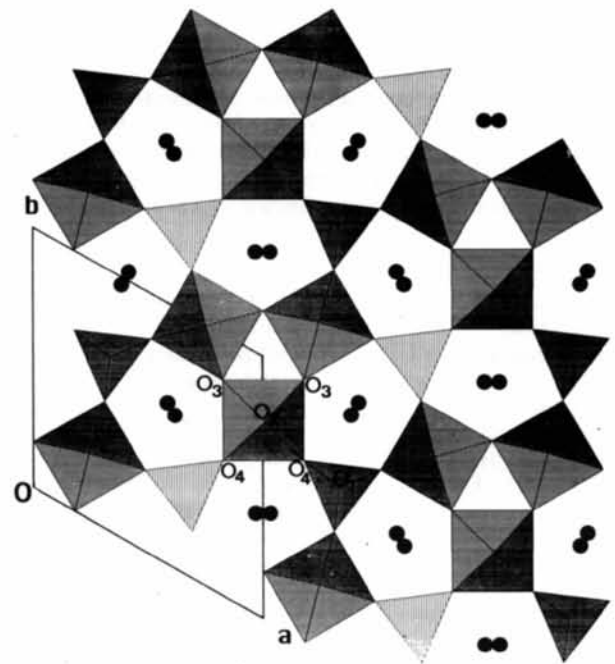


Fig. 1. Projection sur *ab* de l'arrangement planaire des octaèdres NbO<sub>6</sub> et des tétraèdres SiO<sub>4</sub>. Les disques noirs figurent les atomes de potassium.

La superposition de ces plans (001) entraîne le partage de sommets oxygénés axiaux entre polyèdres de même nature d'où l'existence de colonnes (Nb<sub>3</sub>O<sub>12</sub>)<sub>∞</sub> orientées selon [001] et liées entre elles par des groupements Si<sub>2</sub>O<sub>7</sub> indépendants. Cette succession de plans (001) met en évidence deux types de tunnels rectilignes selon l'axe *c*, dont les sections triangulaires ou pentagonales sont clairement visibles sur la Fig. 1. Les atomes de potassium, situés dans les tunnels à section pentagonale, sont à égales distances des plans de polyèdres et s'entourent de 12 atomes d'oxygène distants de 3,25 Å au plus. Deux autres anions O(4) situés à 3,48(1) Å du potassium peuvent être intégrés à son polyèdre de coordination.