American Mineralogist, Volume 76, pages 1455–1458, 1991

A time-of-flight neutron powder diffraction study of $MgAl_2O_4$ at temperatures up to 1273 K

R. C. PETERSON
Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6, Canada
G. A. LAGER
Department of Geology, University of Louisville, Louisville, Kentucky 40292, U.S.A.
R. L. HITTERMAN
IPNS Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

ABSTRACT

Time-of-flight neutron powder diffraction data have been obtained in situ at temperatures up to 1273 K for two samples of $MgAl_2O_4$ (spinel). The samples were synthesized under different experimental conditions (single-crystal boule vs. air-quenched sintered pellet) and exhibited different degrees of cation disorder at room temperature. The Rietveld method was used to fit the data, which were obtained initially at room temperature and then at various temperatures as the samples were cooled from 1273 K. Both samples exhibit statistically equivalent degrees of disorder in the temperature range 973–1273 K. The atomic fraction of Al in the tetrahedral site increases from 0.25(1) at 973 K to 0.35(2) at 1273 K. This amount of disorder is significantly less than that determined by an earlier nuclear magnetic resonance experiment. The slight nonuniform variation of the atomic parameters in this temperature range for both samples may suggest a behavior that is inconsistent with a simple process of cation reordering on cooling.

INTRODUCTION

The spinel group of minerals, with general formula AB_2O_4, has been the subject of investigations using many different experimental techniques. The apparent simplicity of these cubic structures gives way under close scrutiny to complex relationships among chemical composition, structural state, and general thermodynamic parameters. The purpose of this study was to investigate the distribution of cations within the spinel structure ($MgAl_2O_4$) at temperatures up to 1273 K. The spinel structure can be described as a cubic closest-packed array of O atoms, with one-eighth of the tetrahedral sites and one-half of the octahedral sites filled. The formula may be written as

$$^{[4]}(Mg_{1-x}Al_x)^{[6]}(Al_{2-x}Mg_x)O_4 \qquad (1)$$

assuming stoichiometric spinel. The terms "normal" and "inverse" are used to denote spinels for which $x = 0$ and $x = 1$, respectively. For a completely random distribution of +2 and +3 cations among the tetrahedral and octahedral sites, $x = 0.6667$.

PREVIOUS WORK

X-ray diffraction studies (Yamanaka and Takéuchi, 1983), dilatometry (Suzuki and Kumazawa, 1980), and electrical conductivity measurements (Weeks and Sonder, 1980) on spinel have all shown evidence of discontinuous behavior of structural parameters in the temperature range 773–1273 K. In addition, reflections that violate space group *Fd*3*m* have been observed with electron diffraction and by anomalous dispersion effects of synchrotron radiation (e.g., Hwang et al., 1973; Grimes et al., 1983; G. D. Price, personal communication, 1987).

Recently, Wood et al. (1986) evaluated the distribution of Al and Mg among the octahedral and tetrahedral sites in $MgAl_2O_4$ quenched from various temperatures using ^{27}Al nuclear magnetic resonance spectroscopy (NMR). They found the degree of inversion to be inconsistent with the reversed phase-equilibria data and attributed this to short-range order effects. A recent ^{27}Al magic angle spinning (MAS) NMR study (Millard et al., in press) shows that the previous NMR work employed instrumental parameters that led to a systematic overestimation of the degree of disorder. Schmocker and Waldner (1976) determined the inverse or normal character of Cr^{3+}-bearing natural spinels and found a similar temperature dependence but less overall disorder. Gobbi et al. (1985) determined the inverse or normal character of a synthetic and a natural spinel by NMR and found results similar to those of Wood et al. (1986).

EXPERIMENTAL METHOD

The present study employed neutron powder diffraction because, unlike X-rays, neutrons are scattered quite differently by Mg and Al, allowing a more direct measure of the distribution of Mg and Al within the crystal. The geometry of the time-of-flight (TOF) method (i.e., fixed

0003–004X/91/0910–1455$02.00

TABLE 2. Atomic parameters and agreement indices (*R*)*

	T (K)	*a* (Å)	*u*	*B* (OX)	*B* (T)	*B* (O)	*x*	wR_p	R_{exp}
W**	293	8.08435(7)	0.26148(7)	0.70(3)	0.24(5)	0.53(4)	0.32(2)	7.70	6.57
UC†	293	8.07975(5)	0.26264(5)	0.51(2)	0.28(3)	0.33(3)	0.12(2)	7.34	5.20
W	873	8.12501(5)	0.26210(6)	1.09(3)	0.85(5)	0.98(4)	0.23(2)	5.88	4.75
UC	923	8.12508(5)	0.26244(5)	1.07(2)	0.84(3)	0.94(3)	0.20(1)	5.85	3.93
W	973	8.13219(5)	0.26186(6)	1.21(3)	0.97(5)	1.09(4)	0.25(2)	5.78	4.81
UC	973	8.12872(4)	0.26225(5)	1.16(2)	0.84(3)	1.06(3)	0.25(1)	5.65	3.68
UC	1023	8.13235(5)	0.26204(5)	1.25(2)	0.90(4)	1.36(4)	0.27(1)	5.64	3.71
W	1073	8.13927(6)	0.26174(6)	1.37(3)	1.13(6)	1.16(4)	0.27(2)	5.79	4.90
UC	1073	8.13613(5)	0.26190(5)	1.30(2)	0.92(4)	1.14(4)	0.27(2)	5.92	4.20
UC	1123	8.13991(5)	0.26180(5)	1.36(2)	1.04(4)	1.21(4)	0.29(2)	5.51	3.65
W	1173	8.14616(6)	0.26141(7)	1.47(3)	1.19(7)	1.28(5)	0.33(2)	5.83	4.89
UC	1173	8.14369(5)	0.26164(5)	1.45(2)	1.06(4)	1.25(4)	0.31(2)	5.43	3.65
W	1273	8.15409(4)	0.26114(5)	1.60(3)	1.25(5)	1.41(4)	0.36(1)	4.20	3.02
UC	1273	8.15090(5)	0.26144(6)	1.56(3)	1.13(5)	1.41(5)	0.34(2)	5.93	4.51

* Refer to Jorgensen et al. (1989) for definition of agreement indices.
** W = sintered supplied by Wood.
† UC = Union Carbide single-crystal boule.

detector position) allows use of a furnace that is simple in design and stable with respect to temperature fluctuations. These in situ neutron-diffraction experiments on spinel powders at temperatures up to 1273 K allow a unique opportunity to study cation disordering.

A fragment of a large synthetic crystal of $MgAl_2O_4$ (Union Carbide, Electronics Division, San Diego, California) and a sintered pellet of $MgAl_2O_4$ crystallites previously studied by NMR (B. J. Wood, Northwestern University) were ground under acetone in an agate mortar. The samples were packed in a thin-walled V can and mounted inside a Ta resistance furnace. The material supplied by Wood filled only one-third of the sample canister, and the measured intensity from this sample was therefore considerably less than for the Union Carbide material. The diffraction data were obtained in a vacuum ($<10^{-5}$ torr) at temperatures from 273 K to 1273 K using the general purpose powder diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory (Jorgensen et al., 1989; Table 1[1]). Initial data measurement and structure refinements were completed at room temperature for both samples. The first measurements to be made at elevated temperatures were 1273 K for both samples. The changes in the measured parameters (i.e., *a, u, B,* or *x*) reflect the behavior of the spinel on cooling to the various temperatures. The samples were first heated to the highest temperature at which diffraction data would be measured to insure that the cation distributions in the two samples would be as similar as possible. No reversals were completed because of the limited beam time available.

Structure refinements were conducted using the Rietveld method (Rietveld, 1969) modified for TOF neutron data (Von Dreele and Jorgensen, 1982). Neutron scattering lengths were obtained from the compilation of Sears (1986). All high-temperature refinements were based on 128 reflections in the *d* range 0.506–3.120 Å ($2\theta = \pm 90°$) and 15 variable parameters. The latter number included both structural parameters and those parameters that describe the shape of diffraction maxima and the background. The number of reflections in the above *d* range was slightly less at room temperature (124). In addition, there were 16 variable parameters in the room temperature refinement of the Union Carbide sample because both extinction and absorption coefficients were refined. The absorption coefficient was subsequently fixed for this sample in all high-temperature refinements. Mg and Al occupancies of the cation sites were refined with the constraint that the Mg and Al cations were distributed only over the tetrahedral and octahedral sites normally occupied in stoichiometric $MgAl_2O_4$. There was no evidence for cations occupying the normally unfilled tetrahedral and octahedral voids in this closest-packed oxide.

RESULTS

The unit-cell dimension, atomic parameters, and final *R* factors at each temperature for the two samples studied are listed in Table 2. The increase of the *a* unit-cell dimension for each sample is continuous (Fig. 1), and there is no indication of the irregularity in the rate of change of *a* with temperature that has been observed in this temperature interval by other workers (Yamanaka and Takéuchi, 1983); however, fewer measurements of the unit-cell dimension were obtained in the present study.

The O positional parameter (*u*) increases as the spinel becomes more ordered with decreasing temperature (Fig. 2). The observation that *a* is consistently greater for the Union Carbide sample (Fig. 1) and *u* is smaller indicates that a systematic difference exists between the two samples. The cause of these differences is not known. There appears to be a slight variation in the trend of *u* at about 1073 K for both samples. This slight deviation is more apparent in the variation of the temperature factors with temperature as seen in Figure 3. For the Union Carbide sample, the temperature factors for the cations are more

---

[1] To obtain a copy of Table 1, order Document AM-91-471 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

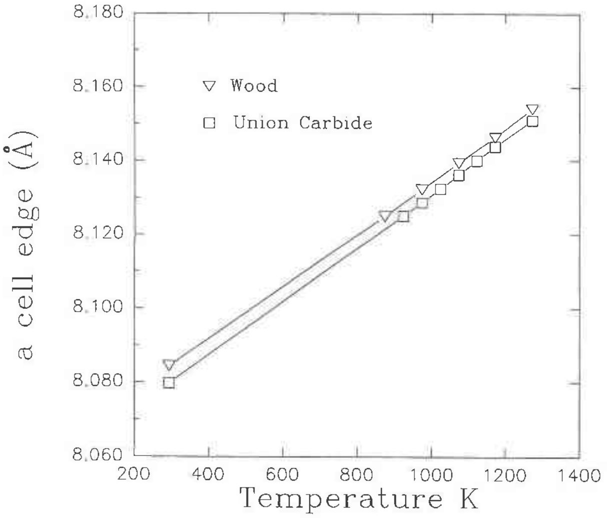

Fig. 1. Variation of the *a* unit-cell dimension (Å) as a function of temperature.

different in the range 973–1073 K, whereas for the Wood sample the temperature factors for the tetrahedral cations and the octahedral cations are equal in magnitude in this range.

The degree of disorder (x), as defined in Equation 1, is plotted as a function of temperature in Figure 4. The two room temperature measurements are included to show the degree of disorder of the starting material. The Wood sample, a small air-quenched sintered pellet, was initially much more disordered than the Union Carbide sample, which, as part of a large crystal boule, cooled much more slowly. Equilibration of the spinel structure at high temperatures (i.e., 1273 K) occurs very quickly. At 1073 K, parameters changed significantly in a few minutes. Therefore, it is likely that cation distributions measured at temperatures greater than 973 K represent equilibrium distributions. In fact, both samples exhibited equal degrees of disorder for all temperatures measured except in the range 873–973 K, in spite of very different methods of synthesis.

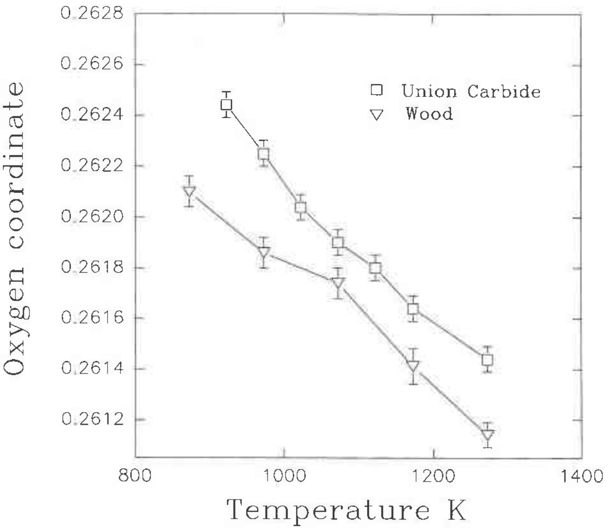

Fig. 2. Variation of the O coordinate (u) as a function of temperature.

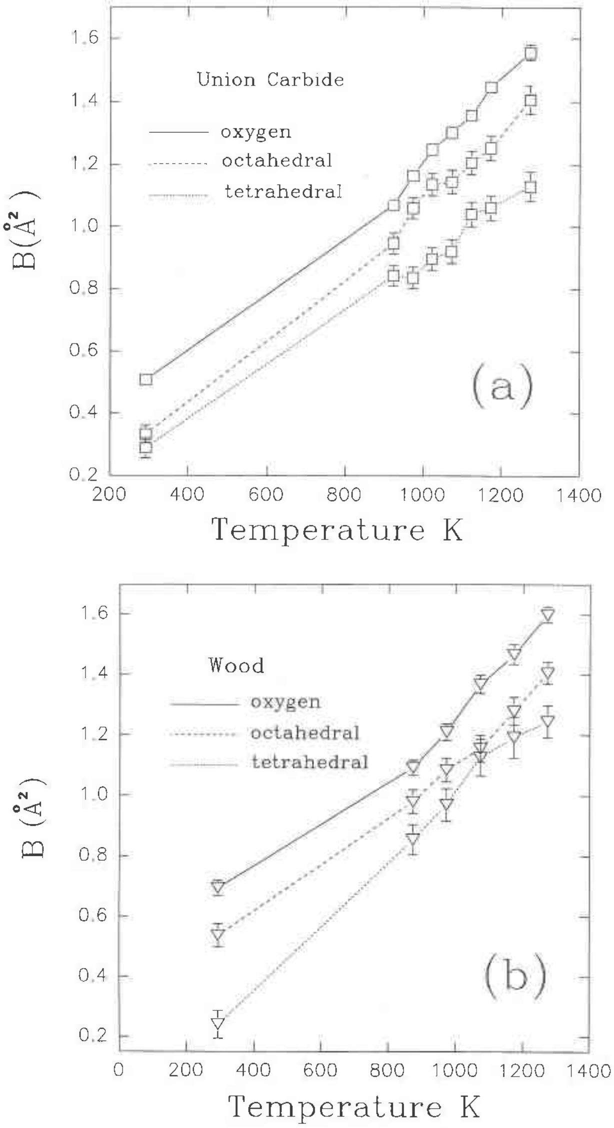

Fig. 3. Variation of isotropic temperature factors (Å²) as a function of temperature. (**a**) Union Carbide sample; (**b**) Wood sample.

DISCUSSION

The amount of disorder determined by neutron diffraction is significantly less than that determined by ^{27}Al MAS NMR by Wood et al. (1986), even though the same material was used. This difference is attributed to a systematic error in the NMR study (Millard et al., unpublished data). O'Neill and Navrotsky (1983) have proposed a modified equilibrium model with a lattice energy

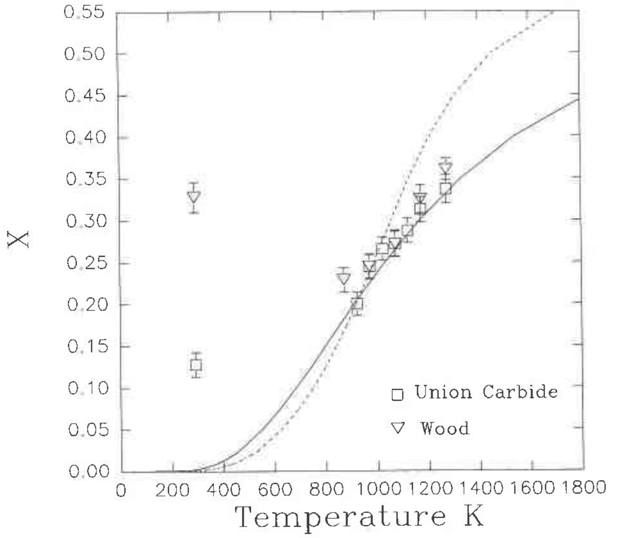

Fig. 4. Variation of the Al content of the tetrahedral site as a function of temperature. The solid curve represents the best fit of the Union Carbide data using the O'Neill and Navrotsky (1983) model with $\alpha = 31(1)$ kJ and $\beta = -10(3)$ kJ. The dashed line represents the fit of Wood et al. (1986) for comparison [$\alpha = 36(1)$, $\beta = -23(2)$].

term, which makes the interchange enthalpy dependent on the degree of inversion:

$$\Delta G^0 = \alpha + 2\beta x = -RT \ln x^2(1 - x)^{-1}(2 - x)^{-1}. \quad (2)$$

A best fit through the Union Carbide data yields $\alpha = 31(1)$ kJ and $\beta = -10(3)$ kJ. The enthalpy of annealing, $\Delta H_{\mathrm{anneal}}$, was recalculated using these coefficients and values of $x = 0.25$ at 973 K and $x = 0.32$ at 1200 K; the result is -1.33 kJ, which is within 1 esd of the experimentally determined $\Delta H_{\mathrm{anneal}}$ values of -1.1 ± 0.7 kJ and -0.7 ± 0.8 kJ for $MgAl_2O_4$ (Navrotsky, 1986).

The slight nonuniform variations of the temperature factors and the O positional parameter in the region 973–1073 K in both samples may suggest a behavior that is inconsistent with a simple process of cation reordering on cooling. This is the same temperature region where Suzuki and Kumazawa (1980) found anomalous thermal expansion on both heating and cooling. Also it is in this temperature range that Weeks and Sonder (1980) found variation in the rate of change of the electrical conductivity with heating. The reversible nature of this phenomenon, as indicated by the dilatometry measurements, shows that it is not simply the result of a failure to achieve equilibrium in the experiments. The present powder neutron diffraction experiments are not precise enough or spaced closely enough in temperature and time to supply an explanation for this unusual behavior. A detailed single-crystal neutron diffraction study in the temperature range 873 K to 1073 K has been scheduled in order to examine this behavior more closely.

ACKNOWLEDGMENTS

We thank B.J. Wood and Union Carbide for generously supplying the samples and F.J. Rotella for help with the data analysis. R.J. Kirkpatrick and A. Navrotsky improved this manuscript with their careful reviews. This research was supported by NSERC-OGP0008009 to R.C.P.

REFERENCES CITED

Gobbi, G.C., Christoffersen, R., Otten, M.T., Miner, B., Buseck, P.R., Kennedy, G.J., and Fyfe, C.A. (1985) Direct determination of cation disorder in $MgAl_2O_4$ spinel by high-resolution ^{27}Al magic-angle-spinning NMR spectroscopy. Chemistry Letters, 771–774.

Grimes, N.W., Thompson, P., and Kay, H.F. (1983) New symmetry and structure for spinel. Proceedings of the Royal Society, London, A386, 333–345.

Hwang, L., Heuer, A.H., and Mitchell, T.E. (1973) On the space group of $MgAl_2O_4$ spinel. Philosophical Magazine, 28, 241–243.

Jorgensen, J.D., Faber, J., Jr., Carpenter, J.M., Crawford, R.K., Haumann, J.R., Hitterman, R.L., Kleb, R., Ostrowski, G.E., Rotella, F.J., and Worlton, T.G. (1989) Electronically-focused time-of-flight powder diffractometer at the Intense Pulsed Neutron Source. Journal of Applied Crystallography, 22, 321–333.

Millard, R.L., Peterson, R.C., and Hunter, B.K. (1992) Temperature dependence of cation disorder in $MgAl_2O_4$ spinel using ^{27}Al and ^{17}O magic-angle spinning NMR. American Mineralogist, 77, in press.

Navrotsky, A. (1986) Cation-distribution energetics and heats of mixing in $MgFe_2O_4$-$MgAl_2O_4$, $ZnFe_2O_4$-$ZnAl_2O_4$ and $NiAl_2O_4$-$ZnAl_2O_4$ spinels: Study by high-temperature calorimetry. American Mineralogist, 71, 1160–1169.

O'Neill, H., and Navrotsky, A. (1983) Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. American Mineralogist, 68, 181–194.

Rietveld, H.M. (1969) A profile refinement method for nuclear and magnetic structures. Journal of Applied Crystallography, 2, 65–71.

Schmocker, U., and Waldner, F. (1976) The inversion parameter with respect to the space group of $MgAl_2O_4$ spinels. Journal of Physics, C9, L235–L237.

Sears, V.F. (1986) Neutron scattering in condensed matter research. In K. Skold and D.L. Price, Eds., Methods of experimental physics, vol. 23, part A, p. 521. Academic Press, Orlando, Florida.

Suzuki, I., and Kumazawa, M. (1980) Anomalous thermal expansion in spinel $MgAl_2O_4$. Physics and Chemistry of Minerals, 5, 279–284.

Von Dreele, R.B., and Jorgensen, J.D. (1982) Rietveld refinement with spallation neutron powder diffraction data. Journal of Applied Crystallography, 15, 581–589.

Weeks, R.A., and Sonder, E. (1980) Electrical conductivity of pure and Fe-doped magnesium-aluminum spinel. Journal of the American Ceramic Society, 63, 92–95.

Wood, B.J., Kirkpatrick, R.J., and Montez, B. (1986) Order-disorder phenomena in $MgAl_2O_4$ spinel. American Mineralogist, 71, 999–1006.

Yamanaka, T., and Takéuchi, Y. (1983) Order-disorder in $MgAl_2O_4$ spinel at high temperatures up to 1700 °C. Zeitschrift für Kristallographie, 165, 65–78.

MANUSCRIPT RECEIVED AUGUST 20, 1990
MANUSCRIPT ACCEPTED MAY 21, 1991