SHORT STRUCTURAL PAPERS

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Structure of Nickel Aluminosilicate (Phase IV): A High-Pressure Phase Related to Spinel

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Abstract. $Ni_3Al_2SiO_8$ (phase IV), orthorhombic, *Imma*, $a = 5{\cdot}665$ (2), $b = 28{\cdot}646$ (9), $c = 8{\cdot}091$ (3) Å, $Z = 10$, $D_x = 4{\cdot}900$ Mg m^{-3}. Crystals are products quenched from $6{\cdot}5 \times 10^3$ MPa and 1553 K. The structure was solved by the Patterson method and refined to $R = 0{\cdot}074$ for 1115 unique reflections from diffractometer data with $|F_o| \geq 3\sigma(F_o)$. The structure is based on a slightly distorted cubic close packing of O atoms and is related to spinel and modified-spinel structures. Both isolated, TO_4, and coupled, T_2O_7, tetrahedra exist; the ratio of the TO_4 to T_2O_7 groups is 1:2. Both single and double columns of MO_6 octahedra run parallel to the *a* axis, while single columns also run parallel to the *b* axis. Partial ordering of cations is found in both octahedral and tetrahedral sites.

Introduction. Phase IV is one of five phases which were observed in the study of the $NiAl_2O_4$–Ni_2SiO_4 system (Ma, 1974; Akaogi, Akimoto, Takahashi, Horiuchi & Morimoto, 1978). The structures of phases I, II and III were reported by Ma, Sahl & Tillmanns (1975), Ma & Tillmanns (1975), and Ma & Sahl (1975), respectively. The structural studies of phase V, the highest-pressure form known at present, were performed by Horioka, Nishiguchi, Morimoto, Horiuchi, Akaogi & Akimoto (1981). All structures of the phases in this system are closely related to the spinel and modified-spinel structures (Morimoto, Akimoto, Koto & Tokonami, 1970; Moore & Smith, 1970). The systematics of their structures, with the introduction of the concept of a 'spinelloid', were reported by Horiuchi, Horioka & Morimoto (1980). Phase relations will be published elsewhere (Horioka, Horiuchi, Akaogi & Akimoto, 1981).

The crystals of phase IV used in this study were prepared from mixtures of powdered NiO, $Al(OH)_3$ and silicic acid in the ratio 3:2:1 at 1553 K and $6{\cdot}5 \times 10^3$ MPa using a tetrahedral anvil press. The run-time was 20 min. The mixture was inserted into a platinum cylindrical heater, of diameter 2 mm and length 6 mm, which was placed in a pyrophyllite tetrahedron with 20 mm edges. The crystals are transparent green with dimensions of *ca* 30–60 μm.

Cell dimensions were determined by the least-squares method using eight high-angle reflections measured on a four-circle diffractometer with Mo $K\alpha_1$ radiation. X-ray photographs indicate systematic absences *hkl* for $h + k + l$ odd and *hk*0 for *h* odd, which are consistent with space group *Imma* or *Im*2*a*. *Imma*, which has a center of symmetry, was assumed in the structure analysis and confirmed to be correct from the final results.

The composition of the specimen was semi-quantitatively confirmed to be in good agreement with the starting bulk composition, $Ni_3Al_2SiO_8$, by means of an analytical electron microscope (Hitachi-12SE). Kyanite (Al_2SiO_5), nickel aluminate spinel ($NiAl_2O_4$) and nickel silicate olivine (Ni_2SiO_4) were used as standard materials. The ratio of the characteristic X-ray intensities of Al to Si is 1·68 for the specimen and 1·60 for kyanite.

The specimen used for intensity measurement was about $0{\cdot}05 \times 0{\cdot}06 \times 0{\cdot}03$ mm. Mo $K\alpha$ radiation monochromatized by pyrolytic graphite was used. The intensities of 1957 independent reflections within the range of $0° < 2\theta \leq 62°$ were obtained using a

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four-circle diffractometer (Rigaku AFC-3) employing the θ–2θ scan technique. Of the reflections measured, 1115 with low standard deviations $[|F_o| \geq 3\sigma(F_o)]$ were used for the structure determination and refinement, while 842 with $|F_o| < 3\sigma(F_o)$ were treated as unobserved and excluded from the refinement. Conventional polarization and Lorentz corrections were applied during the data collection. No absorption correction was made ($\mu r \sim 0{\cdot}35$ for Mo $K\alpha$).

The structure was solved by the Patterson method. The atomic parameters, temperature factors and cation distribution at each site were refined by least squares; they are listed in Table 1. The final R for 1115 reflections $[|F_o| \geq 3\sigma(F_o)]$ is 0·074. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974) for all atoms. The interatomic distances and angles are shown in Table 2.* Computations of the Patterson and Fourier syntheses, least-squares refinements, and interatomic distances and angles were carried out using the programs *3DFR* (Y. Iitaka & T. Matsusaki, private communication), *RFINE* 2 (Finger, 1972), and *UMBADTEA* (Finger, 1968), respectively, at the Computation Center of Osaka University and at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Table 1. *Positional and thermal parameters with their estimated standard deviations in parentheses*

Cation distributions in sites are given by cNi + (1 − c)Al for M and cNi + (0·5 − c)Al + 0·5 Si for T. $B_{\rm eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	Multi-plicity	c (occu-pancies)	x	y	z	$B_{\rm eq}$ (Å^2)
O(1)	0·5		0	−0·0016 (4)	0·2340 (24)	0·6
O(2)	0·5		0	0·1028 (5)	0·2272 (12)	0·4
O(3)	0·5		0	0·2005 (7)	0·2556 (22)	1·2
O(4)	1·0		0·2289 (25)	0·0519 (5)	0·5021 (12)	0·7
O(5)	1·0		0·2574 (27)	0·1553 (3)	0·4980 (12)	0·4
O(6)	0·5		0·2713 (33)	$\frac{1}{4}$	0·5008 (15)	0·4
O(7)	0·5		0	0·1025 (5)	0·7263 (16)	0·5
O(8)	0·5		0	0·1986 (6)	0·7401 (17)	1·0
T(1)	0·5	0·12 (2)	0	0·0486 (2)	0·6210 (7)	0·4
T(2)	0·5	0·01 (2)	0	0·1526 (2)	0·6163 (9)	0·7
T(3)	0·25	0·11 (4)	0	$\frac{1}{4}$	0·3722 (14)	1·3
M(1)	0·5	0·85 (2)	$\frac{1}{4}$	0·0497 (1)	$\frac{1}{4}$	0·7
M(2)	0·5	0·50 (2)	$\frac{1}{4}$	0·1499 (1)	$\frac{1}{4}$	0·2
M(3)	0·25	0·56 (4)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·1
M(4)	0·5	0·85 (2)	$\frac{1}{2}$	0·1002 (1)	0·5255 (3)	0·5
M(5)	0·5	0·69 (3)	$\frac{1}{2}$	0·2003 (1)	0·4994 (4)	0·7
M(6)	0·25	0·78 (3)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0·4

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

Symmetry code

None or (i)	x,	y,	z
(ii)	x,	$-y$,	$-z$
(iii)	x,	$\frac{1}{2}-y$,	z
(iv)	$\frac{1}{2}+x$,	$\frac{1}{2}+y$,	$\frac{1}{2}+z$
(v)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$
(vi)	$\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$
(vii)	$-x$,	y,	z
(viii)	$\frac{1}{2}-x$,	y,	$\frac{1}{2}-z$

		Distance	O–M–O angle
M(1)–O(1)	2×	2·044 (9)	
–O(2)	2×	2·09 (1)	
–O(4)	2×	2·04 (1)	
O(1)–O(1$^{\rm vi}$)		2·844 (4)	88·2 (5)
–O(2$^{\rm i}$)	2×	2·99 (2)	92·7 (4)
–O(4$^{\rm i}$)	2×	2·96 (2)	92·6 (7)
–O(4$^{\rm viii}$)	2×	2·89 (2)	90·0 (7)
O(2)–O(4$^{\rm i}$)	2×	2·96 (2)	91·5 (5)
–O(4$^{\rm viii}$)	2×	2·82 (2)	85·9 (5)
–O(2$^{\rm vi}$)		2·86 (2)	86·4 (6)
M(3)–O(1$^{\rm vi}$)	2×	1·89 (2)	
–O(4)	4×	2·14 (1)	
O(1)–O(4$^{\rm iv}$)	4×	2·89 (2)	91·4 (4)
–O(4$^{\rm v}$)	4×	2·82 (2)	88·6 (4)
O(4)–O(4$^{\rm vii}$)	2×	3·07 (3)	91·8 (7)
–O(4$^{\rm ii}$)	2×	2·98 (3)	88·2 (7)
M(5)–O(3$^{\rm viii}$)		2·06 (2)	
–O(5)	2×	1·88 (1)	
–O(6)	2×	1·92 (1)	
–O(8$^{\rm viii}$)		2·11 (1)	
O(3)–O(5$^{\rm vi}$)	2×	2·79 (2)	89·8 (5)
–O(6$^{\rm vi}$)	2×	2·83 (2)	90·2 (6)
O(5)–O(5$^{\rm vii}$)		2·75 (3)	93·7 (8)
–O(6$^{\rm i}$)	2×	2·71 (1)	90·9 (6)
–O(8$^{\rm v}$)	2×	2·81 (2)	89·4 (5)
O(6)–O(6$^{\rm vii}$)		2·59 (4)	84·6 (8)
–O(8$^{\rm v}$)	2×	2·87 (2)	90·7 (5)

		Distance	O–M–O angle
M(2)–O(2)	2×	1·97 (1)	
–O(3)	2×	2·03 (1)	
–O(5)	2×	2·01 (1)	
O(2)–O(2$^{\rm v}$)		2·856 (3)	93·2 (7)
–O(3$^{\rm i}$)	2×	2·81 (2)	89·4 (5)
–O(5$^{\rm i}$)	2×	3·03 (2)	99·3 (5)
–O(5$^{\rm viii}$)	2×	2·73 (2)	86·8 (5)
O(3)–O(3$^{\rm vi}$)		2·83 (2)	88·7 (8)
–O(5$^{\rm i}$)	2×	2·77 (2)	86·4 (6)
–O(5$^{\rm viii}$)	2×	2·79 (2)	87·3 (6)
T(1)–O(1$^{\rm ii}$)		1·79 (2)	
–O(4)	2×	1·61 (1)	
–O(7)		1·76 (2)	
O(1)–O(4$^{\rm ii}$)	2×	2·88 (2)	115·8 (6)
–O(7$^{\rm ii}$)		2·91 (2)	110·0 (8)
O(4)–O(4$^{\rm vii}$)		2·59 (3)	106·6 (9)
–O(7$^{\rm i}$)	2×	2·66 (2)	103·7 (6)
T(3)–O(3)	2×	1·70 (2)	
–O(6)	2×	1·86 (2)	
O(3)–O(3$^{\rm v}$)		2·84 (4)	112·7 (14)
–O(6$^{\rm i}$)	4×	2·88 (2)	108·1 (4)
O(6)–O(6$^{\rm vii}$)		3·07 (4)	111·8 (11)

		Distance	O–M–O angle
M(4)–O(2$^{\rm viii}$)		2·05 (1)	
–O(4)	2×	2·07 (1)	
–O(5)	2×	2·11 (1)	
–O(7$^{\rm viii}$)		2·01 (1)	
O(2)–O(4$^{\rm viii}$)	2×	2·82 (2)	86·2 (4)
–O(5$^{\rm vi}$)	2×	2·73 (2)	82·4 (4)
O(4)–O(4$^{\rm vii}$)		3·07 (3)	95·5 (8)
–O(5$^{\rm i}$)	2×	2·97 (1)	90·4 (5)
–O(7$^{\rm v}$)	2×	3·05 (2)	96·5 (4)
O(5)–O(5$^{\rm ii}$)		2·75 (3)	81·5 (7)
–O(7$^{\rm v}$)	2×	3·03 (2)	94·6 (4)
M(6)–O(6)	2×	2·02 (1)	
–O(8$^{\rm iii}$)	4×	2·04 (1)	
O(6)–O(8$^{\rm i}$)	4×	2·88 (2)	90·1 (5)
–O(8$^{\rm v}$)	4×	2·87 (2)	89·9 (5)
O(8)–O(8$^{\rm v}$)	2×	2·84 (2)	87·9 (7)
–O(8$^{\rm iii}$)	2×	2·94 (4)	92·1 (7)
T(2)–O(5)	2×	1·75 (1)	
–O(7)		1·69 (2)	
–O(8)		1·65 (2)	
O(5)–O(5$^{\rm vii}$)		2·92 (3)	113·3 (9)
–O(7$^{\rm i}$)	2×	2·80 (2)	109·1 (4)
–O(8$^{\rm i}$)	2×	2·74 (2)	107·3 (5)
O(7)–O(8$^{\rm i}$)		2·76 (2)	111·0 (8)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35753 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A projection on (100) of the structure of phase IV is shown in Fig. 1. The structure is based on a slightly distorted cubic close packing of O atoms. The stacking layers are parallel to (051), $(0\bar{5}1)$, (010) and $(10\bar{1})$. There are six crystallographically independent cations (M) which are octahedrally coordinated by O atoms, where $M(1)$, $M(2)$ and $M(6)$ are located at $x = \frac{1}{4}$ and $\frac{3}{4}$, $M(3)$, $M(4)$ and $M(5)$ at $x = \frac{1}{2}$. The $M(1)$, $M(2)$ and $M(6)$ octahedra form three different columns running parallel to the a axis. The $M(6)$ octahedra form a single column, while the $M(1)$ column shares edges with the adjacent $M(2)$ column to form a double column. $M(3)$, $M(4)$ and $M(5)$ form a single column along the b axis, and this column is connected to both the $M(1)$–$M(2)$ double column and the $M(6)$ single column by sharing edges.

There are three other crystallographically independent cations (T atoms) in the structure, which are on the mirror planes at $x = 0$ and $\frac{1}{2}$ parallel to (100) and tetrahedrally coordinated by O atoms. Of the three tetrahedra, $T(1)O_4$ and $T(2)O_4$ share corners with each other to form T_2O_7 groups, while the $T(3)O_4$ tetrahedra are isolated. Neither shared edges nor faces occur between tetrahedra and octahedra in the structure of phase IV – only shared corners are present.

$T(1)O_4$ and $T(2)O_4$, which form T_2O_7 groups, and the $M(1)$–$M(2)$ double-octahedral column form a band parallel to (010). This band can be considered as a part of a modified-spinel-type (β-phase) structure. On the other hand, isolated $T(3)O_4$ tetrahedra and the $M(6)$ single-octahedral column make another band which can be considered as a part of a spinel-type (γ-phase) structure. Thus, the structure of phase IV can be described as made up of alternating spinel-type modified-spinel-type bands. These features are shown in Fig. 1.

When cation distributions are completely disordered, the M and T sites are occupied by $\frac{3}{4}$Ni + $\frac{1}{4}$Al and $\frac{1}{2}$Si + $\frac{1}{2}$Al, respectively, where Si atoms are assumed to occupy only tetrahedral sites. However, Ni atoms are relatively concentrated in the $M(1)$ and $M(4)$ sites, and Al atoms in the $M(2)$ and $M(5)$ sites. The different distributions of Ni and Al in the M octahedra result in the differences in the mean values of the M—O distances: mean $M(1)$—O, 2·058 (0·85 Ni + 0·15 Al) and $M(4)$—O, 2·070 Å (0·85 Ni + 0·15 Al), in which Ni atoms are relatively concentrated, are greater than $M(2)$—O, 2·020 (0·50 Ni + 0·50 Al) and $M(5)$—O, 1·965 Å (0·69 Ni + 0·31 Al).

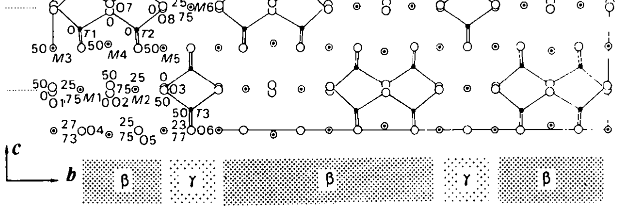

Fig. 1. Crystal structure of phase IV projected on (100). The spinel-type (γ) and modified-spinel-type (β) bands are also illustrated.

The mean $T(3)$—O distance, 1·780 Å, is larger than those in the $T(1)$ and $T(2)$ tetrahedra, which are 1·694 and 1·709 Å, respectively. A small amount of Ni occupies the $T(1)$ and $T(3)$ sites (12% and 11% respectively), but there is almost no Ni in $T(2)$. The differences among the mean values of the T—O distances depend not only on the distribution of the Ni atoms but also on those of the Al and Si atoms. The largest mean T—O value for the $T(3)O_4$ tetrahedra is due to the greater concentration of Al atoms in addition to Ni atoms. The Al content is also greater than the Si content in $T(2)$, because the mean $T(2)$—O distance is much longer than the Si—O distances in spite of the absence of Ni atoms in $T(2)$. On the other hand, $T(1)$ is expected to be enriched with Si atoms, because the large mean value of $T(1)$—O is mostly due to the Ni content on $T(1)$. Therefore, the possibility of combinations such as O_3Al—O—AlO_3 in T_2O_7 groups is scarcely expected.

Furthermore, the results of cation distributions suggest that the $NiAl_2O_4$ component is more enriched in the isolated tetrahedra and their surroundings than in other parts of the structure of phase IV.

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Structure of Nickel Aluminosilicate (Phase V): A High-Pressure Phase Related to Spinel

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Abstract. $Ni_3Al_2SiO_8$ (phase V), orthorhombic, *Pmma*, $a = 5{\cdot}665$ (1), $b = 8{\cdot}590$ (1), $c = 8{\cdot}097$ (2) Å, $Z = 3$, $D_x = 4{\cdot}907$ Mg m^{-3}. The crystals are products quenched from $8{\cdot}6 \times 10^3$ MPa and 1533 K, and are the highest-pressure phase of the $NiAl_2O_4$–Ni_2SiO_4 system known at present. The structure was solved by the Patterson method and refined to an R of 0·059 for 1358 unique reflections from diffractometer data with $|F_o| \geq 3\sigma(F_o)$. The structure is based on a cubic close packing of O atoms and is closely related to phase IV of the $NiAl_2O_4$–Ni_2SiO_4 system, which is an extended spinel and modified-spinel structure. Both isolated TO_4 and coupled T_2O_7 tetrahedra exist and the $TO_4:T_2O_7$ ratio is 1 : 1.

Introduction. Phase V is the highest-pressure form known of five phases which have been observed in studies of the $NiAl_2O_4$–Ni_2SiO_4 system (Ma, 1974; Akaogi, Akimoto, Takahashi, Horiuchi & Morimoto, 1978). The structures of phases I, II, III and IV were reported by Ma, Sahl & Tillmanns (1975), Ma & Tillmanns (1975), Ma & Sahl (1975) and Horioka, Takahashi, Morimoto, Horiuchi, Akaogi & Akimoto (1981), respectively. All phases in this system have spinel-related structures and were classified into 'spinelloids' (Horiuchi, Horioka & Morimoto, 1980). Phase relations of these structures at about 1400 K have been investigated by Horioka, Horiuchi, Akaogi & Akimoto (1981).

The crystals of phase V used in this study were prepared by the following method. An intimate mixture of synthetic Ni_2SiO_4 (olivine) and $NiAl_2O_4$ (spinel) in the ratio 1 : 1 was used as the starting material. The mixture was inserted into a cylindrical platinum heater which was placed in a pyrophyllite tetrahedron of edge 14 mm. High-pressure and high-temperature experiments were carried out at $8{\cdot}6 \times 10^3$ MPa and 1533 K with a tetrahedral press with anvils of edge 9 mm. The run-time was 10 min. The crystals of phase V were transparent green with dimensions of *ca* 20–40 μm. The single crystal used for the X-ray photographic experiments and intensity measurements was about 0·03 × 0·03 × 0·04 mm. Cell dimensions were determined by the least-squares method using 20 high-angle reflections (Mo $K\alpha_1$ and α_2) measured on a four-circle diffractometer.

Photographs indicated *mmm* Laue symmetry; systematic absences were $hk0$, $h = 2n + 1$. These result in the possible space groups *Pmma*, $P2_1ma$ and *Pm*2*a*. The space group *Pmma*, which has a center of symmetry, was assumed for the structure analysis and confirmed to be correct from the final results.

The composition of the specimen was confirmed to be in good agreement with the starting bulk composition, $Ni_3Al_2SiO_8$, by means of an analytical electron microscope (Hitachi-12SE). Kyanite (Al_2SiO_5) was used as a standard. The ratio of the characteristic X-ray intensities of Al to Si is 1·74 for the specimen, whereas it is 1·60 for kyanite.

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