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Crystal Structures of Spinel Polymorphs of Fe_2SiO_4 and Ni_2SiO_4

TAKEHIKO YAGI, FUMIYUKI MARUMO[1], AND SYUN-ITI AKIMOTO

Institute for Solid State Physics, University of Tokyo,
Minato-ku, Tokyo 106, Japan

Abstract

The crystal structures of the spinel polymorphs of Fe_2SiO_4 and Ni_2SiO_4 have been investigated in detail using single crystals synthesized at high pressures and high temperatures.

Fe_2SiO_4 spinel with $a = 8.234(1)$Å had an approximately normal spinel structure. The site occupancy refinement indicates that 2.3 ± 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 1.652Å and 2.137Å, respectively.

Ni_2SiO_4 spinel with $a = 8.044(1)$Å also had a normal spinel structure. Only 0.5 ± 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 1.654Å and 2.063Å respectively.

Introduction

The olivine polymorph of ferromagnesian orthosilicate, $(Mg,Fe)_2SiO_4$, 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 Fe_2SiO_4 (Ringwood, 1958), many other orthosilicates, *e.g.* Ni_2SiO_4 (Ringwood, 1962), Co_2SiO_4 (Ringwood, 1963), Mg_2SiO_4 (Akimoto and Ida, 1966; Suito, 1972; Ito, unpublished data) have been found to transform into spinel structure at high pressures and high temperatures.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 Ni_2SiO_4 spinel from powder diffraction data. Recently, Morimoto *et al* (1974) studied for the first time the crystal structure of the spinel polymorph of Co_2SiO_4.

In the present study, the crystal structures of the spinel polymorphs of Fe_2SiO_4 and Ni_2SiO_4 have been refined from single crystal X-ray data. This may contribute to a better understanding of the silicate spinel structure.

Experimental

(*a*) γ-Fe_2SiO_4

Crystals of the spinel polymorph (γ-phase) of Fe_2SiO_4 were synthesized from the olivine phase of Fe_2SiO_4 at high pressures and high temperatures. Initially, a mixture of Fe_2O_3 and 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 CO_2-H_2 system with a mixing ratio of CO_2 to H_2, P_{CO_2}/P_{H_2}, of 1/1. Fe_2SiO_4 thus synthesized was found to be a single-phase material with the olivine structure. Then dark green, granular γ-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 γ-Fe_2SiO_4. An accurate cell dimension of 8.234(1)Å was determined from powder diffraction data.

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[1] Present address: Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan.

A nearly spherical crystal (0.18 mm in diameter) was used for the intensity collection. Diffraction intensities were measured by the ω-scan technique with a RIGAKU automatic four-circle diffractometer using Mo$K\alpha$ radiation which was monochromatized with a graphite plate, up to $2\theta = 90°$. The scanning speed was 2°/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° for all reflections. The ω-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*) γ-Ni_2SiO_4

Starting materials used to synthesize γ-Ni_2SiO_4 crystals were a mixture of silicic acid and NiO. NiO was obtained by heating nickel nitrate at 500°C. Crystals of the spinel polymorph of Ni_2SiO_4 were synthesized at 55 kbar and 1400°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 γ-Fe_2SiO_4 crystals and were green in color. The cell dimension which was determined from the 2θ angles of seven reflections measured on a four-circle diffractometer was 8.044(1) Å.

Intensities were collected and converted into structure amplitudes in a manner similar to that described for the previous experiment with γ-Fe_2SiO_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, $1.4° + 0.6° \times \tan\theta$. 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 γ-Fe_2SiO_4 and γ-Ni_2SiO_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 ($[(\Sigma\ |\ |F_o| - |F_c|\ |^2)/\Sigma\ |F_o|^2]^{1/2}$) was reduced to 0.037 for γ-Fe_2SiO_4, while the value remained at 0.093 for γ-Ni_2SiO_4. Then, the isotropic extinction parameter was introduced into the calculation, yielding R' values of 0.026 and 0.028 for γ-Fe_2SiO_4 and γ-Ni_2SiO_4 respectively. The rather small extinction effect observed in the γ-Fe_2SiO_4 crystal agrees with the broader reflection width.

The cation distributions over the tetrahedral and octahedral sites were examined by changing the population parameter, α, in the expression $(M_{2-\alpha}, Si_\alpha)(Si_{1-\alpha}, M_\alpha)O_4$, where M stands for Fe or Ni. The least squares refinements initiated with $\alpha = 0$ converged to $\alpha = 0.023(10)$ for γ-Fe_2SiO_4 and to $\alpha = 0.005(12)$ for γ-Ni_2SiO_4, giving R' values of 0.025 and 0.028 for the respective crystals. Since α 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 α-value. To check this, each structure was refined at several fixed α-values and the R' values compared. The result is shown in Figure 1. Clearly, the α-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 Fe^{2+}, Ni^{2+}, and Si^{4+} were taken from *International Tables for X-ray Crystallography*, Vol. 3 (1962). The values used for 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 γ-Ni_2SiO_4 and by Morimoto *et al* (1974) in γ-Co_2SiO_4. Kamb calculated the value of 0.365 for the u-parameter of γ-Fe_2SiO_4 from the cell constant by

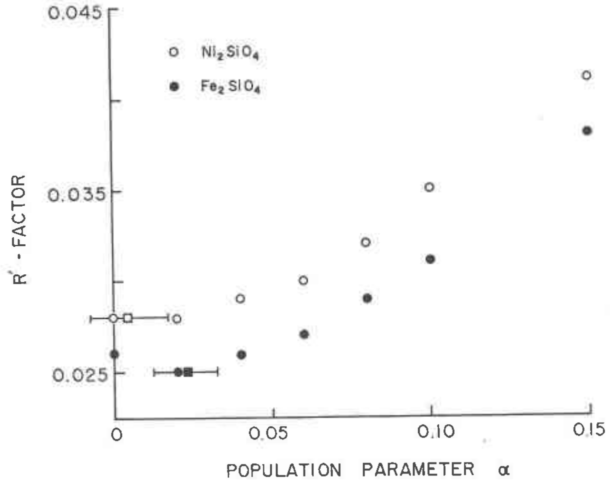

FIG. 1. R' factors are plotted against population parameters, α, in the expression $(M_{2-\alpha}, \mathrm{Si}_\alpha)(\mathrm{Si}_{1-\alpha}, M_\alpha)\mathrm{O}_4$, where M stands for Fe or Ni. Solid square and open square are the results of least-squares calculations for Fe_2SiO_4 and Ni_2SiO_4, respectively.

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 γ-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, γ-Fe_2SiO_4, γ-Co_2SiO_4, and γ-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 γ-Mg_2SiO_4 to be approximately 0.368 by interpolation.

Interatomic distances and angles in γ-Fe_2SiO_4 and γ-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 γ-Fe_2SiO_4 and γ-Ni_2SiO_4 respectively, and are slightly longer than the value 1.646 Å reported for γ-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 γ-Fe_2SiO_4 and γ-Ni_2SiO_4

Atom	Site occupancy	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{31}	β_{23}
γ-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)
γ-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.

TABLE 2. Observed and Calculated Structure Factors

(a) γ-Fe_2SiO_4

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	4	381.88	384.22	1	9	13	38.16	36.24	3	9	9	56.46	55.37
0	0	8	282.61	287.22	1	11	11	40.54	40.19	3	9	11	33.10	32.13
0	0	12	110.63	113.50	2	2	2	139.08	133.97	3	9	13	15.90	14.25
0	0	16	108.58	113.39	2	2	4	64.63	65.91	3	11	11	69.81	68.42
0	2	2	79.65	80.16	2	2	6	130.17	130.30	4	4	4	227.71	226.12
0	2	6	51.28	55.94	2	2	8	45.84	47.53	4	4	6	7.29	3.45
0	2	10	40.27	40.87	2	2	10	90.00	91.24	4	4	8	228.84	225.43
0	2	14	20.76	20.24	2	2	12	28.29	28.58	4	4	12	101.21	100.08
0	4	4	408.19	408.12	2	2	14	63.70	66.11	4	6	6	36.28	36.44
0	4	8	163.86	164.93	2	2	16	17.44	17.78	4	6	10	35.50	35.57
0	4	12	160.01	161.58	2	4	4	6.57	5.51	4	6	14	11.70	12.12
0	6	6	52.69	53.42	2	4	6	52.91	55.09	4	8	8	115.37	113.91
0	6	10	26.05	24.27	2	4	8	7.68	6.23	4	8	10	8.05	3.47
0	6	14	26.89	27.03	2	4	10	31.30	31.97	4	8	12	128.14	126.94
0	8	8	191.41	187.79	2	4	14	24.12	23.72	5	5	5	89.65	88.28
0	8	12	91.44	90.19	2	6	6	105.95	107.85	5	5	7	38.86	39.14
0	10	10	32.12	32.28	2	6	8	37.24	36.45	5	5	9	14.53	14.52
1	1	1	103.45	102.84	2	6	10	78.96	79.72	5	5	11	70.51	71.69
1	1	3	227.33	219.59	2	6	12	26.53	25.63	5	5	13	40.17	39.02
1	1	5	151.37	150.77	2	6	14	60.77	61.22	5	7	7	95.94	94.44
1	1	7	73.57	72.64	2	8	8	11.12	9.29	5	7	9	67.23	67.79
1	1	9	30.00	29.13	2	8	10	29.03	28.56	5	7	11	39.94	39.59
1	1	11	96.87	96.44	2	8	12	11.11	10.30	5	7	13	18.91	20.09
1	1	13	53.37	53.75	2	8	14	15.72	15.61	5	9	9	43.87	43.49
1	1	15	38.83	38.75	2	10	10	67.54	65.63	5	9	11	25.94	27.86
1	3	3	107.51	113.75	2	10	12	18.37	17.37	5	11	11	61.16	58.93
1	3	5	61.77	64.79	3	3	3	208.40	205.16	6	6	6	90.20	91.01
1	3	7	141.57	146.17	3	3	5	147.37	150.02	6	6	8	34.70	35.49
1	3	9	90.09	91.61	3	3	7	75.54	74.69	6	6	10	72.93	71.56
1	3	11	49.41	50.55	3	3	9	36.46	36.88	6	6	12	19.25	18.62
1	3	13	19.09	20.52	3	3	11	96.17	96.72	6	6	14	56.67	57.08
1	3	15	65.37	67.71	3	3	13	58.61	57.02	6	8	10	20.33	17.64
1	5	5	37.32	36.53	3	3	15	40.89	41.46	6	10	10	61.73	60.80
1	5	7	116.75	116.30	3	5	5	114.09	115.32	7	7	7	56.10	55.12
1	5	9	72.55	73.01	3	5	7	54.18	53.72	7	7	9	36.56	33.81
1	5	11	40.84	40.61	3	5	9	26.20	25.74	7	7	11	76.59	76.28
1	5	15	58.60	60.35	3	5	11	82.58	82.31	7	7	13	46.90	48.09
1	7	7	60.69	58.50	3	5	13	49.77	48.73	7	9	9	22.58	22.03
1	7	9	33.13	33.05	3	5	15	34.74	34.83	7	9	11	58.25	56.63
1	7	11	85.02	83.50	3	7	7	113.93	113.98	8	8	8	143.35	142.71
1	7	13	50.82	51.99	3	7	9	79.07	78.84	8	10	10	24.96	24.58
1	9	9	13.88	14.36	3	7	11	49.71	49.11	9	9	9	7.71	7.47
1	9	11	62.05	62.89	3	7	13	24.26	23.89					

(b) γ-Ni_2SiO_4

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	4	421.01	416.34	1	11	11	43.62	45.24	4	8	8	137.10	131.83
0	0	8	302.21	308.93	2	2	2	167.14	167.37	4	8	12	139.88	140.01
0	0	12	127.72	131.51	2	2	4	63.62	65.07	4	10	10	18.47	16.41
0	0	16	126.28	130.65	2	2	6	151.24	152.75	5	5	5	103.57	102.44
0	2	2	81.54	76.98	2	2	8	45.74	45.53	5	5	7	48.74	49.62
0	2	6	54.35	56.23	2	2	10	99.01	101.69	5	5	9	28.97	26.29
0	2	10	37.62	37.68	2	2	12	28.59	27.41	5	5	11	74.21	75.77
0	2	14	21.77	20.50	2	2	14	68.30	69.15	5	5	13	47.93	45.47
0	4	4	437.72	434.51	2	4	4	12.16	4.18	5	7	7	99.23	97.69
0	4	8	187.99	186.65	2	4	6	51.70	51.87	5	7	9	73.96	74.27
0	4	12	174.69	176.46	2	4	10	31.83	31.97	5	7	11	44.96	42.82
0	6	6	47.57	47.94	2	4	14	19.43	21.20	5	7	13	26.73	31.29
0	6	10	28.24	27.10	2	6	6	124.52	122.01	5	9	9	54.05	50.82
0	6	14	22.32	21.96	2	6	8	36.45	35.94	5	9	11	33.76	33.21
0	8	8	207.25	204.09	2	6	10	88.13	86.40	6	6	6	100.91	101.54
0	8	12	106.98	106.55	2	6	12	23.73	23.73	6	6	8	31.60	31.64
0	10	10	25.31	25.68	2	6	14	63.00	65.88	6	6	10	76.39	76.15
1	1	1	126.27	128.47	2	8	10	27.13	26.06	6	6	12	19.64	19.19
1	1	3	232.11	232.78	2	10	10	69.61	68.82	6	8	10	21.33	19.53
1	1	5	167.73	171.43	2	10	12	16.94	17.23	6	10	10	65.87	65.60
1	1	7	80.74	81.17	3	3	3	204.45	207.59	7	7	7	57.24	54.09
1	1	9	42.19	43.64	3	3	5	157.58	161.15	7	7	9	41.36	39.82
1	1	11	96.25	98.93	3	3	7	77.68	77.89	7	7	11	76.12	73.11
1	1	13	61.09	61.59	3	3	9	47.65	48.18	7	9	9	29.88	29.21
1	1	15	39.14	40.78	3	3	11	95.83	95.61	7	9	11	61.39	63.91
1	3	3	123.67	123.34	3	3	13	63.13	63.47	8	8	8	157.89	156.52
1	3	5	82.28	82.57	3	3	15	43.09	46.03					
1	3	7	149.08	149.74	3	5	5	132.12	129.05					
1	3	9	100.55	102.30	3	5	7	62.39	61.53					
1	3	11	52.07	53.52	3	5	9	37.41	37.49					
1	3	13	28.80	29.34	3	5	11	84.33	84.74					
1	3	15	67.13	68.31	3	5	13	55.11	55.37					
1	5	5	57.33	55.49	3	7	7	115.04	112.76					
1	5	7	124.33	123.86	3	7	9	85.74	84.64					
1	5	9	84.17	84.27	3	7	11	51.60	48.71					
1	5	11	45.75	46.03	3	7	13	31.86	30.63					
1	5	13	21.57	22.36	3	9	9	63.33	62.65					
1	5	15	61.15	66.29	3	9	11	38.57	37.51					
1	7	7	65.19	62.12	3	11	11	69.51	70.09					
1	7	9	43.04	42.02	4	4	4	250.08	252.39					
1	7	11	85.67	83.12	4	4	8	244.06	244.31					
1	7	13	57.92	57.50	4	4	12	118.52	117.12					
1	9	9	25.70	24.34	4	6	6	38.66	38.24					
1	9	11	67.15	66.97	4	6	10	29.31	30.26					
1	9	13	43.76	45.89	4	6	14	18.97	15.05					

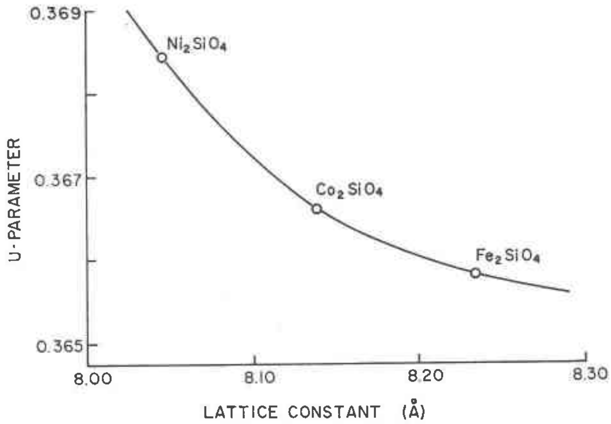

FIG. 2. U-parameter versus lattice constant curve for silicate spinels. For Co_2SiO_4 we used the data obtained by Morimoto *et al* (1974).

Ni_2SiO_4, Fe_2SiO_4, Co_2SiO_4 and Mg_2SiO_4. As suggested by Syono *et al* (1971), it would be necessary to consider the crystal field effect in a discussion of the transition pressure.

The site occupancy analysis of γ-Ni_2SiO_4 showed that the crystal is practically pure normal spinel. Ma (1972) reported that 8 ± 6 percent of silicon ions in γ-Ni_2SiO_4 are in octahedral coordination. However, in view of the large probable error in his determination, it might be said that the two results are consistent. The distribution of cations over tetrahedral and octahedral sites may depend on crystal preparation conditions. According to the investigation by Morimoto *et al* (1974), γ-Co_2SiO_4 is also estimated to be perfectly normal spinel. Alternatively, from the present investigation, a very small amount of Fe^{2+} ions seem to be replaced by Si^{4+} ions in the γ-Fe_2SiO_4 crystal. Since the γ-Fe_2SiO_4 crystals were synthesized at higher pressures and temperatures than the γ-Ni_2SiO_4 crystals, mixing of two kinds of cations in crystallographically equivalent positions would be more likely to occur in the former substance than in the latter. The slight difference in cation site occupancy between γ-Ni_2SiO_4 and γ-Fe_2SiO_4 is probably meaningful, although the determination is rather dependent on the accuracy of the values used for the relevant ions' atomic scattering factors.

TABLE 3. Interatomic Distances and Angles in γ-Fe_2SiO_4 and γ-Ni_2SiO_4

		γ-Fe_2SiO_4	γ-Ni_2SiO_4
SiO_4 tetrahedron			
Si-O	[x4]	1.652(2)Å	1.654(2)Å
O-O	[x6]	2.697(2)	2.701(2)
O-Si-O	[x6]	109.5(1)°	109.5(1)°
MO_6 octahedron			
M-O	[x6]	2.137(2)Å	2.063(2)Å
O-O (shared edge)	[x6]	3.125(2)	2.987(2)
O-O (unshared edge)	[x6]	2.915(2)	2.846(2)
O-O (mean)		3.020	2.917
O-M-O	[x6]	94.0(1)°	92.8(1)°
O-M-O	[x6]	86.0(1)°	87.2(1)°
O-M-O (mean)		90.0°	90.0°

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