

## Cation ordering and structural variations with temperature in $\text{MgAl}_2\text{O}_4$ spinel: An X-ray single-crystal study

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### ABSTRACT

The equilibrium distribution of Mg and Al between the tetrahedral and octahedral sites of a flux grown, stoichiometric  $\text{MgAl}_2\text{O}_4$  spinel was investigated between 600 and 1100 °C by single-crystal X-ray diffraction of quenched samples. The cation distribution for both ordering and disordering runs was obtained by minimizing accurate crystallographic parameters and effective ionic radii. Along with the variation of the degree of inversion from 0.18 to 0.29 between 600 and 1100 °C, both unit cell and oxygen positional parameter decreased linearly. Multiple non-linear least-squares fit of our data with the thermodynamic model of O'Neill and Navrotsky (1983) gave  $\alpha = 23 \pm 2$  KJ/mol and  $\beta = 13 \pm 4$  KJ/mol. The influence of both cation inversion and thermal expansion on T-O and M-O bond length variation was determined by comparison of our data with previous *in situ* studies. In the thermal interval investigated, the inversion accounts for change of  $-0.014$  Å for T-O and  $+0.007$  Å for M-O. Mean linear polyhedral thermal expansion coefficients of  $6.5 \times 10^{-6}$  °C<sup>-1</sup> and  $8.9 \times 10^{-6}$  °C<sup>-1</sup> were calculated for T and M sites, respectively.

### INTRODUCTION

A nearly ideal cubic close-packed array of oxygen atoms with one eighth of tetrahedral (T) and one half of octahedral (M) sites filled by heterovalent cations characterizes multiple oxides with the spinel structure (space group  $Fd\bar{3}m$ ). With origin at  $\bar{3}m$ , T and M sites have fixed coordinates  $1/8$   $1/8$   $1/8$  and  $1/2$   $1/2$   $1/2$ , respectively, and oxygen occupies a  $3m$  point symmetry site with  $u$   $u$   $u$  coordinates. Spinel has the general formula  $(\text{A}_{1-x}\text{B}_x)[\text{A}_x\text{B}_{2-x}]\text{O}_4$ , where parentheses refer to the tetrahedral site, square brackets to the octahedral sites, and  $x$  to the inversion parameter. In common 2-3 spinels several divalent (A) and trivalent (B) cations can enter both T and M sites. Inversion degree  $x$ , defined as the fraction of B-type cations in the tetrahedral site, can vary from 0 to 1 in normal and inverse spinels respectively, assuming the value of  $2/3$  for a completely random distribution. The order-disorder of spinels is "non-convergent" (i.e., the same symmetry is maintained at any inversion), so that  $x$  may be used as a measure for cation disordering since it asymptotically approaches the value of  $2/3$  on increasing temperature (Sack and Ghiorso 1991).

In geologic environments, the chemical and structural variations in spinels have been shown to be dependent on both paragenesis and P-T history and, because of this, they are useful as petrogenetic indicators (Sack 1982; Mattioli and Wood 1988; Princivalle et al. 1989, 1999). Modeling of cation distributions with temperature and composition in the spinel system has been done using various approaches (O'Neill and Navrotsky

1984; Lehmann and Roux 1986; Nell et al. 1989; Della Giusta and Ottonello 1993), but the existing discrepancies need additional and more accurate experimental data to be constrained.

The  $\text{MgAl}_2\text{O}_4$  end-member is one of the most common components of natural spinel solid solutions. Cation ordering as a function of temperature in natural and synthetic  $\text{MgAl}_2\text{O}_4$  has been studied using several analytical methods: ESR of impurity Cr cations (Schmocker and Waldner 1976), X-ray diffraction (Yamanaka and Takéuchi 1983), NMR (Wood et al. 1986; Millard et al. 1992; Maekawa et al. 1997), and neutron diffraction (Peterson et al. 1991; Redfern et al. 1999). Conflicting data exist for the maximum temperature at which an increase of disorder can be observed. According to *in situ* experiments of Schmocker and Waldner (1976) this temperature is 900–950 °C, whereas other works revealed increasing disorder up to 1600 °C (Yamanaka and Takéuchi 1983; Maekawa et al. 1997; Redfern et al. 1999). Discrepancies remain among the published data in terms of inversion degree corresponding to a certain temperature and vice versa. As an example, the same inversion has been attributed to temperatures which may differ by more than 500 °C, thus preventing accurate thermodynamic modeling of Mg-Al disordering with temperature and hence any exploitation of the  $x$ - $T$  relation for petrologic and geophysical purposes. The difference between the methods used to measure inversions as well as some undetected deviations of the studied samples from nominal  $\text{MgAl}_2\text{O}_4$  stoichiometry may be responsible for these discrepancies.

Pure  $\text{MgAl}_2\text{O}_4$  is rare in nature and its synthetic analogue may be prepared by various methods and at different temperatures, which may produce unexpected defects and deviations

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from stoichiometry. When synthetic powders are studied, the intrinsic difficulty of their accurate chemical characterization must be considered because the presence of even very small vacancy contents may strongly affect both the kinetics of order-disorder and the equilibrium value of  $x$  (Redfern et al. 1999). As an alternative approach, synthetic single-crystals may be examined with the advantage of exploiting the high accuracy achieved by single-crystal methods of chemical and structural characterization. Therefore we synthesized stoichiometric  $\text{MgAl}_2\text{O}_4$  crystals and investigated disordering using the quenching technique and crystal X-ray diffraction.

## EXPERIMENTAL TECHNIQUES

### Synthesis

High quality  $\text{MgAl}_2\text{O}_4$  crystals were synthesized via the flux-growth method. The main advantage of this method is that crystals may be grown at relatively low temperatures, which decreases the number of defects and vacancies compared with samples produced by other methods at higher temperatures. The starting materials consisted of analytical grade  $\text{Al}(\text{OH})_3$  and  $\text{MgO}$  powders which were dehydrated at  $1000^\circ\text{C}$  for 12 h and dried before mixing with  $\text{Na}_2\text{B}_4\text{O}_7$ , which was used as flux compound. Around 5 g of starting mixture was thoroughly ground, mixed under acetone in an agate mortar, and then transferred to a pure platinum crucible. The crucible was covered by a platinum lid and placed in a temperature-controlled muffle furnace. The synthesis heating cycle was started by a rather steep increment up to  $1200^\circ\text{C}$ , at which the temperature was kept constant for 24 hours to obtain complete dissolution and homogenization of the oxide mixture. A slow cooling rate was applied down to  $800^\circ\text{C}$ , and then the temperature was decreased rapidly by turning off the power to the heating elements. Different cooling rates were tried from 1 to  $4^\circ\text{C}/\text{h}$ , with both linear and saw-tooth temperature profiles, to improve crystal quality. Experimental conditions were optimized so that the final cooling path involved linear cooling at  $2^\circ\text{C}/\text{h}$ .

Run product (from experiment SP3) consisted of an intergrown network of spinel and magnesium borate crystals embedded in minor glass. The spinel crystals preferentially nucleate on the walls of the crucible and on the surface of the melt, but also in the bulk of the material. The run product was immersed in hot dilute hydrochloric acid for a few days to dissolve the glass and magnesium borate. About 100 mg of spinel single-crystals, most of them gem quality, were recovered from this run. Crystals were colorless and free of inclusions, with regular octahedral shape and sizes ranging from 0.1 to over 0.5 mm. For further details see Andreozzi (1999).

### Sample characterization

Six optically homogeneous and inclusion-free crystals were chemically analyzed by a CAMECA-CAMEBAX microprobe operating at 15 KV and 15 nA sample current, using the wavelength dispersive method. Synthetic  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  standards were used. A PAP-CAMECA program was used to convert X-ray counts into weight percentages of the corresponding oxides. The average and standard deviations of one hundred and thirty analyses performed on the six crystals were: Mg =

1.006(7) and Al = 1.996(4) atoms per formula unit (apfu). No elements other than Mg and Al were detected. The absence of boron was confirmed by Nuclear Reaction Analysis (alpha particles emission stimulated by a proton beam). These results show the SP3 crystals to be, within one standard deviation, stoichiometric  $\text{MgAl}_2\text{O}_4$ .

The cell parameter of some SP3 crystals was determined using three different automated single-crystal diffractometers (Kuma-KM4, Siemens P4, Stoe AED II). The values of  $a$ , measured at room temperature using  $\text{MoK}\alpha_1$  radiation ( $\lambda = 0.70930 \text{ \AA}$ ), ranged from 8.0844(1) to 8.0865(6)  $\text{\AA}$ . The small differences in  $a$  values were consistent with differences in crystal mounting, monochromator alignment, and power applied to the tube. A powder sample was prepared by grinding some homogeneous and inclusion-free crystals from the SP3 run with NBS640B Si as internal standard. A X-ray powder spectrum was collected with a Philips 3710 automatic diffractometer; data were processed by the PC-ADP software program (Philips copyright) and  $2\theta$  values were calculated using the second derivative algorithm of Savitzky and Golay. The cell parameter at room temperature determined from powder data using  $\text{CuK}\alpha_1$  radiation,  $\lambda = 1.5406 \text{ \AA}$ , was  $a = 8.0859(1) \text{ \AA}$  (Salviulo et al., work in progress). As discussed by many authors (e.g., Grimes et al. 1983; Navrotsky et al. 1986; Lucchesi and Della Giusta 1994; Maekawa et al. 1997), the  $a$  values measured on SP3 are consistent with a vacancy-free  $\text{MgAl}_2\text{O}_4$  spinel. As it will be shown later in the text, the quoted  $a$  differences are irrelevant to the cation distribution.

### X-ray data collection

X-ray diffraction data were collected using an automated KUMA-KM4 (K-geometry) diffractometer ( $\text{MoK}\alpha$  monochromatized by a flat graphite crystal). Intensity data were collected up to  $2\theta = 110^\circ$  in the continuous  $\omega$ - $2\theta$  scan mode, with peak-base width of  $2\theta = 1.8^\circ$ , which increased with the  $\theta$  angle. Counting times ranged from 30 to 120 s, according to peak standard deviation, with background measured from both sides of the peak for a total of half peak-time. Because the psi-scan curves were flat, empirical correction for absorption was not applied. Twenty-four equivalents of the 12 8 4 reflection (ca.  $82^\circ$  of  $2\theta$ ) were accurately centered at positive and negative values of  $2\theta$  and used for cell parameter determination. Structure factors tables are available from the authors on request.

Structural refinements, performed with the SHELX-93 program (Sheldrick 1993), were carried out in the  $Fd\bar{3}m$  space group with origin at  $\bar{3}m$ , without chemical constraints. No violations of this symmetry were detected. Refined parameters were: scale factor, secondary extinction coefficient, oxygen positional parameter ( $u$ ), Mg and Al occupancy in T and M sites, respectively, and anisotropic displacement parameters  $U(\text{O})$ ,  $U(\text{M})$ , and  $U(\text{T})$ .

In spinels, the mean atomic number (m.a.n.) determined by least squares refinement of T and M sites is quite sensitive to the ionization level of scattering curves, whereas their ratio remains almost constant (Della Giusta et al. 1986). Table 1 gives an example of structural refinements performed using different degrees of ionization for O atoms. The best values of the

**TABLE 1.** Influence of oxygen and cation ionization level on structural parameters

Oxygen cations	O <sup>0</sup> neutral	O <sup>-2</sup> neutral	O <sup>-1.6</sup> neutral	O <sup>-1.6</sup> +cats ionized
u	0.26177(5)	0.26184(4)	0.26183(4)	0.26184(4)
M occ.	0.958(5)	0.992(4)	0.986(4)	0.989(4)
T occ.	1.003(8)	1.035(7)	1.030(7)	1.033(7)
M m.a.n.	12.45(6)	12.90(5)	12.82(5)	12.86(5)
T m.a.n.	12.0(1)	12.42(9)	12.36(8)	12.40(8)
Tot m.a.n.	36.9(1)	38.2(1)	38.0(1)	38.1(1)
$U_{11}(\text{O}) (\text{\AA}^2)$	0.0085(1)	0.0076(1)	0.0078(1)	0.0078(1)
$U_{12}(\text{O}) (\text{\AA}^2)$	0.0003(1)	0.0003(1)	0.0003(1)	0.0003(1)
$U_{11}(\text{M}) (\text{\AA}^2)$	0.0041(1)	0.0040(1)	0.0040(1)	0.0040(1)
$U_{12}(\text{M}) (\text{\AA}^2)$	-0.0002(1)	-0.0002(1)	-0.0002(1)	-0.0002(1)
$U_{11}(\text{T}) (\text{\AA}^2)$	0.0043(1)	0.0042(1)	0.0042(1)	0.0042(1)
Refl.	178	178	178	178
$R_{\text{int}}\%$	3.79	3.79	3.79	3.79
$R1\%$	2.50	2.42	2.34	2.44
$wR2\%$	5.61	4.61	4.35	4.72
GooF	1.329	1.371	1.328	1.228
Ext.	0.18(1)	0.155(9)	0.160(8)	0.159(9)

Notes: First three columns refer to different oxygen ionization levels and neutral cations, the fourth to fully ionized cations. Refinement data are relative to disordering run performed at 950 °C for 1 day. Estimated standard deviations in brackets. m.a.n. = mean atomic number; Refl. = Number of observed [ $>3\sigma(I)$ ] independent reflections;  $R_{\text{int}}$ ,  $R1$ , and  $wR2$  = disagreement factors according to SHELX-93 program package; GooF = goodness of fit; Ext. = Isotropic secondary extinction coefficient.

statistical descriptors  $R1$ ,  $wR2$ , and GooF in all  $\sin \theta/\lambda$  shells and a total m.a.n. very close to that expected from stoichiometry. Stoichiometry were obtained for  $\text{O}^{-1.6}$  and neutral curves for Mg and Al. The worst fit refers to neutral oxygen, which gave a total m.a.n. more than 2% lower than expected. Changing the ionization level of cations (column 4 in Table 1) led to negligible differences in m.a.n. results, but the statistical descriptors definitely became worse. Therefore, the SP3 crystal was refined, before and after thermal treatments, with partially ionized oxygen and neutral cations (Table 2). In this table, only isotropic displacement parameters are shown, the out-of-diagonal terms being of the same order as their standard deviations.

## Heating runs

Experimental runs were carried out sequentially using the same gem-quality, octahedral, colorless crystal from the SP3 batch, which measured about 0.15 mm across. The crystal was sealed in a thin-wall quartz tube in air. Run temperatures were accurately measured and controlled by means of a calibrated Pt/Pt-Rh thermocouple located near the sample. Uncertainty was about  $\pm 5$  °C up to 600–700 °C and less than  $\pm 10$  °C for higher temperatures. Heating-quenching runs were performed at room pressure in air, because oxidation problems were not expected for the composition investigated in the temperature range studied. No change in crystal color or transparency was observed. Disordering runs were carried out at 800, 850, 900, 950, 1000, and 1100 °C, with heat treatment of 24 hours for each run (Table 2). Ordering runs were carried out at 950, 800, 700, and 600 °C, with progressively increasing times (Table 2). Equilibrium attained at temperatures as low as 600 °C was clearly indicated by kinetic data (work in progress). The crystal was quenched by dropping the quartz tube with the sample to cold water (20 cm of free fall). Cooling time from 1100 to 400 °C was estimated to be less than 0.5 s (Molin et al. 1991; Della Giusta et al. 1996).

## Cation partitioning

Intracrystalline cation distributions were calculated on the basis of the bond distances and m.a.n. of T and M sites. The latter can give little information about Mg and Al distributions, since their X-ray scattering power is very similar. Instead, Mg and Al can easily be distinguished by their very different crystal radii in the same coordination (Shannon 1976; O'Neill and Navrotsky 1983).

It is known that cation site fractions have linear relations with site m.a.n., but not necessarily with bond distances. Strong non-linearity effects between site cation content and bond distances have recently been shown in iron-rich compositions (Waerenborgh et al. 1994; Lucchesi et al. 1999). Using a data-

**TABLE 2.** Results of structure refinements of thermally treated  $\text{MgAl}_2\text{O}_4$  spinel with neutral cations and partially ionized O atoms

T °C	SP3	800 D	850 D	900 D	950 D	1000 D	1100 D	950 O	800 O	700 O	600 O
Time	—	1 d	1 d	1 d	1 d	1 d	1 d	3 d	7 d	90 d	45 d
a (Å)	8.0844(1)	8.0845(1)	8.0841(1)	8.0840(1)	8.0838(1)	8.0835(1)	8.0829(1)	8.0837(1)	8.0846(1)	8.0851(1)	8.0856(1)
u	0.26223(5)	0.26222(6)	0.26212(4)	0.26193(6)	0.26183(4)	0.26171(4)	0.26152(5)	0.26183(4)	0.26223(4)	0.26251(4)	0.26286(4)
M occ.	0.990(5)	0.989(5)	0.986(4)	0.986(5)	0.986(4)	0.986(5)	0.981(4)	0.984(3)	0.984(5)	0.992(4)	0.990(3)
T occ.	1.024(9)	1.026(9)	1.032(7)	1.033(9)	1.030(7)	1.034(8)	1.042(7)	1.034(8)	1.033(7)	1.021(7)	1.025(6)
M m.a.n.	12.87(6)	12.85(7)	12.82(5)	12.82(6)	12.82(5)	12.81(6)	12.75(5)	12.80(4)	12.79(6)	12.89(5)	12.88(4)
T m.a.n.	12.3(1)	12.3(1)	12.38(9)	12.4(1)	12.36(8)	12.4(1)	12.50(9)	12.4(1)	12.40(9)	12.25(9)	12.30(7)
Tot m.a.n.	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.0(1)	38.05(9)
$U(\text{O}) (\text{\AA}^2)$	0.0072(1)	0.0075(2)	0.0077(1)	0.0079(1)	0.0078(1)	0.0080(1)	0.0080(1)	0.0075(1)	0.0073(1)	0.0065(1)	0.0059(1)
$U(\text{M}) (\text{\AA}^2)$	0.0042(1)	0.0042(1)	0.0042(1)	0.0043(1)	0.0040(1)	0.0041(1)	0.0038(1)	0.0042(1)	0.0039(1)	0.0038(1)	0.0037(1)
$U(\text{T}) (\text{\AA}^2)$	0.0043(2)	0.0045(2)	0.0046(1)	0.0046(2)	0.0042(1)	0.0043(2)	0.0041(1)	0.0045(1)	0.0044(1)	0.0041(1)	0.0043(1)
Refl.	181	184	181	183	178	183	183	181	181	183	182
$R_{\text{int}}\%$	3.59	3.38	3.41	3.41	3.79	3.16	4.15	4.66	4.43	2.53	2.84
$R1\%$	3.23	3.32	2.87	2.81	2.34	2.94	2.36	2.31	2.60	2.71	2.15
$wR2\%$	6.16	7.07	5.26	6.80	4.35	6.22	4.69	3.65	4.46	5.25	4.04
GooF	1.421	1.439	1.325	1.546	1.328	1.417	1.379	1.256	1.347	1.442	1.341
Ext.	0.19(1)	0.15(1)	0.17(1)	0.19(1)	0.160(8)	0.15(1)	0.164(9)	0.140(7)	0.161(9)	0.17(1)	0.174(8)

Notes: Estimated standard deviations in brackets. SP3 = untreated crystal; D = disordering; O = ordering; m.a.n. = mean atomic number; Refl. = Number of observed [ $>3\sigma(I)$ ] independent reflections;  $R_{\text{int}}$ ,  $R1$ , and  $wR2$  = disagreement factors according to SHELX-93 program package; GooF = goodness of fit; Ext. = Isotropic secondary extinction coefficient.

base of about 200 spinels with well characterized compositions and structural parameters, the influence of the cations in the second coordination sphere was determined and a new set of cation-to-oxygen bond distances was refined (Della Giusta et al. in preparation).

The new refined distances (in angstroms) are  $D_{\text{Mg(T)}} = 1.966$ ,  $D_{\text{Al(T)}} = 1.774$ ,  $D_{\text{Mg(M)}} = 2.081$ , and  $D_{\text{Al(M)}} = 1.908$ . Cation distributions were calculated by minimizing the following function which takes into account structural and chemical data (Carbonin et al. 1996):

$$F(X_i) = \sum_j \{ [O_j - C_j(X_i)] / \sigma_j \}^2 \quad (1)$$

where  $O_j$  are observed quantities—i.e., T-O and M-O bond lengths, m.a.n. of T and M sites, and atomic proportions obtained from microprobe analysis—and  $\sigma_j$  their standard deviations. Variables  $X_i$  are cation fractions  $\text{Mg(T)}$ ,  $\text{Al(T)}$ ,  $\text{Mg(M)}$ , and  $\text{Al(M)}$ , related by means of inversion  $x$ . The quantities  $C_j$  are the same already described for  $O_j$  calculated from variable parameters  $X_i$ . Refinement is restricted to  $\text{MgAl}_2\text{O}_4$  stoichiometry. Results were considered acceptable when the differences between observed and calculated parameters were within  $2\sigma$  of each observed quantity. For every refinement, observed and calculated structural quantities are shown in Table 3, together with the value of  $F(X_i)$ . Agreement between observed and calculated values is very high, confirming the consistency of the cation distributions obtained.

## RESULTS

Structural parameters, sequentially measured on the quenched SP3 crystal, turned out to be sensitive to equilibration temperature. All the data from disordering and ordering runs were in excellent agreement as they matched within one standard deviation.

The  $a$  values obtained from the same instrument and the same crystal mounted as accurately as possible with the same orientation, show a significant trend decreasing by  $0.0027 \text{ \AA}$  from 600 to 1100 °C (Fig. 1a). A comparable cell parameter decrease was observed by powder diffraction in a natural spinel very close to  $\text{MgAl}_2\text{O}_4$ , after quenching from 1100 °C (Salviulo et al. 1999). The oxygen positional parameter  $u$  decreases significantly from 0.26286(4) to 0.26152(5) when equilibration temperature increases from 600 to 1100 °C (Fig. 1b). Notably, the crystal SP3 shows to have reached equilibrium at 800 °C, the final temperature at which it was synthesized. The variation of both  $a$  and  $u$  with  $T$  are well described by linear relations ( $R^2 = 0.99$ ). Because both  $a$  and  $u$  parameters at equilibrium depend linearly on  $T$ , they are also related to each other through the linear relationship  $u = 0.4983 a - 3.766$  ( $R^2 = 0.98$ ) for the investigated  $T$  range.

For the spinel structure, T-O and M-O bond distances are related to  $a$  and  $u$  by

$$\text{T-O} = a \sqrt{3(0.125 - u)^2} \quad (2)$$

and

$$\text{M-O} = a \sqrt{(0.5 - u)^2 + 2(0.25 - u)^2} \quad (3)$$

Both distances show a regular variation with  $T$ , well approximated by a linear fit (Fig. 1c). The two distances cross each other, with T-O larger than M-O at temperatures lower than 700 °C and vice versa. Close to this temperature, T-O and M-O distances become equal,  $u$  being 0.2625, as required by spinel structure. From 600 to 1100 °C the T-O distance decreases from 1.931 to 1.911 Å, showing almost double the variation compared with M-O, which increases from 1.923 to 1.932 Å. Due to the very small standard deviations of T-O and M-O compared with their relative variations, sensitivity with mean bond-length changes is sufficient to show temperature differences of 50°. Mean atomic numbers in both T and M sites show a limited but significant variation trend with equilibration temperature (Fig. 1d): in spite of the small scattering difference between Mg and Al, the m.a.n. of T site increases and that of M site decreases as a consequence of Al-Mg exchange in the two sites. Even more precise results were obtained by Grimes et al. (1983), who accurately defined the inversion of  $\text{MgAl}_2\text{O}_4$  on the basis of m.a.n. alone by collecting 3968 reflections. Figure 1e shows that the displacement parameters  $U(\text{T})$  and  $U(\text{M})$  of the cation sites (the former constantly larger than the latter) are not affected by variations in charge distribution between T and M sites determined by temperature. Instead, the displacement parameter relative to the oxygen site  $U(\text{O})$  displays a definite increase with configurational disorder.

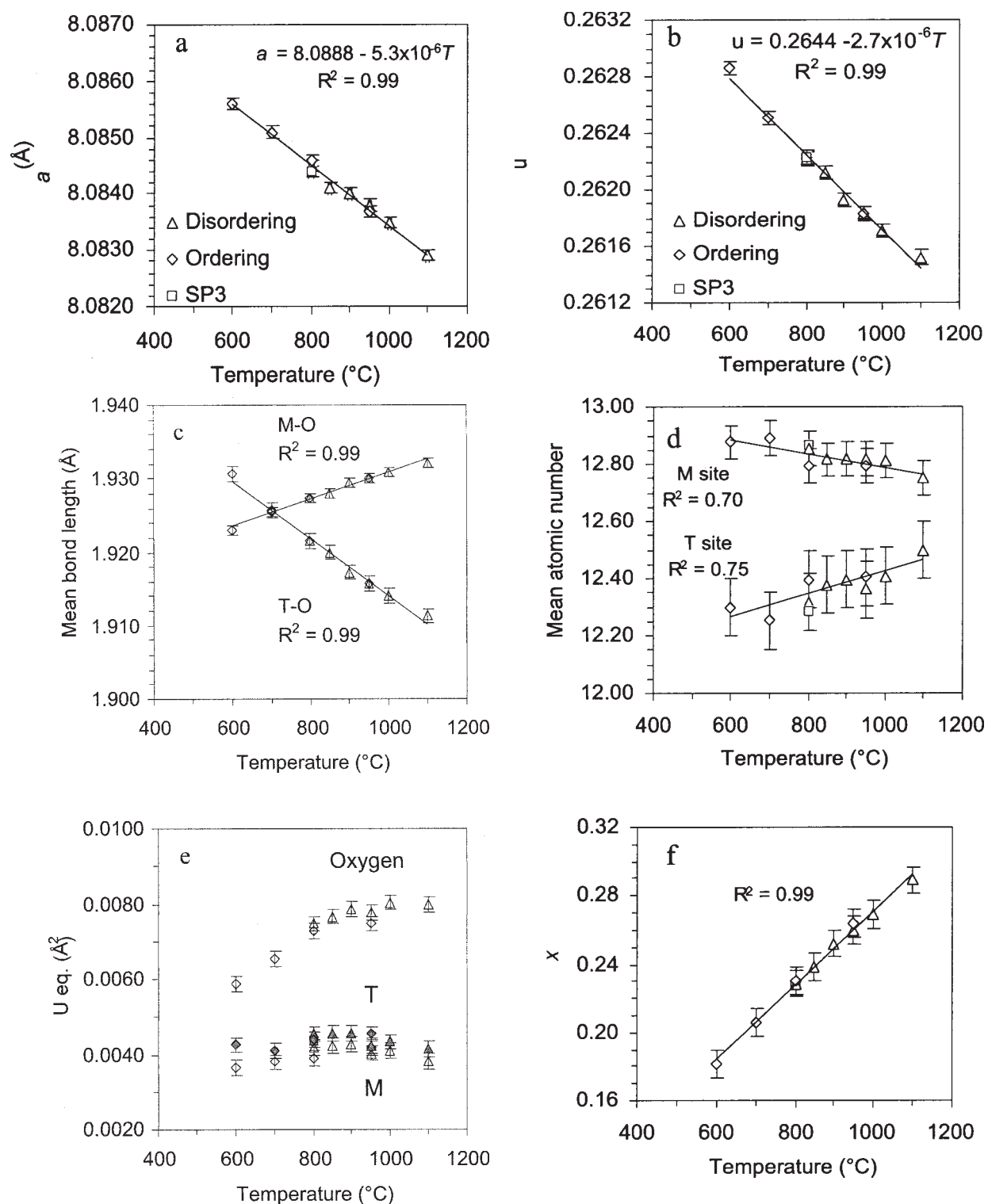
Inversion degree  $x$ , calculated by Equation 1, regularly increases with equilibration temperature, ranging from 0.18 to 0.29 at 600 and 1100 °C, respectively (Table 3 and fig. 1f). The quoted differences in cell parameter  $a$  hardly influenced final  $x$  values: variations of  $a \pm 0.0020 \text{ \AA}$  only produced variations in  $x$  of less than 0.001, i.e., five to ten times less than its estimated standard deviation (Table 3). Linear relationship of  $x$  with temperature, on both heating and cooling, shows an increase of almost 0.1  $x$  for every 50 °C. However, this trend cannot be extrapolated out of the examined  $T$  range, because the relationships between  $x$  and  $T$ , as discussed later, are more complex.

## DISCUSSION

Stoichiometric  $\text{MgAl}_2\text{O}_4$  was studied with the aim to explore thermally induced cation order-disorder and related structural modifications. No deviations from equilibrium curves were observed in either disordering or ordering runs at 800 °C, i.e. the temperature at which the crystal was grown. Thus, the crystal did not retain any “memory” of synthesis run conditions, a phenomenon revealed in synthetic powders by Redfern et al. (1999).

Because  $a$  decreases and  $x$  increases with temperature, a strongly correlated inverse linear relationship was observed between them ( $R^2 = 0.98$ ), all data plotting on the regression line within  $2\sigma$  for  $a$  and  $1\sigma$  for  $x$  (Fig. 2a). The small but significant  $a$  decrease observed with inversion ( $0.0027 \text{ \AA}$ ) was only detectable using the quenching technique, as this effect is overwhelmed by the greater thermal expansion in the in situ experiments. This  $a$  decrease was determined by T-O contraction greater than the M-O increment, consequent upon Mg-Al exchange between T and M sites (see Fig. 1c).

As observed for  $a$ , the values of  $u$  and  $x$  at equilibrium are closely correlated, experimental data falling on the regression



**FIGURE 1.** Structural parameters and inversion degree variations with temperature measured from ordering and disordering runs: (a) cell parameter; (b) oxygen positional parameter; (c) mean bond lengths of T-O and M-O; (d) mean atomic numbers of T and M sites; (e) displacement parameters of oxygen and T and M sites; (f) inversion degree. In (b), (c), and (f) diagrams ordering and disordering data perfectly overlap. Open square = untreated crystal SP3; open triangle = disordering; open diamond = ordering;



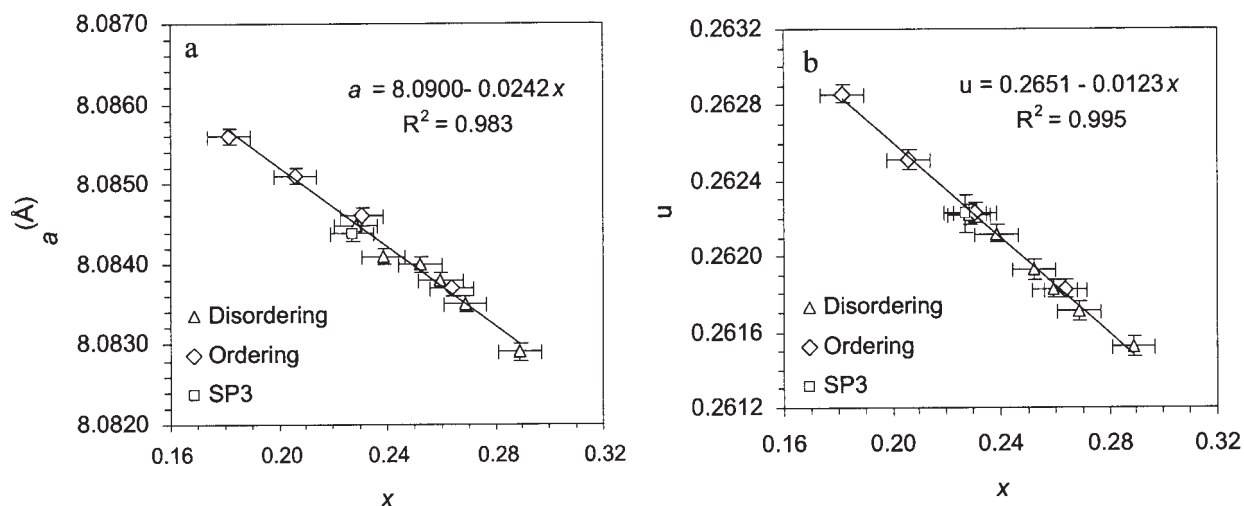


FIGURE 2. Structural parameter variations with inversion degree measured from ordering and disordering runs: (a) cell parameter; (b) oxygen positional parameter. Open square = untreated crystal SP3; open triangle = disordering; open diamond = ordering.

line within  $1\sigma$  for both (Fig. 2b). This inverse relationship is well described by the linear equation:

$$u = 0.2651 - 0.0123x \quad (R^2 = 0.995) \quad (4)$$

The above equation can be used to obtain the inversion degree of MgAl<sub>2</sub>O<sub>4</sub> at equilibrium simply by measuring the oxygen positional parameter, which is less sensitive than  $a$  to varying experimental conditions. Furthermore, the maximum value of 0.2651 is derived for perfectly ordered MgAl<sub>2</sub>O<sub>4</sub> crystals, i.e.,  $x = 0$ . This limit has been approached, but never reached, by natural spinels compositionally very close to MgAl<sub>2</sub>O<sub>4</sub> from low grade metamorphic environments (Tsirel'son et al. 1987; Carbonin et al. 1996; Lucchesi and Della Giusta 1997).

In the 700–1100 °C interval, comparing our T-O and M-O bond lengths measured after quenching with the same quantities measured in situ by Redfern et al. (1999), the different

influence of (a) disordering and (b) thermal expansion to tetrahedral and octahedral bond length variations could be separated. From the in situ data, in the quoted temperature interval, T-O decreases from 1.926 to 1.918 Å ( $\Delta = -0.008$  Å) and M-O increases from 1.941 to 1.956 Å ( $\Delta = +0.015$  Å) as a consequence of (a + b). In the same interval, our data revealed a contribution due to disordering of  $-0.014$  Å for T-O and  $+0.007$  Å for M-O. Consequently, thermal expansions between 700 and 1100 °C are 0.006 Å for T-O and 0.008 Å for M-O. The same quantities were calculated using the mean linear polyhedral thermal coefficient proposed by Hazen and Finger (1982):

$$\alpha = 32.9(0.75 - z/n)10^{-6} \text{ } ^\circ\text{C}^{-1} \quad (5)$$

where  $z/n$  is the Pauling bond strength. With  $z$  values corresponding to the cation distributions obtained between 700 and 1100 °C,  $\alpha$  of the T site is about  $6.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  and  $\alpha$  of the M site is about  $8.9 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . Calculated thermal expansions in

TABLE 3. Inversion degrees and calculated and observed structural parameters of heat-treated MgAl<sub>2</sub>O<sub>4</sub>

T °C	Time	x		a (Å)	u	T-O (Å)	M-O (Å)	T m.a.n.	M m.a.n.	F(x <sub>i</sub> )
SP3	—	0.229(6)	cal.	8.0844	0.26223	1.9216	1.9273	12.2	12.88	1.0
			obs.	8.0844(1)	0.26223(5)	1.9216(7)	1.9273(4)	...	12.87(6)	
800 D	1 d	0.231(8)	cal.	8.0845	0.26222	1.9214	1.9274	12.2	12.88	2.2
			obs.	8.0845(1)	0.26222(6)	1.9215(8)	1.9274(4)	12.3(1)	12.85(7)	
850 D	1 d	0.24(1)	cal.	8.0841	0.26212	1.9199	1.9280	12.2	12.88	6.9
			obs.	8.0841(1)	0.26212(4)	1.9200(6)	1.9280(3)	12.38(9)	12.82(5)	
900 D	1 d	0.25(1)	cal.	8.0840	0.26193	1.9172	1.9294	12.3	12.87	5.2
			obs.	8.0840(1)	0.26193(6)	1.9173(8)	1.9294(4)	...	12.82(6)	
950 D	1 d	0.262(9)	cal.	8.0838	0.26183	1.9158	1.9301	12.3	12.87	4.0
			obs.	8.0838(1)	0.26183(4)	1.9158(6)	1.9301(3)	12.36(8)	12.82(5)	
1000 D	1 d	0.27(1)	cal.	8.0835	0.26171	1.9141	1.9309	12.3	12.86	5.2
			obs.	8.0835(1)	0.26171(4)	1.9141(6)	1.9309(3)	...	12.81(7)	
1100 D	1 d	0.29(1)	cal.	8.0829	0.26152	1.9112	1.9321	12.3	12.85	22.7
			obs.	8.0829(1)	0.26152(5)	1.9113(7)	1.9321(4)	12.50(9)	...	
950 O	3 d	0.266(9)	cal.	8.0837	0.26183	1.9158	1.9301	12.3	12.86	12.8
			obs.	8.0837(1)	0.26183(4)	1.9158(6)	1.9300(3)	12.4(1)	12.80(4)	
800 O	7 d	0.23(1)	cal.	8.0846	0.26223	1.9216	1.9274	12.2	12.88	10.1
			obs.	8.0846(1)	0.26223(4)	1.9216(6)	1.9274(3)	12.40(9)	12.79(6)	
700 O	90 d	0.208(5)	cal.	8.0851	0.26251	1.9257	1.9255	12.2	12.89	1.0
			obs.	8.0851(1)	0.26251(4)	1.9257(6)	1.9255(3)	12.25(9)	...	
600 O	45 d	0.18(1)	cal.	8.0856	0.26286	1.9307	1.9231	12.2	12.90	5.3
			obs.	8.0856(1)	0.26286(4)	1.9307(6)	1.9230(3)	12.30(7)	12.88(4)	

Notes: Estimated standard deviations in brackets. SP3 = untreated crystal; D = disordering; O = ordering;  $F(x_i)$  = sum of square residuals, (Eq. 1).

the quoted temperature interval turn out to be 0.005 Å and 0.007 Å for T and M sites, respectively, which are quite satisfactory values as they closely match the thermal expansions obtained by comparing quench and in situ data.

As shown for bond lengths, the combined effect of thermal expansion and inversion degree can also be distinguished for the oxygen displacement parameter. According to in situ data,  $U(\text{O})$  increases regularly with temperature up to about 700 °C, then showing a slope increment after Mg-Al disorder is thermally activated (Yamanaka and Takéuchi 1983; Peterson et al. 1991; Redfern et al. 1999). This bimodal trend may be explained considering the thermal effect to which is added up the increment of  $U(\text{O})$  due to configurational disorder, i.e. the quantity measured by quenching (Fig. 1e).

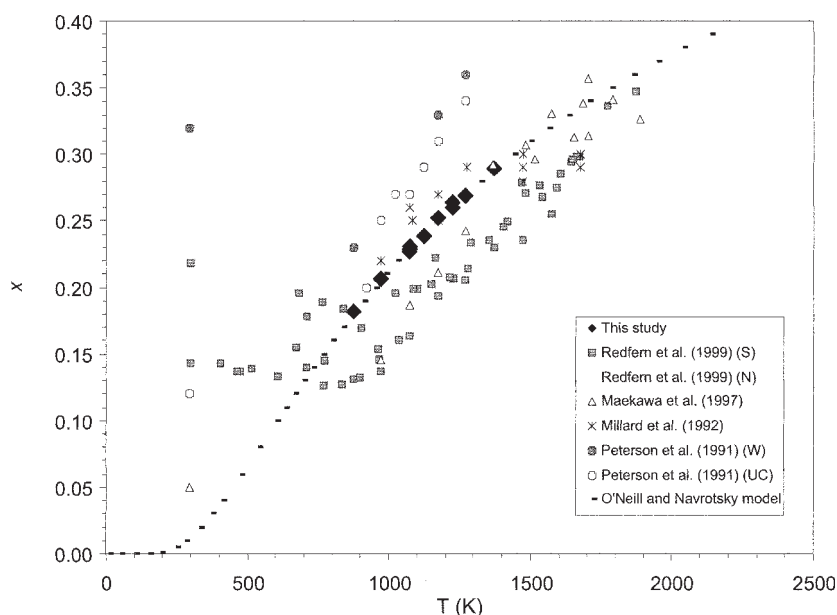
Inversion data with respect to temperature available in the literature for  $\text{MgAl}_2\text{O}_4$  spinel are often conflicting. The anomalous inversion values of Wood et al. (1986) were discussed by Millard et al. (1992). Yamanaka and Takéuchi (1983) did not determine absolute inversion values, but only their increments with temperature. Schmocker and Waldner (1976) did not find any disorder at temperatures higher than 950 °C, in contrast with all subsequent works.

Figure 3 shows the results from recent studies, obtained from room temperature up to 1873 K. Data below 800 K clearly reveal that equilibrium was not reached. Those between 800 and 1000 K need to be carefully considered, due to the slow kinetics of the order-disorder reaction at these temperatures: in the present study, several days were needed to achieve equilibrium at 873 K, which is a very long time compared with in situ experiments. For  $T \geq 1000$  K, a large scattering of inversion data is observed. Inversions as different as 0.15 correspond to a given equilibrium temperature, a large span which is almost comparable with the whole inversion range experimentally measured by every single work. The quoted discrepancies occur not only when different analytical methods were used, but also with the same method. For example, synthetic powders and a natural

$\text{MgAl}_2\text{O}_4$  crystal were studied using  $^{27}\text{Al}$  MAS NMR spectroscopy by Millard et al. (1992) and Maekawa et al. (1997). Although the same calibration procedure was used in both cases, the results differed significantly. Even more disagreement may be observed between the inversion values measured using in situ neutron powder diffraction by Peterson et al. (1991) and Redfern et al. (1999). The disagreement was attributed by the latter authors to suspected non-stoichiometry of the samples analyzed by Peterson et al. (1991), who examined a synthetic crystal from Union Carbide (UC) and the  $\text{MgAl}_2\text{O}_4$  powder synthesized by B. Wood (W). It is known that spinel deviation from stoichiometry is possible along the  $\text{MgAl}_2\text{O}_4 - \square_{1/3}\text{Al}_{8/3}\text{O}_4$  solid solution and this is recorded by a cell parameter decrease from 8.084 to 7.908 Å (Viertel and Seifert 1979; Lucchesi and Della Giusta 1994). The non-stoichiometry of the UC sample is evidenced by the low cell parameter  $a = 8.079$  Å, corresponding to about 3% of the  $\square_{1/3}\text{Al}_{8/3}\text{O}_4$  component (about 0.01 vacancies per four O atoms). On the contrary, no evidence of non-stoichiometry is shown by the W sample, for which  $a = 8.0842$  Å, as measured by Wood et al. (1986) using X-ray diffraction with Si as internal standard. Considering also that Redfern et al. (1999) studied both a stoichiometric (S) and a slightly non-stoichiometric (N) sample, the large difference of inversion at the same  $T$  ( $0.10 < \Delta x < 0.15$ ) measured by neutron diffraction by Peterson et al. (1991) and Redfern et al. (1999), still remains unclear.

In the present study, an approach based on accurate crystallographic parameters and effective ionic radii was used. The optimized bond distances for spinels allowed the highly accurate reproduction of both structural parameters and cation distributions of existing data on spinels. Compared with Shannon's distances, a strong decrease in the residuals of the minimization function (1) was observed for all samples in the database (Della Giusta et al. in preparation). Therefore, we are highly confident in the inversion values obtained using this approach.

Our inversion data show an almost linear trend between 873



**FIGURE 3.** Variation in inversion degree with temperature. Size of the symbol used for our inversion data is comparable with the estimated standard deviation. Gray and open squares used for data from Redfern et al. (1999) refer to stoichiometric and non-stoichiometric samples respectively. Gray and open circles used for data from Peterson et al. (1991) refer to B. Wood and the Union Carbide samples, respectively.

and 1373 K and plot approximately in the middle of all previous data. We obtained  $x$  values from 0.18 to 0.29 which are lower than those of both Millard et al. (1992) and Peterson et al. (1991) and higher than those of both Redfern et al. (1999) and Maekawa et al. (1997) in the same  $T$  range. In particular, our data run parallel to those of Millard et al. (1992), at least up to 1273 K. After this temperature the latter authors did not measure changes in inversion, which indicates that their quenching technique could not prevent cation reordering. In any case, the slope of our trend compares well with that of the previous works, the relative increases in inversion ( $\Delta x$ ) being between 0.10 and 0.13, independently of materials and methods used.

Following O'Neill and Navrotsky's (1983) thermodynamic model, the internal energy change upon disordering is presumed to have a quadratic dependence on inversion  $x$  in the form  $\Delta U_D = \alpha x + \beta x^2$ . The multiple non-linear least-squares fit of our inversion data in the 873–1373 K interval yields values for thermodynamic parameters  $\alpha = +23(2)$  KJ/mol and  $\beta = +13(4)$  KJ/mol, which fit the experimental data closely (Fig. 3). The sign of our  $\beta$  is positive, in contrast with the common assumption that enthalpy in all 2–3 spinels can be described with an almost constant value of  $\beta = -20$  KJ/mol (O'Neill and Navrotsky 1983). A similar positive  $\beta$  was obtained by both Millard et al. (1992) ( $\alpha = +25$  KJ/mol,  $\beta = +6$  KJ/mol) and Redfern et al. (1999) ( $\alpha = +33$  KJ/mol,  $\beta = +5$  KJ/mol) for  $\text{MgAl}_2\text{O}_4$  and by Harrison et al. (1998) for  $\text{FeAl}_2\text{O}_4$  ( $\alpha = +31$  KJ/mol,  $\beta = +19$  KJ/mol).

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## REFERENCES CITED

- Andreozzi, G.B. (1999) Synthetic spinels in the  $(\text{Mg}, \text{Fe}^{2+}, \text{Zn})(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$  system: I. Flux Growth of single-crystals. *Periodico di Mineralogia*, 68, 43–51.
- Carbonin, S., Russo, U., and Della Giusta, A. (1996) Cation distribution in some natural spinels by X-ray diffraction and Mössbauer spectroscopy. *Mineralogical Magazine*, 60, 355–368.
- Della Giusta, A. and Ottonello, G. (1993) Energy and long-range disorder in simple spinels. *Physics and Chemistry of Minerals*, 20, 228–241.
- Della Giusta, A., Princivalle, F., and Carbonin, S. (1986) Crystal chemistry of a suite of natural Cr-bearing spinels with  $0.15 \leq \text{Cr} \leq 1.07$ . *Neues Jahrbuch für Mineralogie Abhandlungen*, 155, 319–330.
- Della Giusta, A., Carbonin, S., and Ottonello, G. (1996) Temperature-dependent disorder in a natural Mg–Al– $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  spinel. *Mineralogical Magazine*, 60, 603–616.
- Grimes, N.W., Thompson, P., and Kay, H.F. (1983) New symmetry and structure for spinel. *Proceedings of the Royal Society London*, A 386, 333–345.
- Harrison, R.J., Redfern, S.A.T., and O'Neill, H.St.C. (1998) The temperature dependence of the cation distribution in synthetic hercynite ( $\text{FeAl}_2\text{O}_4$ ) from in-situ neutron diffraction refinements. *American Mineralogist*, 83, 1092–1099.
- Hazen, R.M. and Finger, L.W. (1982) *Comparative Crystal Chemistry*. Wiley, New York.
- Lehmann, J. and Roux, J. (1986) Experimental and theoretical study of  $(\text{Fe}^{2+}, \text{Mg})(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$  spinels: Activity-composition relationships, miscibility gaps, vacancy contents. *Geochimica et Cosmochimica Acta*, 50, 1765–1783.
- Lucchesi, S. and Della Giusta, A. (1994) Crystal chemistry of non-stoichiometric Mg–Al synthetic spinels. *Zeitschrift für Kristallographie*, 209, 714–719.
- Lucchesi, S. and Della Giusta, A. (1997) Crystal chemistry of a highly disordered Mg–Al natural spinel. *Mineralogy and Petrology*, 59, 91–99.
- Lucchesi, S., Russo, U., and Della Giusta, A. (1999) Cation distribution in natural Zn-spinels: Franklinites. *European Journal of Mineralogy*, 11, 501–511.
- Maekawa, H., Kato, S., Kawamura, K., and Yokokawa, T. (1997) Cation mixing in natural  $\text{MgAl}_2\text{O}_4$  spinel: A high-temperature  $^{27}\text{Al}$  NMR study. *American Mineralogist*, 82, 1125–1132.
- Mattioli, G.S. and Wood, B.J. (1988) Magnetite activities across the  $\text{MgAl}_2\text{O}_4$ – $\text{Fe}_3\text{O}_4$  spinel join, with application to thermobarometric estimates of upper mantle oxygen fugacity. *Contributions to Mineralogy and Petrology*, 98, 148–162.
- Millard, R.L., Peterson, R.C., and Hunter, B.K. (1992) Temperature dependence of cation disorder in  $\text{MgAl}_2\text{O}_4$  spinel using  $^{27}\text{Al}$  and  $^{17}\text{O}$  magic-angle spinning NMR. *American Mineralogist*, 77, 44–52.
- Molin, G.M., Saxena, S.K., and Brizi, E. (1991) Iron-magnesium order-disorder in an orthopyroxene crystal from the Johnstown meteorite. *Earth and Planetary Science Letters*, 105, 260–265.
- Navrotsky, A., Wechsler, B.A., Geisinger, K., and Seifert, F. (1986) Thermochemistry of  $\text{MgAl}_2\text{O}_4$ – $\text{Al}_{8/3}\text{O}_4$  defect spinels. *Journal of the American Ceramic Society*, 69, 418–422.
- Nell, J., Wood, B.J., and Mason, T.O. (1989) High-temperature cation distributions in  $\text{Fe}_3\text{O}_4$ – $\text{MgAl}_2\text{O}_4$ – $\text{MgFe}_2\text{O}_4$ – $\text{FeAl}_2\text{O}_4$  spinels from thermopower and conductivity measurements. *American Mineralogist*, 74, 339–351.
- O'Neill, H.St.C. and Navrotsky, A. (1983) Simple spinels: crystallographic parameters, cation radii, lattice energies, and cation distribution. *American Mineralogist*, 68, 181–194.
- (1984) Cation distribution and thermodynamic properties of binary spinel solid solutions. *American Mineralogist*, 69, 733–753.
- Peterson, R.C., Lager, C.A., and Hitterman, R.L. (1991) A time-of-flight neutron powder diffraction study of  $\text{MgAl}_2\text{O}_4$  at temperatures up to 1273 K. *American Mineralogist*, 76, 1455–1458.
- Princivalle, F., Della Giusta, A., and Carbonin, S. (1989) Comparative crystal chemistry of spinels from some suites of ultramafic rocks. *Mineralogy and Petrology*, 40, 117–126.
- Princivalle, F., Della Giusta, A., De Min, A., and Piccirillo, E.M. (1999) Crystal chemistry and significance of cation ordering in Mg–Al rich spinels from high-grade hornfels (Predazzo-Monzoni, NE Italy). *Mineralogical Magazine*, 63(2) 257–262.
- Redfern, S.A.T., Harrison, R.J., O'Neill, H.St.C., and Wood, D.R.R. (1999) Thermodynamics and kinetics of cation ordering in  $\text{MgAl}_2\text{O}_4$  spinel up to 1600 °C from in situ neutron diffraction. *American Mineralogist*, 84, 299–310.
- Sack, R.O. (1982) Spinel as petrogenetic indicators: Activity-composition relations at low pressures. *Contributions to Mineralogy and Petrology*, 79, 169–186.
- Sack, R.O. and Ghiorso, M.S. (1991) An internally consistent model for the thermodynamic properties of Fe–Mg–titanomagnetite–aluminate spinels. *Contributions to Mineralogy and Petrology*, 106, 474–505.
- Salviulo, G., Russo, U., Della Giusta, A., and Carbonin, S. (1999) Intracrystalline disorder in spinels: sensitivity of cell parameter  $a$  and Mossbauer data. *Neues Jahrbuch für Mineralogie Monatshefte*, 4, 167–179.
- Schmocker, U. and Waldner, F. (1976) The inversion parameter with respect to the space group of  $\text{MgAl}_2\text{O}_4$  spinels. *Journal of Physics C: Solid State Physics*, 9, L235–L237.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sheldrick, G.M. (1993) SHELX-93. Program for crystal structure refinement, University of Göttingen, Germany.
- Tsirel'son, V.G., Belokoneva, Ye.L., Nozik, Yu.Z., and Urusov, V.S. (1987) Precision X-ray diffraction data on the structure of  $\text{MgAl}_2\text{O}_4$  spinel. *Geochemistry International*, 24, 124–130.
- Viertel, H.U. and Seifert, F. (1979) Physical properties of defect spinels in the system  $\text{MgAl}_2\text{O}_4$ – $\text{Al}_2\text{O}_3$ . *Neues Jahrbuch für Mineralogie Abhandlungen*, 134, 167–182.
- Waerenborgh, J.C., Figueiredo, M.O., Cabral, J.M.P., and Pereira, L.C.J. (1994) Temperature and composition dependence of the cation distribution in synthetic  $\text{ZnFe}_3\text{Al}_{2-y}\text{O}_4$  ( $0 < y < 2$ ) spinels. *Journal of Solid State Chemistry*, 111, 300–309.
- Wood, B.J., Kirkpatrick, R.J., and Montez, B. (1986) Order-disorder phenomena in  $\text{MgAl}_2\text{O}_4$  spinel. *American Mineralogist*, 71, 999–1006.
- Yamanaka, T. and Takéuchi, Y. (1983) Order-disorder transition in  $\text{MgAl}_2\text{O}_4$  spinel at high temperatures up to 1700 °C. *Zeitschrift für Kristallographie*, 165, 65–78.

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