

## Crystal Structures of Spinel Polymorphs of $\text{Fe}_2\text{SiO}_4$ and $\text{Ni}_2\text{SiO}_4$

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### Abstract

The crystal structures of the spinel polymorphs of  $\text{Fe}_2\text{SiO}_4$  and  $\text{Ni}_2\text{SiO}_4$  have been investigated in detail using single crystals synthesized at high pressures and high temperatures.

$\text{Fe}_2\text{SiO}_4$  spinel with  $a = 8.234(1)\text{\AA}$  had an approximately normal spinel structure. The site occupancy refinement indicates that  $2.3 \pm 1.0$  percent of the total silicon atoms are found in the octahedral sites. The  $u$ -parameter is 0.3658(2). The final  $R'$  value is 0.025 for all 128 observed reflections. The average Si–O and Fe–O distances are 1.652 $\text{\AA}$  and 2.137 $\text{\AA}$ , respectively.

$\text{Ni}_2\text{SiO}_4$  spinel with  $a = 8.044(1)\text{\AA}$  also had a normal spinel structure. Only  $0.5 \pm 1.2$  percent of the total silicon atoms are octahedrally coordinated. The  $u$ -parameter is 0.3687(2) and the final  $R'$  value is 0.028 for all 116 observed reflections. The average Si–O and Ni–O distances are 1.654 $\text{\AA}$  and 2.063 $\text{\AA}$  respectively.

### Introduction

The olivine polymorph of ferromagnesian orthosilicate,  $(\text{Mg,Fe})_2\text{SiO}_4$ , is believed to be the most abundant mineral in the earth's upper mantle. The olivine-spinel transformation of orthosilicates has been intensively investigated in view of its great importance in interpreting the rapid increase in seismic wave velocities at depths of around 400 km in the mantle. Following the first successful synthesis of the spinel polymorph of  $\text{Fe}_2\text{SiO}_4$  (Ringwood, 1958), many other orthosilicates, e.g.  $\text{Ni}_2\text{SiO}_4$  (Ringwood, 1962),  $\text{Co}_2\text{SiO}_4$  (Ringwood, 1963),  $\text{Mg}_2\text{SiO}_4$  (Akimoto and Ida, 1966; Suito, 1972; Ito, unpublished data) have been found to transform into spinel structure at high pressures and high temperatures.

The structural basis of the olivine-spinel transformation was first given by Kamb (1968). The stability of silicate spinel was also discussed by Syono, Tokonami, and Matsui (1971) on the basis of crystal field theory. Although exact information about coordinates of oxygen atoms and distributions of cations among metal-ion sites is indispensable for a detailed discussion of stability, only a few structures of silicate spinels have been refined by the X-ray diffraction method. Ma (1972) attempted to determine both cation distributions and the oxygen parameter in  $\text{Ni}_2\text{SiO}_4$  spinel from powder diffraction data. Recently,

Morimoto *et al* (1974) studied for the first time the crystal structure of the spinel polymorph of  $\text{Co}_2\text{SiO}_4$ .

In the present study, the crystal structures of the spinel polymorphs of  $\text{Fe}_2\text{SiO}_4$  and  $\text{Ni}_2\text{SiO}_4$  have been refined from single crystal X-ray data. This may contribute to a better understanding of the silicate spinel structure.

### Experimental

#### (a) $\gamma\text{-Fe}_2\text{SiO}_4$

Crystals of the spinel polymorph ( $\gamma$ -phase) of  $\text{Fe}_2\text{SiO}_4$  were synthesized from the olivine phase of  $\text{Fe}_2\text{SiO}_4$  at high pressures and high temperatures. Initially, a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  powders in the orthosilicate ratio was formed into a tablet and heated at 1150°C for about three hours under a controlled atmosphere. The control of partial pressure of oxygen was obtained by the mixed gas technique, using the  $\text{CO}_2\text{-H}_2$  system with a mixing ratio of  $\text{CO}_2$  to  $\text{H}_2$ ,  $P_{\text{CO}_2}/P_{\text{H}_2}$ , of 1/1.  $\text{Fe}_2\text{SiO}_4$  thus synthesized was found to be a single-phase material with the olivine structure. Then dark green, granular  $\gamma$ -phase crystals were obtained from the olivine phase at 75 kbar and 1500°C using a tetrahedral anvil, high-pressure apparatus with graphite capsules. The cell dimension and the space group,  $Fd3m$ , obtained from preliminary measurements of precession photographs, confirmed the crystal to be  $\gamma\text{-Fe}_2\text{SiO}_4$ . An accurate cell dimension of 8.234(1) $\text{\AA}$  was determined from powder diffraction data.

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A nearly spherical crystal (0.18 mm in diameter) was used for the intensity collection. Diffraction intensities were measured by the  $\omega$ -scan technique with a RIGAKU automatic four-circle diffractometer using  $\text{MoK}\alpha$  radiation which was monochromatized with a graphite plate, up to  $2\theta = 90^\circ$ . The scanning speed was  $2^\circ/\text{min}$ , and scanning was repeated up to three times when the standard deviation of a structure amplitude due to the counting statistics,  $\sigma(|F|)$ , was larger than 2 percent of the amplitude ( $|F|$ ). The scanning width was  $2.5^\circ$  for all reflections. The  $\omega$ -scan technique was employed because of the rather broad diffraction width. The intensities were corrected for Lorentz, polarization, and absorption factors assuming a sphere of 0.18 mm in diameter for the crystal shape. Extinction corrections were made in the course of refinement. In total, 150 independent reflections were measured, among which 22 had zero intensity. The remaining 128 reflections were used for the structure refinement.

#### (b) $\gamma\text{-Ni}_2\text{SiO}_4$

Starting materials used to synthesize  $\gamma\text{-Ni}_2\text{SiO}_4$  crystals were a mixture of silicic acid and NiO. NiO was obtained by heating nickel nitrate at  $500^\circ\text{C}$ . Crystals of the spinel polymorph of  $\text{Ni}_2\text{SiO}_4$  were synthesized at 55 kbar and  $1400^\circ\text{C}$  using these starting materials and the tetrahedral anvil press. Nickel capsules and a graphite heater were used for the high-pressure and high-temperature experiments. The crystals obtained were finer grained than the  $\gamma\text{-Fe}_2\text{SiO}_4$  crystals and were green in color. The cell dimension which was determined from the  $2\theta$  angles of seven reflections measured on a four-circle diffractometer was  $8.044(1) \text{ \AA}$ .

Intensities were collected and converted into structure amplitudes in a manner similar to that described for the previous experiment with  $\gamma\text{-Fe}_2\text{SiO}_4$ . The following are the main differences in data collection. (1) The size of the crystal used is 0.08 mm in diameter. (2) The  $\omega - 2\theta$  scan technique was adopted, and the scanning width was determined according to the formula,  $1.4^\circ + 0.6^\circ \times \tan \theta$ . In all, 127 reflections were measured, of which 11 reflections have zero intensity. The remaining 116 reflections were used in the structure refinement.

#### Structure Refinement

Structural refinements of  $\gamma\text{-Fe}_2\text{SiO}_4$  and  $\gamma\text{-Ni}_2\text{SiO}_4$  were calculated using a local version of a full-matrix least-squares program LINUS (Coppens and Hamilton,

1970). The first stage of the program refined for each crystal the so-called  $u$ -parameter (the positional parameter of oxygen atoms), individual anisotropic temperature factors, and the scale factor assuming a normal spinel structure. The  $R'$  value ( $(\sum | |F_o| - |F_c| |^2) / \sum |F_o|^2$ )<sup>1/2</sup> was reduced to 0.037 for  $\gamma\text{-Fe}_2\text{SiO}_4$ , while the value remained at 0.093 for  $\gamma\text{-Ni}_2\text{SiO}_4$ . Then, the isotropic extinction parameter was introduced into the calculation, yielding  $R'$  values of 0.026 and 0.028 for  $\gamma\text{-Fe}_2\text{SiO}_4$  and  $\gamma\text{-Ni}_2\text{SiO}_4$  respectively. The rather small extinction effect observed in the  $\gamma\text{-Fe}_2\text{SiO}_4$  crystal agrees with the broader reflection width.

The cation distributions over the tetrahedral and octahedral sites were examined by changing the population parameter,  $\alpha$ , in the expression  $(M_{2-\alpha}, \text{Si}_\alpha)(\text{Si}_{1-\alpha}, M_\alpha)\text{O}_4$ , where  $M$  stands for Fe or Ni. The least squares refinements initiated with  $\alpha = 0$  converged to  $\alpha = 0.023(10)$  for  $\gamma\text{-Fe}_2\text{SiO}_4$  and to  $\alpha = 0.005(12)$  for  $\gamma\text{-Ni}_2\text{SiO}_4$ , giving  $R'$  values of 0.025 and 0.028 for the respective crystals. Since  $\alpha$  shifted very little from the value of the ideally normal spinel structure in both crystals, it was uncertain if the refinements converged to real minima, or if they stopped at subsidiary ones near the initial  $\alpha$ -value. To check this, each structure was refined at several fixed  $\alpha$ -values and the  $R'$  values compared. The result is shown in Figure 1. Clearly, the  $\alpha$ -value obtained with the least-squares procedure gives the best fit between observed and calculated structure amplitude in both crystals.

In the above refinements, the atomic scattering factors of  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Si}^{4+}$  were taken from *International Tables for X-ray Crystallography*, Vol. 3 (1962). The values used for  $\text{O}^{2-}$  were those given by Tokonami (1965). Unit weight was assigned for all the reflections in the least squares calculations. The final parameters are listed in Table 1, and the observed and calculated structure amplitudes are compared in Table 2.

#### Discussion

In both crystals, the  $u$ -parameter is markedly smaller than 0.375, corresponding to the ideal closest-packed arrangement of oxygen ions and contrary to ordinary normal spinels. This particular property of silicate spinels was first suggested by Kamb (1968) and recently confirmed experimentally by Ma (1972) in  $\gamma\text{-Ni}_2\text{SiO}_4$  and by Morimoto *et al* (1974) in  $\gamma\text{-Co}_2\text{SiO}_4$ . Kamb calculated the value of 0.365 for the  $u$ -parameter of  $\gamma\text{-Fe}_2\text{SiO}_4$  from the cell constant by

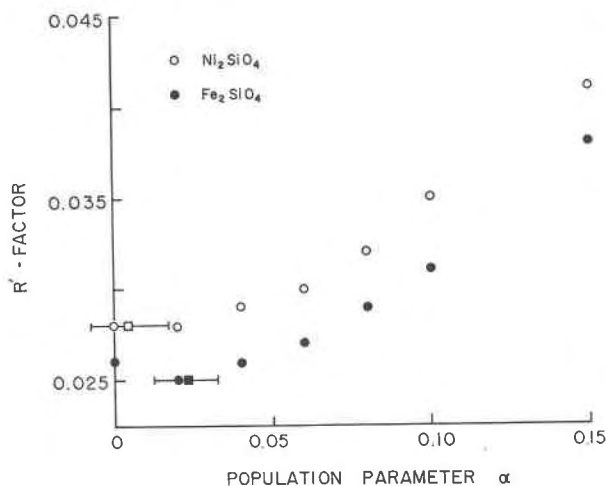


FIG. 1.  $R'$  factors are plotted against population parameters,  $\alpha$ , in the expression  $(M_{2-\alpha}, Si_{\alpha})(Si_{1-\alpha}, M_{\alpha})O_4$ , where  $M$  stands for Fe or Ni. Solid square and open square are the results of least-squares calculations for  $Fe_2SiO_4$  and  $Ni_2SiO_4$ , respectively.

assuming the Si-O distance to be 1.634 Å, the same as in the olivine form. The  $u$ -parameter is in surprisingly good agreement with the experimental one of 0.3658(2) obtained in this study. The small discrepancy is due to a slight expansion of  $SiO_4$  tetrahedra in the spinel form. The  $u$ -parameter of  $\gamma$ - $Ni_2SiO_4$  is 0.3687(2) and is a little larger than the value, 0.367(3), determined by Ma (1972) from powder diffraction data.

In Figure 2 the  $u$ -parameters of three silicate spinels,  $\gamma$ - $Fe_2SiO_4$ ,  $\gamma$ - $Co_2SiO_4$ , and  $\gamma$ - $Ni_2SiO_4$  are plotted

against cell dimensions. As seen from Figure 2, the  $u$ -parameter decreases with increasing cell dimension. Since Si-O distances are more or less the same in these silicate spinels, the observed correlation suggests that the  $u$ -parameter and cell dimension change significantly with octahedral metal-oxygen distance in silicate spinels. We can deduce the value of the  $u$ -parameter of  $\gamma$ - $Mg_2SiO_4$  to be approximately 0.368 by interpolation.

Interatomic distances and angles in  $\gamma$ - $Fe_2SiO_4$  and  $\gamma$ - $Ni_2SiO_4$  are listed in Table 3. As a result of the small  $u$ -parameters, the shared edges of  $FeO_6$  and  $NiO_6$  octahedra are remarkably longer than the unshared ones. As pointed out by Kamb (1968), this does not satisfy Pauling's rule for edge sharing by coordination polyhedra, and this could be a reason why silicate spinels are unstable at atmospheric pressure. The Si-O distances of  $SiO_4$  tetrahedra are 1.654 Å and 1.652 Å in  $\gamma$ - $Fe_2SiO_4$  and  $\gamma$ - $Ni_2SiO_4$  respectively, and are slightly longer than the value 1.646 Å reported for  $\gamma$ - $Co_2SiO_4$  by Morimoto *et al* (1974). Under high pressures, it is likely that the Si-O distance remains almost unchanged while the M-O distance decreases more easily. Consequently, the  $u$ -parameter increases gradually, and under very high pressures the spinel structure becomes stable. However, we cannot account for the differences of the silicate olivine-spinel transition pressures in this manner alone. The transition pressures at 1000°C from olivine to spinel increase in the sequence

TABLE 1. Final Atomic Coordinates, Anisotropic Temperature Factors, and Extinction Parameter in  $\gamma$ - $Fe_2SiO_4$  and  $\gamma$ - $Ni_2SiO_4$

Atom	Site occupancy	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{11}$	$\beta_{23}$
$\gamma$ - $Fe_2SiO_4$		$G = 0.049(5) \times 10^4$								
M	Fe 0.989(5) Si 0.011	5/8	5/8	5/8	0.0015(1)	0.0015(1)	0.0015(1)	-0.0001(1)	-0.0001(1)	-0.0001(1)
T	Fe 0.023 Si 0.977	0	0	0	0.0010(1)	0.0010(1)	0.0010(1)	0	0	0
O		0.3658(2)	0.3658(2)	0.3658(2)	0.0015(1)	0.0015(1)	0.0015(1)	-0.0001(1)	-0.0001(1)	-0.0001(1)
$\gamma$ - $Ni_2SiO_4$		$G = 0.925(59) \times 10^4$								
M	Ni 0.990(6) Si 0.010	5/8	5/8	5/8	0.0013(1)	0.0013(1)	0.0013(1)	-0.0003(1)	-0.0003(1)	-0.0003(1)
T	Ni 0.005 Si 0.995	0	0	0	0.0011(2)	0.0011(2)	0.0011(2)	0	0	0
O		0.3687(2)	0.3687(2)	0.3687(2)	0.0014(1)	0.0014(1)	0.0014(1)	0.0005(3)	0.0005(3)	0.0005(3)

M and T represent octahedral and tetrahedral sites respectively.

The following constraints are required from the symmetry:  $\beta_{11} = \beta_{22} = \beta_{33}$  and  $\beta_{12} = \beta_{23} = \beta_{31}$  for all the atoms, and  $\beta_{12} = \beta_{23} = \beta_{31} = 0$  for the T-atom.



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