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bond lengths and angles with estimated standard deviations were calculated with the program *SADIAN* (Baur & Wenniger, unpublished) and are listed in Table 2.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 $x=0{\cdot}0$ 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.

Che-Bao Ma is grateful to the Alexander von Humboldt Foundation (Bad Godesberg) for a fellowship and to Professor W. Schreyer for his interest and support.

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Acta Cryst. (1975). B**31**, 2139

Nickel Aluminosilicate, Phase II

By Che-Bao Ma and Ekkehart Tillmanns*

Institut für Mineralogie, Ruhr-Universität Bochum, D-463 Bochum, Germany (BRD)

(*Received* 9 *April* 1975; *accepted* 12 *April* 1975)

Abstract. $Ni_{17.0}Al_{13.9}Si_{5.1}O_{48}$, orthorhombic, *Imma*, $a=5{\cdot}6603(7)$, $b=17{\cdot}298(2)$, $c=8{\cdot}110(1)$ Å, $Z=1$, $D_x=4{\cdot}78$ 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 $R=0{\cdot}036$ for 348 observed reflexions. Phase II is isostructural with manganostibite (Mn_7SbAsO_{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 SiO_2–NiO–$NiAl_2O_4$. Crystals used in this study were grown by Ma at 18·6 kbar, 1550°C from a multiphase assemblage of bulk composition $11NiO.2Al_2O_3.7SiO_2$ 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

* Present address: Institut für Mineralogie der Universität, 65 Mainz, Germany (BRD).

a composition within analytical error on the join $NiAl_2O_4$–Ni_2SiO_4. It was normalized to 100% and projected onto the join to give the formula used in the present refinement. Full accounts of crystal growth and microprobe analysis have been given (Ma, 1972).

A crystal, approximately 0·075 × 0·075 × 0·090 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 ($\mu = 104$ 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 0·43–0·62. Standard deviations of intensities were calculated in the usual manner. No extinction correction was applied.

The equivalent reflexions were averaged giving 687 independent reflexions, of which 339 with $I < 2\sigma(I)$ were treated as unobserved and excluded from the refinement.

The refinement was carried out by full-matrix least-squares calculations with a local version of *ORFLS* (Busing, Martin & Levy, 1962). The initial atomic coordinates were those of manganostibite (Moore, 1970). An ordering scheme of Ni and Al in octahedral sites was assumed and later modified from time to time based on the calculated temperature factors of the atoms involved. Successive refinement of scale factor, atomic coordinates and temperature factors readily converged to an R of 0·046. The results showed, however, some incorrect details including unreasonable temperature factors for two O atoms [O(4): 3·2(6), O(5): 0·0(1) Å^2] and too short an average interatomic distance for T(2)–O [1·57(2) Å]. The refinement had apparently reached a false minimum in the least-squares calculation. A Fourier synthesis was then calculated with the program *SFS* (Neukäter & Biedl, unpublished). The atomic coordinates obtained from the least-squares refinement were checked against the peak positions and the ordering scheme of Ni and Al was modified by the relative peak heights in the

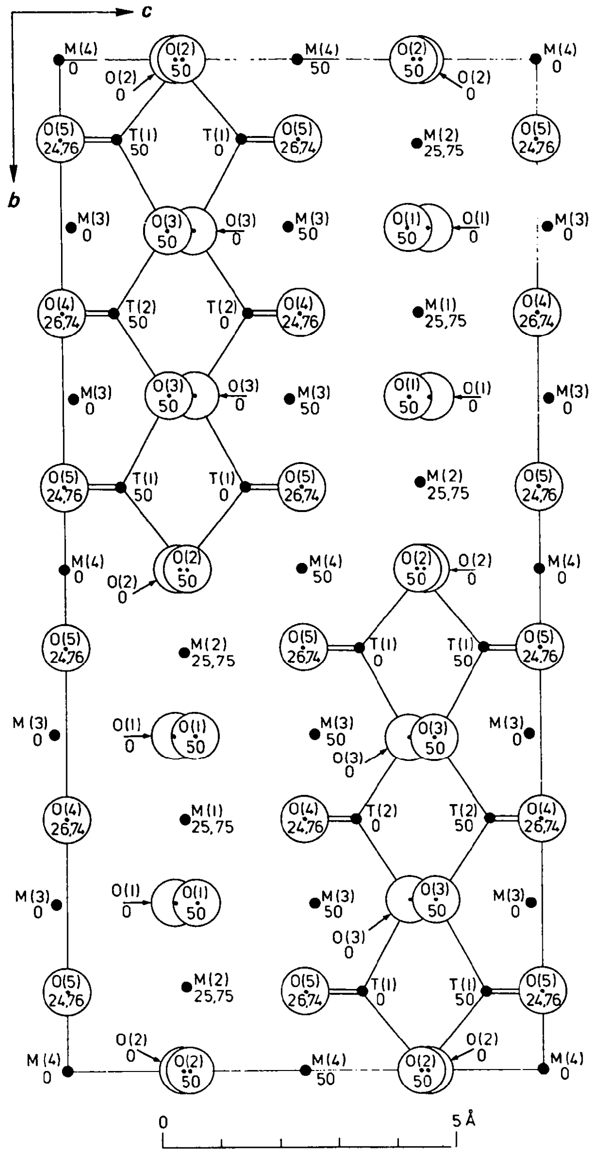

Fig. 1. Projection of the crystal structure of phase II on (100). Heights of atoms are shown by x coordinates (×100).

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

		x	y	z	B (Å^2)
M(1)	2·6Ni + 1·4Al	0·25	0·25	0·75	0·47 (6)
M(2)	5·8Ni + 2·2Al	0·25	0·0840 (1)	0·75	0·40 (4)
M(3)	6·6Ni + 1·4Al	0·0	0·1658 (2)	0·0231 (3)	0·41 (4)
M(4)	2·0Ni + 2·0Al	0·0	0·0	0·0	0·4 (1)
T(1) }	6·9Al + 5·1Si	0·0	0·4216 (2)	0·3788 (6)	0·34 (7)
T(2) }		0·0	0·25	0·3878 (8)	0·4 (1)
O(1)		0·0	0·8318 (6)	0·228 (1)	1·0 (2)
O(2)		0·0	0·0003 (4)	0·243 (2)	1·4 (4)
O(3)		0·0	0·1690 (6)	0·275 (1)	0·7 (2)
O(4)		0·261 (4)	0·25	0·000 (1)	1·5 (4)
O(5)		0·244 (2)	0·0785 (5)	0·0004 (6)	0·5 (2)

Fourier map. A few additional cycles converged to the final $R=0{\cdot}036$ and $R_w=0{\cdot}043$ for 348 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 O^-, Al^{2+}, Si^{4+} and Ni^{2+} were taken from *International Tables for X-ray Crystallography* (1968).

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.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31043 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

M(1)–O(1)	4×	2·01 (1)			
M(1)–O(4)	2×	2·03 (1)			
O(1)–O(1)	2×	2·85 (1)	O(1)–M(1)–O(1)	2×	90·4 (3)
O(1)–O(1)	2×	2·83 (2)	O(1)–M(1)–O(1)	2×	89·6 (3)
O(1)–O(4)	4×	2·76 (2)	O(1)–M(1)–O(4)	4×	86·3 (5)
O(1)–O(4)	4×	2·95 (2)	O(1)–M(1)–O(4)	4×	93·7 (5)
M(2)–O(2)	2×	2·03 (1)			
M(2)–O(5)	2×	2·03 (1)			
M(2)–O(1)	2×	2·04 (1)			
O(2)–O(2)	1×	2·83 (1)	O(2)–M(2)–O(2)	1×	88·3 (2)
O(2)–O(5)	2×	2·89 (2)	O(2)–M(2)–O(5)	2×	90·5 (6)
O(2)–O(5)	2×	2·76 (2)	O(2)–M(2)–O(5)	2×	85·7 (6)
O(2)–O(1)	2×	2·92 (1)	O(2)–M(2)–O(1)	2×	91·5 (3)
O(5)–O(1)	2×	2·78 (1)	O(5)–M(2)–O(1)	2×	86·3 (4)
O(5)–O(1)	2×	3·06 (1)	O(5)–M(2)–O(1)	2×	97·6 (4)
O(1)–O(1)	1×	2·85 (1)	O(1)–M(2)–O(1)	1×	88·8 (3)
M(3)–O(1)	1×	2·04 (1)			
M(3)–O(3)	1×	2·05 (1)			
M(3)–O(5)	2×	2·05 (1)			
M(3)–O(4)	2×	2·08 (2)			
O(1)–O(5)	2×	2·78 (1)	O(1)–M(3)–O(5)	2×	85·7 (3)
O(1)–O(4)	2×	2·76 (2)	O(1)–M(3)–O(4)	2×	84·1 (3)
O(3)–O(5)	2×	3·05 (1)	O(3)–M(3)–O(5)	2×	96·3 (3)
O(3)–O(4)	2×	3·02 (2)	O(3)–M(3)–O(4)	2×	94·0 (3)
O(5)–O(5)	1×	2·76 (1)	O(5)–M(3)–O(5)	1×	84·4 (4)
O(5)–O(4)	2×	2·97 (1)	O(5)–M(3)–O(4)	2×	91·7 (5)
O(4)–O(4)	1×	2·96 (3)	O(4)–M(3)–O(4)	1×	90·4 (6)
M(4)–O(5)	4×	1·94 (1)			
M(4)–O(2)	2×	1·97 (2)			
O(5)–O(5)	2×	2·76 (1)	O(5)–M(4)–O(5)	2×	90·9 (4)
O(5)–O(5)	2×	2·72 (1)	O(5)–M(4)–O(5)	2×	89·1 (4)
O(5)–O(2)	4×	2·76 (2)	O(5)–M(4)–O(2)	4×	90·2 (2)
O(5)–O(2)	4×	2·76 (2)	O(5)–M(4)–O(2)	4×	89·8 (2)
T(1)–O(2)	1×	1·75 (1)			
T(1)–O(5)	2×	1·75 (1)			
T(1)–O(3)	1×	1·78 (1)			
O(2)–O(5)	2×	2·88 (2)	O(2)–T(1)–O(5)	2×	110·8 (4)
O(2)–O(3)	1×	2·93 (1)	O(2)–T(1)–O(3)	1×	112·5 (6)
O(5)–O(5)	1×	2·90 (1)	O(5)–T(1)–O(5)	1×	112·0 (4)
O(5)–O(3)	2×	2·81 (1)	O(5)–T(1)–O(3)	2×	105·3 (4)
T(2)–O(4)	2×	1·63 (2)			
T(2)–O(3)	2×	1·67 (1)			
O(4)–O(4)	1×	2·70 (3)	O(4)–T(2)–O(4)	1×	112·3 (8)
O(4)–O(3)	4×	2·67 (2)	O(4)–T(2)–O(3)	4×	107·7 (3)
O(3)–O(3)	1×	2·80 (2)	O(3)–T(2)–O(3)	1×	113·8 (6)

Discussion. Phase II has the same space group and approximately the same cell dimensions as manganostibite. The success of the refinement proves that phase II and manganostibite are isostructural. 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 (031). There are four crystallographically independent octahedrally coordinated (M) cation sites. M(1) and M(2) atoms occur at heights $x=0{\cdot}25$ and $0{\cdot}75$ and form octahedral columns running parallel to **a**. The M(1) octahedral column shares edges with two adjacent M(2) columns to form a wall three octahedra wide along **b**. The walls of triple columns are cross-linked by single columns of M(3) and M(4) octahedra which run parallel to **b**. Of the two crystallographically independent tetrahedrally coordinated (T) cation sites, T(2) tetrahedra share corners with two adjacent T(1) tetrahedra to form T_3O_{10} groups.

The proposed distribution of Ni and Al was derived by trial-and-error and hence involves a large uncertainty. Since the 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 2·02(1), M(2)–O 2·03(1), M(3)–O 2·06(1), M(4)–O 1·95(1) Å], however, compare well with literature values for the proposed cation distribution.

During the course of refinement, complete disordering was assumed for Al and Si in tetrahedral sites. The average bond distances [T(1)–O 1·76(1), T(2)–O 1·65(2) Å] suggest that Al is enriched predominantly in T(1) sites.

Che-Bao Ma is grateful to the Alexander von Humboldt Foundation (Bad Godesberg) for a fellowship, to Professor K. Sahl for discussions and to Professor W. Schreyer for his interest and support.

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