Zeitschrift für Kristallographie 194, 111–119 (1991)

Cation and vacancy distribution in a synthetic defect spinel

R. Basso

Dipartimento di Scienze della Terra, Corso Europa, 26, I-16132 Genova, Italy

S. Carbonin and A. Della Giusta

Dipartimento di Mineralogia, Corso Garibaldi, 37, I-35122 Padova, Italy

Received: April 23, 1990

Defect spinel / Vacancies

Abstract. Crystal structure refinement was carried out on a defect spinel with composition $Mg_{0.388}Al_{2.408}O_4$ synthesized at 2050°C. Combining information from site occupancies and bond distances for tetrahedral and octahedral sites, the following cation and vacancy distribution were obtained: $(Al_{0.653}Mg_{0.347})(Al_{1.755}Mg_{0.041}\square_{0.204})O_4$. Structural analysis performed after heating the same crystal at 1150°C led to the same result, suggesting that the obtained distribution is stable over a wide range of temperatures.

Introduction

Spinel structure consists of a close-packed array of 32 oxygen atoms in a cubic cell with $Fd\bar{3}m$ symmetry, and a cell edge of about 8 Å units. This cell accommodates cations in the $8a$ (Wyckoff notation) tetrahedral (T) site with $\bar{4}3m$ point symmetry, and in the $16d$ octahedral (M) site with $\bar{3}m$ point symmetry. Several cations like Mg, Fe^{2+}, Fe^{3+} and Al can be accommodated in both T and M sites, while others have a strong preference for one of them (Hafner, 1960; Hill, Craig, and Gibbs, 1979; Ursov, 1983). In spinels with di- and trivalent cations part of the positions occupied by divalent cations may be vacant, giving rise to defect spinels. A well-known example among natural terms is maghemite, $Fe^{3+}_{2.67}O_4$, which can be formed

---

Correspondence to: R. Basso, Dipartimento di Scienze della Terra, Corso Europa 26, I-16132 Genova, Italy.

from magnetite under oxidizing conditions: in this case, 21.33 cations and 2.67 vacancies are present per 32 oxygen anions. The problem of vacancy distribution between the two sites has been faced by several authors, and is fully discussed by Lindsley (1976). This problem is very important in defect crystal chemistry, due to its relevance in determining diffusivity and electric properties in solid state compounds. A detailed investigation of synthetic defect spinels in the system $MgAl_2O_4-Al_{8/3}O_4$ was performed by Viertel and Seifert (1979). Here we investigate the distribution of Mg, Al and vacancies in a defect spinel with 0.61 molar fraction of $Al_{8/3}O_4$.

Cation distribution and temperature dependence in stoichiometric spinel $(Mg_{1-i}Al_i)(Al_{2-i}Mg_i)O_4$.

Yamanaka and Takeuchi (1983) showed that, on heating a spinel grown by the flux technique at 900°C to 1620°C, a relevant amount of Mg ($i =$ about 0.16 atoms per formula unit) moves from T to M, being substituted by aluminum. The exchange between Mg(T) and Al(M) is accompanied by a small decrease in cell edge and by a more relevant decrease in x, the positional parameter of oxygen. These changes can easily be computed if the bond distances of Mg and Al in both tetrahedral and octahedral coordinations are known, since the following relations hold in the atomic framework of spinel structure:

$$a_o = [5\cdot(\mathrm{T-O}) + \sqrt{33\cdot(\mathrm{M-O})^2 - 8\cdot(\mathrm{T-O})^2}]\cdot\frac{8}{11\cdot\sqrt{3}} \tag{1}$$

$$x = \frac{\frac{3}{4}\cdot\frac{(\mathrm{M-O})^2}{(\mathrm{T-O})^2} - 2 + \sqrt{\frac{33}{16}\cdot\frac{(\mathrm{M-O})^2}{(\mathrm{T-O})^2} - \frac{1}{2}}}{6\cdot\left[\frac{(\mathrm{M-O})^2}{(\mathrm{T-O})^2} - 1\right]} \tag{2}$$

where (T − O) and (M − O) are T and M bond distances, which are assumed to be linearly dependent upon the atomic fractions and crystal radii of the cations entering each site (Hill et al., 1979). Knowledge of Mg − Al intracrystalline distribution from structure analysis strictly depends on knowledge of their T and M bonding distances; site electron density cannot give appreciable help, being very similar for these elements the atomic numbers.

Shannon's (1976) crystal radii give excellent approximations for a very large number of structures, but are inadequate for detailed investigations of spinels, as shown by O'Neill and Navrotsky (1984). To obtain sufficiently accurate values of bond distances for the cations entering natural spinels, we performed a simultaneous minimization of the normalized residuals (a obs − a calc) and (x obs − x calc) using Eqs. (1) and (2) over about 40

Table 1. Data on stoichiometric spinel. Inversion (*i*), cell edge (*a* calc) and oxygen positional parameter (*x* calc) obtained from minimization of (*a* obs − *a* calc) and (*x* obs − *x* calc) in samples 1, 2, 12, 14. In samples 3, 7 inversion obtained by NMR technique. s = synthesis temperature, q = quench temperature.

a obs(A)	*a* calc(A)	*x* obs	*x* calc	*i*	*T* (°C)
1 8.0898(9)	8.089	0.2633	0.2633	0.14	natural
2 8.0858(4)	8.088	0.2626	0.2626	0.19	–
3 8.0855(6)	8.085	–	0.2599	0.39	q > 900
4 8.0855(11)	–	–	–	–	s 1400
5 8.0844(3)					s 1300–1500
6 8.0843(12)	–	–	–	–	–
7 8.0834(5)	8.087	–	0.2623	0.21	q 700
8 8.0826(3)					s 1450 1 kb
9 8.0826(3)	–	–	–	–	s 1500
10 8.0814(1)					s 1490 20 kb
11 8.0813(1)	–	–	–	–	s 1250 25 kb
12 8.0806(4)	8.087	0.2623	0.2623	0.21	s 900
13 8.0805(2)					s 1290 20 kb
14 8.0788(5)	8.087	0.2615	0.2615	0.27	q 1200

1 Finger et al. (1986); 2 Grimes et al. (1983); 3–7 Wood et al. (1986); 4 Mattioli et al. (1987); 5 Navrotsky et al. (1986); 6 Allen (1966); 8–10–13 Viertel, Seifert (1979); 9 Sharma et al. (1973); 11 Oka et al. (1984); 12–14 Yamanaka, Takeuchi (1983).

samples well characterized from structural and chemical points of view. Samples are mainly those reported by Della Giusta, Princivalle and Carbonin (1987). Princivalle, Della Giusta and Carbonin (1989), and others not yet published. Concerning Mg and Al, results are as follows: (Mg–O)T = 1.963; (Al–O)T = 1.773; (Mg–O)M = 2.095; (Al–O)M = 1.908 Å. These data were used to compute the *i* values and consequently the *a* and *x* values of Table 1, where they are compared with the existing data measured at room temperature. There is some disagreement in these experimental data. For instance, measurements by Wood, Kirkpatrik and Montez (1986) using high resolution ^{27}Al NMR spectroscopy give an inversion near 0.40 at 900° C. All their experiments up to 1425° C gave the same amount of inversion, contrary to the results of Yamanaka and Takeuchi (1983), who measured different inversions at 900 and 1200° C from quenched samples, and directly by high-temperature X-ray diffractometry up to 1700° C. Moreover, Wood et al.'s (1986) cell edge measurements do not seem to be self-consistent, since the increase in *i* from 0.21 to 0.39 (Table 1) is accompanied by a cell edge change of +0.002 Å. This is contrary to evidence from Eq. (1) in which it can be calculated – no matter what crystal radii are adopted – that the quoted increase of *i* causes a change of about −0.002 Å in cell edge.

It is interesting to note that only sample 1, the only natural sample, which underwent very slow cooling under metamorphic conditions, reached high Mg—Al ordering and consequently low inversion, high T—O and a high x value. Its cell edge is definitely higher than that of the synthetic samples. Sample 1 does contain small amounts of Zn (0.005 a.f.u.) and Fe^{2+} (0.005 a.f.u.), but their substitution for Mg can only cause an enlargement of the cell edge of 0.0004 Å with respect to pure MgAl spinel. Instead, all the synthetic samples have observed cell edges shorter than that of the natural spinel by amounts ranging from 0.004 to 0.011 Å. This fact can be explained neither by strong changes of inversion nor by non-stoichiometry, due to the relatively low synthesis temperatures (Viertel and Seifert, 1980). We presume therefore that the actual uncertainties within the reported data are definitely higher than 3 σ.

The calculated inversions of Table 1 agree well with those predicted according to the model of Novrotsky and Kleppa (1967), that is, about 0.14 at 800° C and 0.25 at 1200° C. This suggests that an inversion of about 0.14 represents the maximum ordering that spinel can reach, even under very slow cooling rates, and consequently that a temperature of about 700—800° C represents the minimum temperature at which Mg—Al exchange can occur.

Here, in the light of the accurate values of bond distances in the spinel structure, we define the distribution of Mg, Al and vacant positions in the studied defect spinel using crystal structure refinement data.

Source material and physical properties

Our specimen was a synthetic spinel boule about 25 mm wide and 40 mm long. It was kindly supplied by DJEVA, Industrie de Pierres Scientifiques, Switzerland, which manufactures crystals for high-tech industrial applications and for the jewellery trade. This spinel was obtained by melting alumina and magnesia at about 2050° C at room pressure and growing the crystal by means of a processing blowpipe following Verneuil's method. The crystal is colourless, transparent and optically isotropic. Its refractive index, measured by Becke's method using Cargille's liquids and Na-light at 25° C, is 1.730(3). This value agrees well with that calculated according to Viertel and Seifert (1979) using the chemical formula from microprobe analysis ($n = 1.726$). Specific gravity, measured with a torsion balance, is 3.61 g cm^{-3} slightly lower than the calculated value of 3.63 g cm^{-3}.

Chemical composition

Chemical analysis was performed on a thin slice of the boule, from which fragments for all other determinations were also obtained. Spot analyses were performed on a PHILIPS 515 SEM electron microscope equipped with an EDAX PV 9100 in energy dispersive mode, with an accelerating

Table 2. Chemical data.

	Measured weight percents			
	Range	Average	Atoms	Atoms[a]
MgO	10.81 – 11.62 ($\sigma = 0.80$)	11.30	0.388	0.408
Al_2O_3	88.17 – 89.02 ($\sigma = 0.25$)	88.60	2.408	2.395
Total		99.90		
Charges			8.000	8.002

[a] Calculated according to Viertel and Seifert (1979).

voltage of 15 KV and beam current of about 2 nA. Reference samples olivine Fo90 and K-anorthoclase (Jarosewich, Nelen and Norberg, 1980) were used as standards for Mg and Al, respectively. No other element was detected. The analyzed material was very homogeneous; the range of variation of weight percent measured in several spots was within 1σ for MgO and 4σ for Al_2O_3. Results are shown in Table 2.

X-ray powder diffraction pattern

The X-ray powder pattern was obtained using Ni filtered CuK_α radiation on a SIEMENS diffractometer with NaF as internal standard. Peaks from corundum were completely absent. Least squares refinement of the lines measured up to $\vartheta = 51$ degrees gave a cell edge of 7.974 Å. The equation for predicting the lattice constant of defect spinels in this system (polynomial II from Viertel and Seifert, 1979) gives a value of 7.975 Å for this composition.

The X-ray powder pattern was also calculated using the LAZY PULVERIX computer program (Yvon, Jeitschko and Parthé, 1977). The calculated intensities, based on CuK_α radiation, were obtained using scattering curves for half ionized atoms, and structural model and thermal factors according to single crystal structure refinement (see Table 4). Table 3 reports observed and calculated powder diffraction data. Comparing with data in J.C.P.D.S. card 21-1152 for a synthetic sample of $MgAl_2O_4$, two reflections, 1 1 1 and 4 4 0, show appreciable intensity differences.

Crystal structure refinement

Diffraction data were collected on a fragment measuring $0.27 \times 0.34 \times 0.15$ mm by a SIEMENS AED2 four circle diffractometer with graphite monochromatized MoK_α radiation up to $\vartheta = 45$ degrees. The ω mode was used with peak-base widths of 2 degrees 2ϑ, 45 steps integration and 0.6 s counting time per step. Six equivalent reflections were measured and corrected for absorption (ψ scan method) and background according to

Table 3. Comparison between observed and calculated X-ray powder diffraction data (*d* in Å).

h	*k*	*l*	*d* obs	*I*/*Io* obs	*d* calc	*I*/*Io* calc
1	1	1	4.61	15	4.604	15
2	2	0	2.822	36	2.819	34
3	1	1	2.406	100	2.404	100
2	2	2	(masked by NaF)		2.302	5
4	0	0	1.994	51	1.994	58
4	2	2	1.627	11	1.628	11
5	1	1	1.535	59	1.535	49
4	4	0	1.408	83	1.410	77
5	3	1	1.347	1	1.348	2
6	2	0	1.260	4	1.261	4
5	3	3	1.216	5	1.216	10
4	4	4	1.150	5	1.151	7
7	1	1	1.116	1	1.116	2
6	4	2	1.065	3	1.066	6
7	3	1	1.038	7	1.038	17
8	0	0	0.9964	4	0.9968	11

North, Phillips and Scott-Mathews (1968) and Blessing, Coppens and Becker (1972), respectively. Several authors, such as Hafner (1960), Schmocker and Waldner (1976), Tokonami and Horiuchi (1980), Grimes, Thompson and Kay (1983) have discussed the correct interpretation of space groups for spinels. As our data set showed no violation of $Fd\bar{3}m$ symmetry, this space group was retained for crystal structure refinement. Only reflections with $I > 5\sigma(I)$ were used, and unitary weights were assigned. Data were corrected for Lorentz and polarization effects and isotropic secondary extinction. The latter turned out to be very strong, and a careful examination of the intensities of symmetry equivalent reflections suggested the possibility of anisotropic extinction. Twenty-two accurately centred reflections with $10 < \vartheta < 36°$ were used for cell parameter determination. Following Della Giusta, Princivalle and Carbonin (1986), scattering curves for half ionized atoms were used (International Tables for X-ray Crystallography). The derived parameters were Al occupancies in both T and M sites, oxygen positional parameter, and anisotropic thermal factors. No chemical constraint was used during refinement. The results of structure refinement, performed with STRUCSY programs (STOE copyright), are shown in Table 4.[1]

---

[1] Additional material to this paper can be ordered referring to the no. CSD 54364, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 4. Crystal data and results of crystal structure refinement. Cell parameter and bond distances in Å units, thermal factors $\times 10^4(\text{Å}^2)$.

a	7.9783(4)
ext.	0.12×10^{-4}
$\mu(\mathrm{Mo}K_\alpha, \mathrm{cm}^{-1})$	12.2
x oxygen	0.2582(2)
(T) $U11 = 76(4)$	
(M) $U11 = 80(3)$	$U12 = -3(2)$
(O) $U11 = 106(4)$	$U12 = 14(4)$
occ Al(T)	0.98(1)
occ Al(M)	0.88(1)
T−O	1.839
M−O	1.932
tet. edge	3.003
oct. edge (shared)	2.638
oct. edge (unsh.)	2.824
measur. refl.	173
refl. with $I > 5\sigma(I)$	115
R unw.	0.037
R all refl.	0.050

Discussion

Combining the information on T and M site occupancies and bond distances gives us a sufficiently reliable picture of site population also for cations very close in atomic number, like Mg and Al. T site occupancy (0.98 Al, corresponding 12.7 e^-) may suggest the presence of very few, if any, vacancies. In fact, to justify both the high number of electrons and a small (about 0.02) number of vacancies, we must admit a): the presence of Al only; and b): a T-vacancy to oxygen distance close to half the cell parameter, to fit the observed T−O distance. Point a) contrast with the generally ascertained preference of Mg with respect to Al for tetrahedral coordination in spinel structure. Point b) is quite unrealistic for a cubic closest packed structure: data from Kullerud, Donnay and Donnay (1969) for an end-member maghemite with tetrahedral vacancies only and $a = 8.45$ Å give a T-vacancy to oxygen distance of about 2.30 Å. We consequently presume full T-site occupancy by Al + Mg: namely $\mathrm{Al}_{0.653} + \mathrm{Mg}_{0.347}$ occupancies result from the observed T−O value, using our quoted values for bond distances. In this way be have 12.7 e^-, in agreement with the observed T site electron density.

On the other hand, the number of electrons in M site is about 11.4, and since M site must contain almost exclusively Al, this is clear evidence of the presence of vacancies. The crystal chemical formula of this sample is consequently $(\mathrm{Al}_{0.653}\mathrm{Mg}_{0.347})(\mathrm{Al}_{1.755}\mathrm{Mg}_{0.041}\square_{0.204})\mathrm{O}_4$. (We retain three digits after the decimal point for site occupancies simply in order to respect the mean chemical analysis.) The number of electrons in M site, 11.7 from chemical formula, is within 2σ of the Al occupancy from the refinement. This structural arrangement with vacancies only in M site is very close to the "D" model suggested by Navrotsky, Wechsler, Geisinger and Seifert (1986).

The strong cell edge decrease with respect to stoichiometric spinel is due to the shortening of T – O distance, because of the relevant amount of Al in this site. Instead, the M – O distance is very similar to that of a low-inversion stoichiometric spinel.

We can tentatively calculate the "bond distance" of octahedral vacancy in spinel structure from the proposed cation distribution. With our bond distances for (Mg – O)M and (Al – O)M we obtain a value of 2.11 Å to fit the experimental (M – O) distance. It should be noted that, for a hypothetical end-member maghemite with only octahedral vacancies, this value gives $a = 8.29$ Å, which is not inconsistent with the minimum value of 8.32 Å (Lindsley, 1976) measured in natural samples that probably contained some amounts of Fe_3O_4 ($a = 8.396$ Å).

In conclusion, in the investigated composition Mg seems to be almost completely ordered in T site, while vacancies are virtually present only in the octahedral site. Structure refinement performed on the same crystal under the same conditions after heating for 30 min at 1150°C led to the same results within 1σ, suggesting that the proposed cations and vacancy distribution is stable over a wide range of temperatures.

References

Allen, W. C.: An X-ray method for defining composition of magnesium spinel. Am. Mineral. **51** (1966) 239 – 243.

Blessing, R. H., Coppens, P., Becker, P.: Computer analysis of step-scanned X-ray data. J. Appl. Crystallogr. **7** (1972) 488 – 492.

Della Giusta, A., Princivalle, F., Carbonin S.: Crystal chemistry of a suite of natural Cr-bearing spinels with 0.15 < Cr < 1.07. Neues Jahrb. Mineral., Abh. **155** (1986) 319 – 330.

Della Giusta, A., Princivalle, F., Carbonin, S.: Crystal structure and cation distribution in some natural magnetites. Mineral. Petrol. **37** (1987) 315 – 321.

Finger, L. W., Hazen, R. M., Hofmeister, A. M.: High-pressure crystal chemistry of spinel ($MgAl_2O_4$) and magnetite (Fe_3O_4): comparisons with silicate spinels. Phys. Chem. Miner. **13** (1986) 215 – 220.

Grimes, N. W., Thompson, P., Kay, H. F.: New symmetry and structure for spinel. Proc. R. Soc. London **A386** (1983) 333 – 345.

Hafner, S.: Metalloxyde mit Spinellstruktur. Schweiz. Mineral. Petrogr. Mitt. **40** (1960) 208 – 240.

Hill, R. J., Craig, J. R., Gibbs, G. V.: Systematics of the spinel structure type. Phys. Chem. Miner. **4** (1979) 317 – 339.

International Tables for X-ray Crystallography. Vol. 4. Birmingham: Kynoch Press 1974.

Jarosewich, E., Nelen, J. A., Norberg, DJ. A.: Reference samples for electron microprobe analysis. Geostand. Newslett. **4** (1980) 43 – 47.

Kullerud, G., Donnay, G., Donnay, J. D. H.: Omission solid solution in magnetite: Kenotetrahedral magnetite. Z. Kristallogr. **128** (1969) 1–17.

Lindsley, D. H.: The crystal chemistry and structure of oxide minerals as exemplified by the Fe–Ti oxides. In: *Oxide Minerals* (Mineralogical Society of America, Ed. Douglas Rumble) p. L1–L52. Blacksburg: Southern Printing Company 1976.

Mattioli, G. S., Wood, B. J., Garmichael, I. S. E.: Ternary spinel volumes in the system Mg Al_2 O_4–Fe_3O_4–$\gamma Fe_{8/3}O_4$: implications for the effect of P on intrinsic fO_2 measurements of mantle-xenolith spinels. Am. Mineral. **72** (1987) 468–480.

Navrotsky, A., Kleppa, O. J.: The thermodynamics of cation distribution in simple spinels. J. Inorg. Nucl. Chem. **29** (1967) 2701–2714.

Navrotsky A., Wechsler, B. A., Geisinger, K., Seifert F.: Thermochemistry of Mg Al_2O_4–$Al_{8/3}O_4$ defect spinel. J. Am. Ceram. Soc. **69** (1986) 418–422.

North, A. C. T., Phillips, D. C., Scott-Mathews, F.: A semi-empirical method of absorption correction. Acta Crystallogr. **A24** (1968) 351–359.

Oka, Y., Steinke, P., Chatterjee, N. D.: Thermodynamic mixing properties of Mg $(Al,Cr)_2O_4$ spinel crystalline solution at high temperatures. Contrib. Mineral. Petrol. **87** (1984) 196–204.

O'Neill, H. St. C., Navrotsky A.: Cation distribution and thermodynamic properties of spinel solid solutions. Am. Mineral. **69** (1984) 733–753.

Princivalle, F., Della Giusta, A., Carbonin, S.: Comparative crystal chemistry of spinels from some suites of ultramafic rocks. Mineral. Petrol. **40** (1989) 117–126.

Schmocker, U., Waldner, F.: The inversion parameter with respect to the space group of $MgAl_2O_4$ spinel. J. Phys. C. Solid State Phys. **9** (1976) L235–L237.

Shannon, R. D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. **A32** (1976) 751–767.

Sharma, K. K., Langer, K., Seifert, F.: Some properties of spinel phases in the binary system $MgAl_2O_4$–$MgFe_2O_4$. Neues Jahrb. Mineral. Monatsh. **10** (1973) 442–449.

Tokonami, M., Horiuchi, H.: On the space group of spinel $MgAl_2O_4$. Acta Crystallogr. **A36** (1980) 122–126.

Urusov, V. S.: Interaction of cations on octahedral and tetrahedral sites in simple spinels. Phys. Chem. Miner. **9** (1983) 1–5.

Viertel, H. U., Seifert, F.: Physical properties of defect spinels in the system $MgAl_2O_4$–Al_2O_3. Neues Jahrb. Mineral., Abh. **134** (1979) 167–182.

Viertel, H. U., Seifert, F.: Thermal stability of defect spinels in the system $MgAl_2O_4$–Al_2O_3. Neues Jahrb. Mineral., Abh. **140** (1980) 89–101.

Wood, B. J., Kirkpatrik, R. J., Montez, B.: Order-disorder phenomena in $MgAl_2O_4$ spinel. Am. Mineral. **71** (1986) 999–1006.

Yamanaka, T., Takeuchi, Y.: Order-disorder transition in $MgAl_2O_4$ spinel at high temperatures up to 1700°C. Z. Kristallogr. **165** (1983) 65–78.

Yvon, K., Jeitschko, W., Parthé, E.: LAZY PULVERIX, a computer program for calculating X-ray and neutron diffraction powder patterns. J. Appl. Crystallogr. **10** (1977) 73–74.