

Acta Cryst. (1975). B31, 2137**Nickel Aluminosilicate, Phase I**BY CHE-BAO MA, KURT SAHL AND EKKEHART TILLMANN^{*}*Institut für Mineralogie, Ruhr-Universität Bochum, D-463 Bochum, Germany (BRD)*

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Abstract. $\text{Ni}_{10.3}\text{Al}_{11.4}\text{Si}_{2.3}\text{O}_{32}$, orthorhombic, *Pmma*, $a = 5.6664(5)$, $b = 11.496(2)$, $c = 8.0983(7)$ Å, $Z = 1$, $D_x = 4.69$ g cm⁻³. Crystals are a quench product from 30 kbar and 1300°C. The structure was solved by Patterson and Fourier methods and refined by least-squares calculations to a final $R = 0.040$ for 434 observed reflexions. The structure is based on cubic close-packing of O atoms, and contains single and triple octahedral columns running parallel to **a** cross-linked by single octahedral columns running parallel to **b**. The tetrahedra are either isolated or linked in T_3O_{10} groups. Partial ordering of cations occurs in both octahedral and tetrahedral cation sites. Some Ni may be tetrahedrally coordinated.

Introduction. Phase I is one of three nickel aluminosilicate phases first described by Ma (1972) in connexion with a phase-equilibrium study of the system $\text{SiO}_2\text{-NiO-NiAl}_2\text{O}_4$. Crystals used in this study were grown by Ma at 30 kbar, 1300°C from a multiphase assemblage of bulk composition $7\text{NiO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with a piston-cylinder type pressure apparatus. Precession photographs show Laue symmetry *mmm* and lead to the space group *Pmma* if centrosymmetry is assumed. Electron-microprobe analysis on the same crystals yields: NiO = 57.31, $\text{Al}_2\text{O}_3 = 30.97$, $\text{SiO}_2 = 12.78$ mol.%; total = 101.06 mol.%. The analysis represents a composition within analytical error on the join $\text{NiAl}_2\text{O}_4\text{-Ni}_2\text{SiO}_4$. It was normalized to 100% and projected onto the join to give the formula used

in the present structure refinement. Full accounts of crystal growth and microprobe analysis have been given (Ma, 1972).

A prismatic crystal, approximately $0.06 \times 0.075 \times 0.11$ mm, was chosen for data collection on an automatic Hilger and Watts four-circle diffractometer (graphite monochromator, scintillation counter). Cell dimensions were obtained by a least-squares fit to the setting angles of 12 high-angle reflexions (Mo $K\alpha_1$ radiation). Four octants of integrated intensities were collected to a 2θ limit of 61° by the θ - 2θ step-scan technique. Two standard reflexions were monitored after every 100 reflexion measurements.

A local version of the data-reduction program *DATAPH* (a Brookhaven crystallographic program) was used to correct intensities for Lorentz and polarization factors and for absorption ($\mu = 94.5$ cm⁻¹ for Mo $K\alpha$ radiation). For the latter (Coppens, Leiserowitz & Rabinovich, 1965) the crystal was approximated by six boundary planes. The transmission factors were in the range 0.35–0.56. Standard deviations of intensities were calculated in the usual manner. No extinction correction was applied.

The equivalent reflexions were averaged giving 923 independent reflexions, of which 489 with $I < 2\sigma(I)$ were treated as unobserved and excluded from the refinement.

A Patterson synthesis with the Fourier program *SFS* (Neukäter & Biedl, unpublished) led to a model which gave $R = 0.273$ after initial scaling by least-squares calculations. Fourier synthesis with the same program yielded atomic coordinates for further refinement, which was carried out by full-matrix least-

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Table 1. Atomic coordinates, temperature factors and the proposed cation distribution with standard deviations

		x	y	z	B (Å ²)
M(1)	1.6Ni + 0.4Al	0.0	0.0	0.0	0.32 (7)
M(2)	1.5Ni + 0.5Al	0.0	0.5	0.5	0.31 (7)
M(3)	2.0Ni + 2.0Al	0.0	0.2497 (3)	0.0	0.34 (6)
M(4)	3.8Ni + 0.2Al	0.25	0.1269 (4)	0.2728 (4)	0.28 (6)
M(5)	0.9Ni + 3.1Al	0.25	0.376 (1)	0.2491 (4)	0.3 (1)
T(1)	0.5Ni + 1.5Al	0.75	0.5	0.1215 (8)	0.3 (1)
T(2) }	3.7Al + 2.3Si	0.75	0.0	0.362 (1)	0.4 (2)
T(3) }		0.75	0.2582 (5)	0.3690 (8)	0.3 (1)
O(1)		0.25	0.131 (1)	0.022 (2)	1.2 (3)
O(2)		0.25	0.370 (2)	0.010 (2)	1.1 (3)
O(3)		0.25	0.122 (1)	0.528 (2)	0.8 (3)
O(4)		0.25	0.378 (2)	0.493 (2)	0.7 (3)
O(5)		0.00 (1)	0.0	0.252 (2)	0.6 (6)
O(6)		0.019 (9)	0.5	0.253 (1)	0.9 (6)
O(7)		0.001 (9)	0.257 (1)	0.247 (1)	1.4 (5)

squares calculations with a local version of *ORFLS* (Busing, Martin & Levy, 1962). Three cycles varying scale factor and atomic coordinates reduced *R* to 0.113.

Table 2. Bond lengths (Å) and angles (°) with standard deviations

M(1)–O(5)	2 × 2.05 (1)		
M(1)–O(1)	4 × 2.08 (1)		
O(5)–O(1)	4 × 2.78 (3)	O(5)–M(1)–O(1)	4 × 84.9 (1.2)
O(5)–O(1)	4 × 3.04 (3)	O(5)–M(1)–O(1)	4 × 95.1 (1.2)
O(1)–O(1)	2 × 2.86 (1)	O(1)–M(1)–O(1)	2 × 86.9 (0.4)
O(1)–O(1)	2 × 3.01 (2)	O(1)–M(1)–O(1)	2 × 93.1 (0.4)
M(2)–O(4)	4 × 2.00 (1)		
M(2)–O(6)	2 × 2.00 (1)		
O(4)–O(4)	2 × 2.84 (1)	O(4)–M(2)–O(4)	2 × 90.4 (0.5)
O(4)–O(4)	2 × 2.81 (2)	O(4)–M(2)–O(4)	2 × 89.6 (0.5)
O(4)–O(6)	4 × 2.73 (3)	O(4)–M(2)–O(6)	4 × 86.1 (1.1)
O(4)–O(6)	4 × 2.92 (3)	O(4)–M(2)–O(6)	4 × 93.9 (1.1)
M(3)–O(1)	2 × 1.98 (1)		
M(3)–O(2)	2 × 1.99 (1)		
M(3)–O(7)	2 × 2.00 (1)		
O(1)–O(1)	1 × 2.86 (1)	O(1)–M(3)–O(1)	1 × 92.6 (0.5)
O(1)–O(2)	2 × 2.75 (2)	O(1)–M(3)–O(2)	2 × 88.1 (0.5)
O(1)–O(7)	2 × 2.98 (3)	O(1)–M(3)–O(7)	2 × 97.1 (1.2)
O(1)–O(7)	2 × 2.72 (3)	O(1)–M(3)–O(7)	2 × 86.4 (1.2)
O(2)–O(2)	1 × 2.84 (1)	O(2)–M(3)–O(2)	1 × 91.3 (0.5)
O(2)–O(7)	2 × 2.71 (3)	O(2)–M(3)–O(7)	2 × 85.8 (1.2)
O(2)–O(7)	2 × 2.84 (3)	O(2)–M(3)–O(7)	2 × 90.7 (1.2)
M(4)–O(1)	1 × 2.03 (2)		
M(4)–O(5)	2 × 2.04 (4)		
M(4)–O(3)	1 × 2.07 (1)		
M(4)–O(7)	2 × 2.07 (4)		
O(1)–O(5)	2 × 2.78 (3)	O(1)–M(4)–O(5)	2 × 86.3 (0.5)
O(1)–O(7)	2 × 2.72 (3)	O(1)–M(4)–O(5)	2 × 83.2 (0.4)
O(5)–O(5)	1 × 2.82 (8)	O(5)–M(4)–O(5)	1 × 87.7 (1.7)
O(5)–O(3)	2 × 2.99 (3)	O(5)–M(4)–O(3)	2 × 93.5 (0.5)
O(5)–O(7)	2 × 2.96 (1)	O(5)–M(4)–O(7)	2 × 92.2 (1.6)
O(3)–O(7)	2 × 3.10 (3)	O(3)–M(4)–O(7)	2 × 97.0 (0.4)
O(7)–O(7)	1 × 2.82 (7)	O(7)–M(4)–O(7)	1 × 85.9 (1.6)
M(5)–O(6)	2 × 1.94 (4)		
M(5)–O(2)	1 × 1.94 (2)		
M(5)–O(7)	2 × 1.96 (4)		
M(5)–O(4)	1 × 1.97 (2)		
O(6)–O(6)	1 × 2.62 (7)	O(6)–M(5)–O(6)	1 × 85.1 (1.6)
O(6)–O(2)	2 × 2.80 (3)	O(6)–M(5)–O(2)	2 × 92.4 (0.6)
O(6)–O(7)	2 × 2.79 (1)	O(6)–M(5)–O(7)	2 × 91.5 (1.5)
O(6)–O(4)	2 × 2.73 (3)	O(6)–M(5)–O(4)	2 × 88.6 (0.6)
O(2)–O(7)	2 × 2.71 (3)	O(2)–M(5)–O(7)	2 × 88.2 (0.5)
O(7)–O(7)	1 × 2.82 (7)	O(7)–M(5)–O(7)	1 × 91.9 (1.6)
O(7)–O(4)	2 × 2.80 (3)	O(7)–M(5)–O(4)	2 × 90.9 (0.5)
T(1)–O(2)	2 × 1.83 (2)		
T(1)–O(6)	2 × 1.86 (4)		
O(2)–O(2)	1 × 2.98 (3)	O(2)–T(1)–O(2)	1 × 108.8 (0.8)
O(2)–O(6)	4 × 3.01 (3)	O(2)–T(1)–O(6)	4 × 109.5 (0.5)
O(6)–O(6)	1 × 3.05 (7)	O(6)–T(1)–O(6)	1 × 110.0 (1.3)
T(2)–O(3)	2 × 1.66 (2)		
T(2)–O(5)	2 × 1.68 (5)		
O(3)–O(3)	1 × 2.80 (2)	O(3)–T(2)–O(3)	1 × 115.0 (0.9)
O(3)–O(5)	4 × 2.67 (3)	O(3)–T(2)–O(5)	4 × 106.5 (0.6)
O(5)–O(5)	1 × 2.85 (8)	O(5)–T(2)–O(5)	1 × 116.2 (1.7)
T(3)–O(7)	2 × 1.73 (4)		
T(3)–O(4)	1 × 1.77 (2)		
T(3)–O(3)	1 × 1.78 (2)		
O(7)–O(7)	1 × 2.85 (7)	O(7)–T(3)–O(7)	1 × 110.4 (1.5)
O(7)–O(4)	2 × 2.90 (3)	O(7)–T(3)–O(4)	2 × 111.5 (0.7)
O(7)–O(3)	2 × 2.79 (3)	O(7)–T(3)–O(3)	2 × 105.3 (0.6)
O(4)–O(3)	1 × 2.95 (2)	O(4)–T(3)–O(3)	1 × 112.7 (0.8)

Further refinement was made varying temperature factors also and assuming partial ordering of Ni and Al. The initial ordering scheme was approximated from the relative peak heights in the Fourier map. Adjustments were made to this scheme by trial-and-error in subsequent cycles to reduce *R* and to equalize approximately the temperature factors of the atoms involved. Several cycles converged to the final *R* = 0.040 and *R_w* = 0.054 for 434 observed reflexions.* The function minimized was $\sum w(|F_o| - |F_c|)^2$. Unit weights were assumed initially, but a weighting scheme $w = 1/\sigma^2(F_o)$ was used in the final stage. Scattering factors for O²⁻, Al²⁺, Si⁴⁺ and Ni²⁺ were taken from *International Tables for X-ray Crystallography* (1968).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31042 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

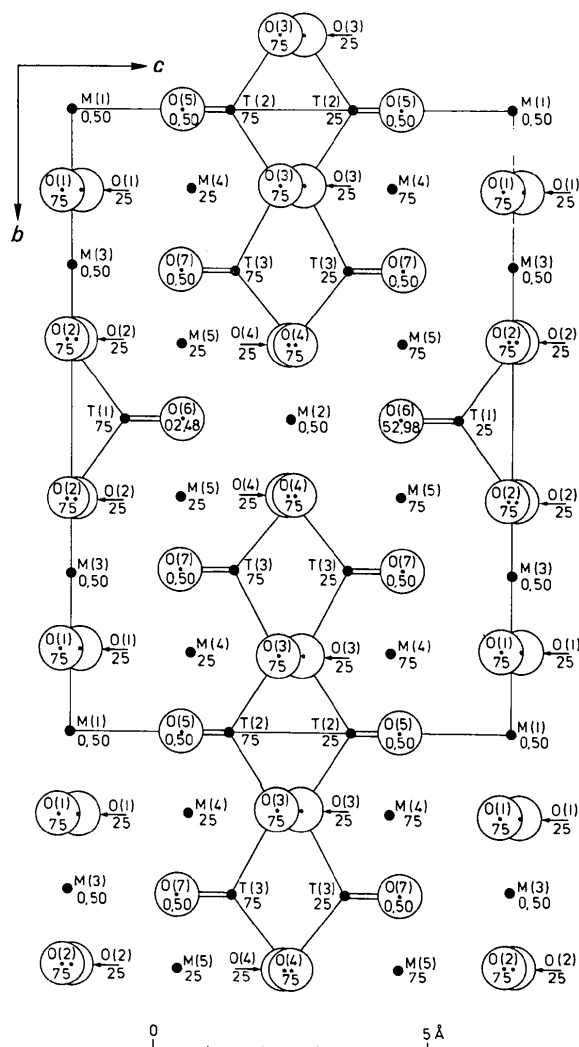


Fig. 1. Projection of the crystal structure of phase I on (100). Heights of atoms are shown by *x* coordinates ($\times 100$).

The final atomic coordinates, temperature factors, and proposed cation distribution are listed in Table 1. The bond lengths and angles with estimated standard deviations were calculated with the program *SADIAN* (Baur & Wenniger, unpublished) and are listed in Table 2.

Discussion. Fig. 1 shows a projection on (100). The structure is based on a distorted cubic close-packing of O atoms with layers stacked parallel to (021). There are five crystallographically independent octahedrally coordinated (M) cation sites. M(1), M(2) and M(3) occur at heights $x=0.0$ and 0.5 and form octahedral columns running parallel to **a**. While the M(2) octahedral column stands by itself as a single column, the M(1) column shares edges with two adjacent M(3) columns to form a wall three octahedra wide along **b**. The walls of triple columns and the single M(2) columns are connected to each other by single columns of M(4) and M(5) octahedra which run parallel to **b**.

Of the three crystallographically independent tetrahedrally coordinated (T) cation sites, T(1) constitute isolated TO_4 tetrahedra, while T(2) tetrahedra share corners with two adjacent T(3) tetrahedra to form T_3O_{10} groups. No edges or faces of the tetrahedral groups are shared with each other or with octahedral groups.

The proposed distribution of Ni and Al was derived by trial-and-error and hence involves a large uncertainty. Since temperature factors of the atoms involved are strongly correlated with the cation distribution,

their values cannot be taken too seriously. The average metal–oxygen distances of octahedral sites [M(1)–O 2.07(1), M(2)–O 2.00(1), M(3)–O 1.99(1), M(4)–O 2.05(3), M(5)–O 1.95(3) Å], however, compare well with literature values for the proposed cation distribution. Furthermore, the average distance T(1)–O 1.85(3) Å is larger than the generally accepted upper limit of the Al–O distance in tetrahedral coordination (1.77 Å) and thus supports the proposed presence of some tetrahedrally coordinated Ni.

During the course of refinement, complete disordering was assumed for Al and Si in T(2) and T(3) sites. The average bond distances [T(2)–O 1.67(3), T(3)–O 1.75(3) Å] suggest that Al is partially enriched in T(3) sites.

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Nickel Aluminosilicate, Phase II

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Abstract. $\text{Ni}_{17.0}\text{Al}_{13.9}\text{Si}_{5.1}\text{O}_{48}$, orthorhombic, *Imma*, $a=5.6603(7)$, $b=17.298(2)$, $c=8.110(1)$ Å, $Z=1$, $D_x=4.78$ g cm⁻³. Crystals are a quench product from 18.6 kbar and 1550°C. The structure was refined by a combination of least-squares calculations and Fourier synthesis to a final $R=0.036$ for 348 observed reflexions. Phase II is isostructural with manganostibite ($\text{Mn}_7\text{SbAsO}_{12}$, $Z=4$). The structure is based on cubic close packing of O atoms and contains triple octahedral columns running parallel to **a** cross-linked by single octahedral columns running parallel to **b**. The tetrahedra are linked in T_3O_{10} groups. Partial ordering

of cations occurs between Ni and Al in octahedral sites and between Al and Si in tetrahedral sites.

Introduction. Phase II is one of three nickel aluminosilicate phases first described by Ma (1972) in connexion with a phase-equilibrium study of the system $\text{SiO}_2\text{--NiO--NiAl}_2\text{O}_4$. Crystals used in this study were grown by Ma at 18.6 kbar, 1550°C from a multiphase assemblage of bulk composition $11\text{NiO} \cdot 2\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ with a piston-cylinder type pressure apparatus. Precession photographs show Laue symmetry *mmm* and lead to the space group *Imma* if centrosymmetry is assumed. Electron-microprobe analysis on the same crystals yields: NiO = 58.98, Al_2O_3 = 23.67, SiO_2 = 17.27 mol. %: total = 99.92 mol. %. The analysis represents

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