

## Structural variation in nickel aluminate spinel (NiAl<sub>2</sub>O<sub>4</sub>)

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### ABSTRACT

The variation in the *a* cell edge, degree of inversion, O positional parameter, and thermal parameters of nickel aluminate spinel (NiAl<sub>2</sub>O<sub>4</sub>) have been determined for samples annealed at temperatures between 800 and 1500 °C by Rietveld refinement using X-ray powder diffraction data. The nickel aluminate spinels were grown in air from oxide mixtures and rapidly quenched in liquid N<sub>2</sub>. As the temperature at which the samples were annealed increased, the *a* cell edge increased and the cation distribution within the spinel became more random. Structural reequilibration during the quench procedure was observed, as all measured structural parameters are equivalent for samples annealed at temperatures above 1200 °C. Above 1200 °C, these results are significantly different from those of Mocala and Navrotsky (1989), who found a decrease in the *a* cell edge and a constant degree of inversion.

### INTRODUCTION

The general formula for an oxide spinel is



where A and B represent differently charged cations and *x* represents the degree of inversion. The two end-members are normal spinel (*x* = 0; AB<sub>2</sub>O<sub>4</sub>) and inverse spinel (*x* = 1; B[AB]O<sub>4</sub>). At high temperatures, spinels tend toward the random distribution



Spinel is classified by cation valence, where A is 2+, 4+, or 6+ and B is 3+, 2+, or 1+. The two most common spinel types are 2-3 (the spinel contains 2+ and 3+ cations) and 4-2 spinels. Nickel aluminate spinel is one example of a partially inverse 2-3 spinel. In many spinels such as nickel aluminate, the degree of inversion varies with temperature (Porta et al., 1978).

The simple crystallographic structure and the ease of solid solution between end-members have been the basis for extensive studies of spinels (Verwey and Heilmann, 1947; Porta et al., 1974, 1978; O'Neill and Navrotsky, 1983, 1984; Navrotsky, 1986). Structural variation studies (e.g., cation distribution) have improved the understanding of the correlation between crystal structure and physical properties in spinels (Eppler, 1982). In particular, intracrystalline cation distribution is an important

parameter when attempting to model the thermodynamic behavior of minerals (Navrotsky and Kleppa, 1967; O'Neill and Navrotsky, 1983, 1984). In this paper, we document the changes in cation distribution of nickel aluminate spinel as a function of quench temperature by Rietveld structure analysis using X-ray powder diffraction data.

### PREVIOUS STUDIES

Previous X-ray powder diffraction studies on nickel aluminate spinel are listed in Table 1. The *a* cell edges determined by various studies are presented in Figure 1, where a wide variation in cell edge can be observed. It is difficult to compare these results as many experimental differences exist, such as sample quench rate and method of synthesis, which may introduce systematic errors. Only two major studies have determined *a* cell edge values from differently quenched materials. Porta et al. (1974), Pepe et al. (1976), and Porta et al. (1978) described a series of closely related experiments on NiAl<sub>2</sub>O<sub>4</sub> quenched from various temperatures. They found that the *a* cell edge increased with the temperature of quench until 1200 °C. Above this temperature, the *a* cell edge remained constant (trend 2 on Fig. 1). This plateau is due to an inadequate rate of quench of the spinel (Navrotsky, 1986). The study of Mocala and Navrotsky (1989) also found that the *a* cell edge increased with an increase in quench temperature up to 1100 °C. However, above 1100 °C, they found that the *a* cell edge decreased as the quench temperature increased. This surprising result is trend 1 in Figure 1.

In general, previous structural studies (Table 1) show that nickel aluminate spinel becomes more random (less inverse) as the quench temperature is increased (Datta

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and Roy, 1967; Cooley and Reed, 1972; Mocala and Navrotsky, 1989). The present study investigates the structural variation of nickel aluminate spinel quenched from 800 to 1500 °C in order to examine the differences exhibited by the work of Porta and coworkers and Mocala and Navrotsky (1989).

## EXPERIMENTAL METHODS

### Synthesis and equilibration

The starting mixtures were prepared from stoichiometric green nickel oxide (AESAR 99.998%) and aluminum oxide (Aldrich 99.99%) that had been preheated in air at 800–1000 °C for 24 h. Equimolar amounts of NiO and Al<sub>2</sub>O<sub>3</sub> were ground together in an agate mortar. Twelve dry-pressed pellets (each of 150 mg) were sintered in air for four 24-h periods at 1300 °C to ensure complete reaction. The pellets were then placed in a Pt wire basket and hung in a Deltech (DT-31 series) furnace. Each sintering period was interspersed with optical examination, X-ray powder diffraction using a Picker diffractometer, and regrinding.

Final X-ray and optical examination revealed only nickel aluminate spinel. The pellets were separated into two groups to bracket the equilibrium conditions. One group of seven pellets was annealed at 800 °C for 352 h

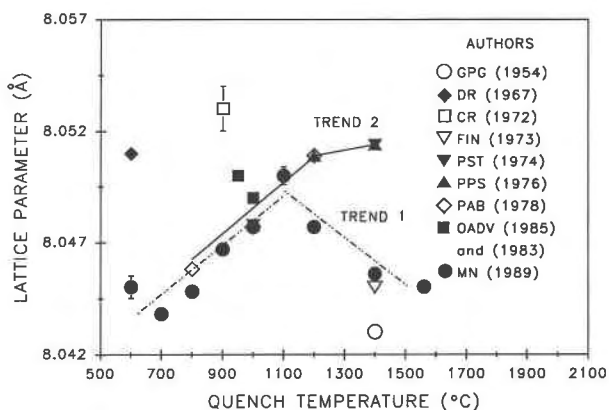


Fig. 1. Results of previous studies of *a* cell edges vs. quench temperature for nickel aluminate spinel. All lines on this and all other graphs were formed from an unweighted least-squares linear fit. The dotted and dashed line represents the study of Mocala and Navrotsky (1989). The solid line represents the studies of Porta and coworkers (Porta et al., 1974; Pepe et al., 1976; Porta et al., 1978). FIN—Furuhashi et al. (1973), PST—Porta et al. (1974), PAB—Porta et al. (1978), DR—Datta and Roy (1967), GPG—Greenwald et al. (1954), OADV—Otero Arean and Diez Vinuela (1985) and Otero Arean et al. (1983), MN—Mocala and Navrotsky (1989), PPS—Pepe et al. (1976), CR—Cooley and Reed (1972).

TABLE 1. Previous structural studies on nickel aluminate spinel

Reference	Method of synthesis	Temperature (°C)	Lattice parameter (Å)	Degree of inversion
Mocala and Navrotsky (1989)	Samples in Pt foil tubes Solid-state reaction between the oxides Quenched in liquid N <sub>2</sub>	600–1560	1. 600–1100 °C increases from 8.0450(5) to 8.0500(4) 2. 1100–1530 °C decreases from 8.0500(4) to 8.0450(3)	0.82(1)–0.775(15)
Otero Arean and Diez Vinuela (1985)	Solid-state reaction between the oxides Quenched in liquid N <sub>2</sub>	950	8.050	0.844(2)
Otero Arean et al. (1983)	Solid-state reaction between the oxides Quenched in liquid N <sub>2</sub>	1000	8.049	0.836(2)
Porta et al. (1978)	Al <sub>2</sub> O <sub>3</sub> soaked in nickel nitrate followed by solid-state reaction between the oxides Quenched in H <sub>2</sub> O	1200 1000 800	8.0509 8.0477 8.0458	0.77 0.80 0.84
Pepe et al. (1976)	Solid-state reaction between the oxides Quenched in H <sub>2</sub> O	1400 1200 1000	8.0514 8.0509 8.0478	0.79 0.77 0.78
Porta et al. (1974)	Solid-state reaction between initially moist oxides that were dried and pelletized Quenched in H <sub>2</sub> O	1400 1000	8.0514 8.0478	0.79 0.78
Furuhashi et al. (1973)	Samples in a Pt envelope Solid-state reaction between the oxides Quenched in H <sub>2</sub> O	1400	8.045	0.84
Cooley and Reed (1972)	Samples in Pt foil tubes and boats Several hydrothermal reaction techniques: 1. mixed nitrate decomposition 2. freeze drying of mixed sulfates Quenched in H <sub>2</sub> O	595–1391	900 °C—8.053	595 °C—0.93 1391 °C—0.74
Datta and Roy (1967)	Samples in Pt or Au tubes Hydrothermally reacted oxide mixtures in Au tubes Dry experiments above 930 °C in Pt or Au tubes	600–1550	600 °C—8.051 1550 °C—8.056	1.00 0.75
Schmalzried (1961)	Samples wrapped in Pt foil NiO produced from its hydrous nitrate Solid-state reaction of oxides Quenched in H <sub>2</sub> O	850–1500		1480 °C—0.745 850 °C—0.818
Greenwald et al. (1954)	Hydrous mixtures of oxides dried before heating Very short experimental time	1400	8.043	annealed 0.85 quenched 0.80

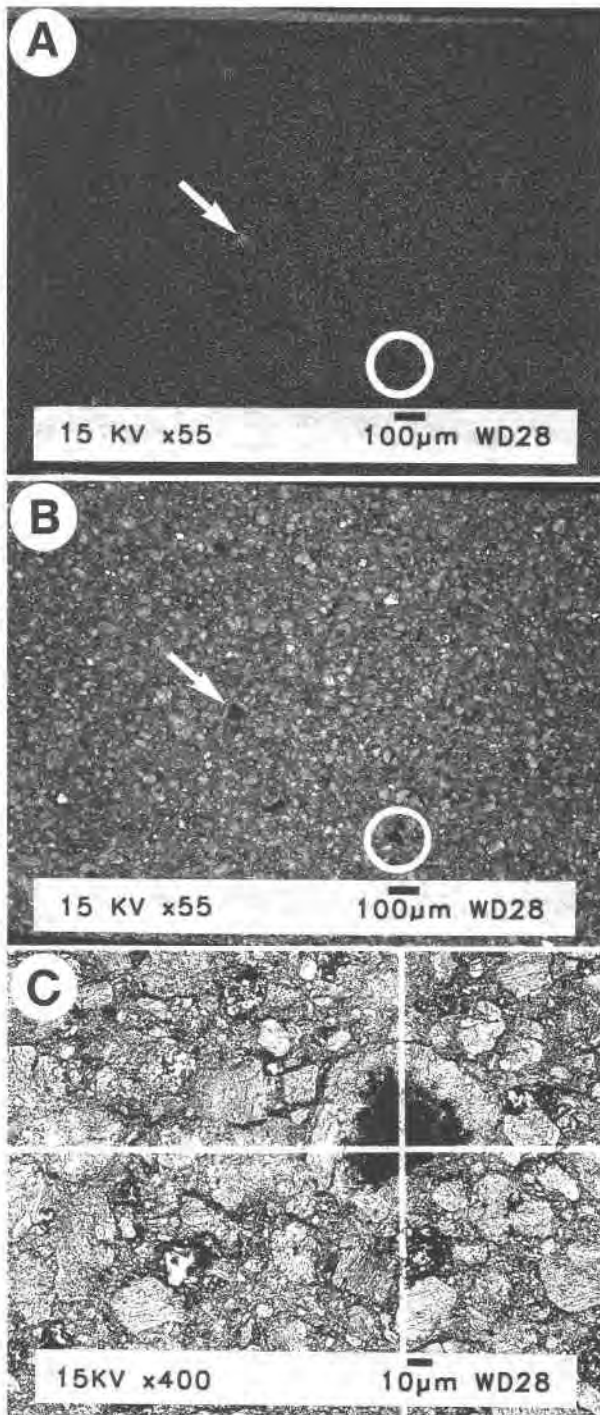


Fig. 2. Scanning electron micrographs of the nickel aluminate spinel samples. (A)  $\text{AlK}\alpha$  X-ray map produced on a previous sintering experiment. The brighter regions are alumina rich (at the tip of the arrow). The circled area is a region of no alumina concentration. (B) Backscattered electron image of the same region as A. (C) Backscattered electron image of the alumina-rich region pointed to in A. The alumina particle is surrounded by nickel aluminate spinel.

TABLE 2. Pellet annealing times

T (°C)	Time (h)
800	352
900	141
1000	116
1100	60
1200	41
1300	24
1400	24
1500	4

and air quenched. To approach equilibrium from a more and less disordered state, one pellet from each group was equilibrated and annealed in air at a temperature between 800 and 1500 °C followed by drop quenching in liquid  $\text{N}_2$ . The annealing times are listed in Table 2. Difficulties were encountered in rapidly quenching the first 1500 °C sample, so the method was repeated for two additional 1500 °C samples initially annealed at 1300 °C.

To verify whether the spinels were equimolar, various pellets were analyzed by neutron activation analysis (NAA) and scanning electron microscopy (SEM). The composition determined by NAA (on five samples) was 41.3(5)%  $\text{NiO}$  and 58.4(5)%  $\text{Al}_2\text{O}_3$ , which corresponds to a spinel with formula  $\text{Ni}_{1.098}\text{Al}_{2.02}\text{O}_4$ . No significant difference in chemical composition was observed between samples annealed at high and low temperatures. The SEM analyses were performed on two pieces of pellets from previous sintering experiments. An  $\text{AlK}\alpha$  map of a large area of one spinel sample revealed small regions (25  $\mu\text{m}$  in diameter) of high alumina content and other equal-area, alumina-poor regions (Figs. 2A, 2B). A point analysis of one alumina-rich region revealed only alumina (Fig. 2C). The alumina is rimmed by nickel aluminate spinel that has, apparently, become an effective retardant to further spinel formation. The alumina-poor region circled in Figures 2A and 2B is a hole in the sample caused by removal of a grain during the sample preparation process.

Transmission X-ray powder diffraction was performed (on a STOE diffractometer) to determine the extent of oxide excess. Very small peaks suggesting an  $\text{NiO}$  concentration of less than 1.0% were observed, but no  $\text{Al}_2\text{O}_3$  peaks were observed. These results indicate the presence of small amounts of unreacted oxides (<1%).

#### X-ray powder diffraction data collection

Step-scan powder diffraction data were measured on a Philips automated diffractometer system PW1710. A PW1050 Bragg-Brentano goniometer (equipped with incident- and diffracted-beam Soller slits, 1° divergence and antiscatter slits, a 0.2-mm receiving slit and a curved graphite diffracted-beam monochromator) was used. The normal-focus  $\text{Cu}$  X-ray tube was operated at 40 kV and 40 mA with a takeoff angle of 6°. The samples were front loaded. The data were measured with a step size of  $0.10^\circ 2\theta$ , a  $2\theta$  range of  $17.00$ – $143.00^\circ$ , and a 2-s counting time at each step (see Hill and Howard, 1987).

TABLE 3A. Final results of Rietveld refinements

	Quench temperatures for samples initially annealed at 800 °C (°C)						
	1500	1400	1200	1100	1000	900	800
<i>a</i> (Å)	8.05154(6)	8.05221(5)	8.05146(5)	8.05038(5)	8.04899(5)	8.04741(5)	8.04622(5)
<i>u</i>	0.2564(2)	0.2563(2)	0.2558(2)	0.2562(2)	0.2555(2)	0.2552(2)	0.2552(2)
<i>x</i>	0.806(5)	0.797(5)	0.804(5)	0.821(5)	0.840(5)	0.859(5)	0.864(5)
$\beta$ -tet	0.31(4)	0.34(4)	0.36(5)	0.33(4)	0.35(5)	0.32(5)	0.36(5)
$\beta$ -oct	0.40(3)	0.38(3)	0.39(3)	0.39(3)	0.40(3)	0.39(3)	0.42(3)
$\beta$ -O	0.70(5)	0.76(5)	0.75(5)	0.71(5)	0.71(5)	0.72(5)	0.70(5)
<b>Various errors and measures of fit</b>							
<i>R</i> -Bragg	2.36	2.90	2.95	2.93	3.28	3.14	3.52
<i>R</i> -WP	7.58	7.50	8.35	7.63	8.84	8.29	8.89
<i>d</i>	1.31	1.37	1.33	1.28	1.37	1.29	1.37
GOF	1.70	1.69	1.88	1.71	1.98	1.85	2.00

Note: *x* is defined as (Ni<sub>1-x</sub>Al<sub>x</sub>)<sup>2+</sup>[Ni<sub>x</sub>Al<sub>2-x</sub>]<sup>3+</sup>O<sub>4</sub>.

### Rietveld structure refinement

The Rietveld method (Rietveld, 1969) as implemented in the DBW 3.2S program, version 8804 (Wiles et al., 1988), was used to characterize the structure of these fine-grained nickel aluminate spinels. Rietveld refinements were conducted in three stages using space group *Fd3m* with the origin at  $\bar{3}$ . Occupancies of the Ni<sup>2+</sup> and Al<sup>3+</sup> cations at the tetrahedral and octahedral sites were allowed to vary within the constraints of the ideal formula and full site occupancy, although they were initially fixed assuming a degree of inversion of 0.80. Initially, the isotropic thermal parameters, monochromator polarization correction, and peak full-width at half-maximum (FWHM) values were also fixed. First, the scale factor, sample displacement, and the first three background parameters were refined. The background was refined according to the function stated in Wiles et al. (1988). The fourth background parameter and *a* cell edge were then added to the refinement. In subsequent refinements, the following parameters were added: the FWHM parameter (*W*), O positional parameter (described by a single parameter, *u*), and the first parameter of the pseudo-Voigt function. In later stages, refinements were performed by allowing each parameter [the remaining FWHM parameters (*U* and *V*), asymmetry correction, the second pseu-

do-Voigt parameter, the isotropic thermal parameters, and the site occupancies] to vary successively. Refinement was continued until the parameter shifts were less than 0.2 $\sigma$ . The final refinement cycles involved 18 variables. During a further refinement with variable O occupancy, no significant variation was observed. Refinement of the preferred orientation parameters (as defined in Wiles et al., 1988) had no effect on the final results. The results for the various refined variables are listed in Table 3.

As a check of the *a* cell edges determined by Rietveld refinement, *a* cell edges were also determined for five samples using a transmission STOE/CSS STADI 2/PL automatic powder X-ray diffractometer with a horizontal X-ray CuK $\alpha$  tube and an incident-beam graphite focusing monochromator. The cell edges were determined with the use of the ELST program (Gabe, 1982) and an Si internal standard. All *a* cell edges determined for samples initially annealed at 800 °C were identical to those determined by Rietveld refinement, whereas *a* cell edges for samples initially annealed at 1300 °C showed a 2–3 $\sigma$  difference.

### DISCUSSION

In this study, the *a* cell edge increases with increasing quench temperature from 800 to 1200 °C but is constant between 1200 and 1500 °C (Fig. 3). This increase is caused

TABLE 3B. Final results of Rietveld refinements

	Quench temperatures for samples initially annealed at 1300 °C (°C)					
	1500	1300	1200	1100	1000	900
<i>a</i> (Å)	8.05263(6)	8.05199(5)	8.05145(5)	8.05059(5)	8.04897(5)	8.04751(5)
<i>u</i>	0.2565(2)	0.2557(2)	0.2562(2)	0.2562(2)	0.2557(2)	0.2555(2)
<i>x</i>	0.793(5)	0.802(5)	0.799(5)	0.814(5)	0.833(5)	0.855(5)
$\beta$ -tet	0.40(5)	0.36(4)	0.36(4)	0.39(4)	0.36(4)	0.33(4)
$\beta$ -oct	0.43(3)	0.36(3)	0.38(3)	0.40(3)	0.37(3)	0.39(3)
$\beta$ -O	0.72(6)	0.73(5)	0.71(5)	0.71(5)	0.75(5)	0.74(5)
<b>Various errors and measures of fit</b>						
<i>R</i> -Bragg	3.03	2.71	2.97	2.80	2.81	3.04
<i>R</i> -WP	8.28	7.54	7.83	7.73	8.12	8.18
<i>d</i>	1.20	1.21	1.35	1.18	1.33	1.29
GOF	1.84	1.67	1.73	1.72	1.82	1.82

Note: *x* is defined as (Ni<sub>1-x</sub>Al<sub>x</sub>)<sup>2+</sup>[Ni<sub>x</sub>Al<sub>2-x</sub>]<sup>3+</sup>O<sub>4</sub>.

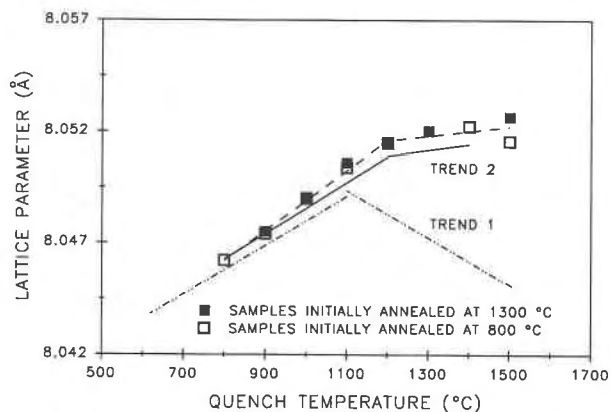


Fig. 3. Comparison of the observed  $a$  cell edge vs. quench temperature with previous cell-edge determinations. The observed  $a$  cell edge increases with quench temperature until 1200 °C, followed by a plateau between 1200 and 1500 °C. This trend is similar to trend 2. (For a description of the origin of the lines, see Fig. 1.)

by structural expansion due to displacement of the larger Ni cation from the octahedral site to the tetrahedral site (O'Neill and Navrotsky, 1983). The plateau is due to the previously mentioned sample reequilibration during the quench procedure (Navrotsky, 1986) and is also observed in other spinels such as magnesioferrite (MgFe<sub>2</sub>O<sub>4</sub>) (Mozzi and Paladino, 1963; Allen, 1966; Faller and Birchenall, 1970).

Our results are similar to those of Porta and coworkers (Porta et al., 1974; Pepe et al., 1976; Porta et al., 1978) (trend 2, Figs. 1, 3). We could not reproduce the results of Mocala and Navrotsky (1989), and we have no explanation as to why their samples showed such a different trend. Some possible explanations were addressed by Mocala and Navrotsky (1989) and discounted. They were the partial solubility of Al<sub>2</sub>O<sub>3</sub> in spinel (Phillips et al.,

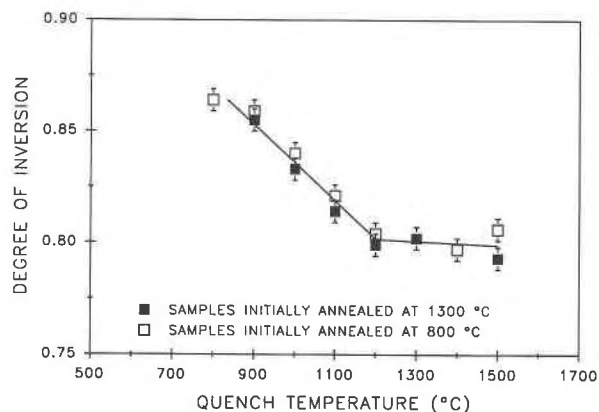


Fig. 4. Observed degree of inversion vs. quench temperature. Note the decreasing degree of inversion with quench temperature until 1200 °C, followed by a constant value between 1200 and 1500 °C.

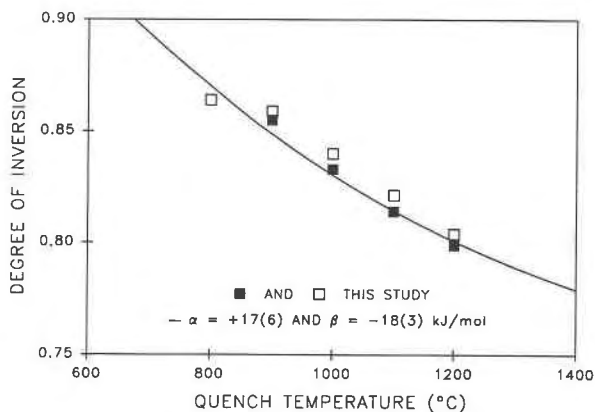


Fig. 5. Comparison between observed and calculated degrees of disorder with quench temperature. The simple quadratic model of O'Neill and Navrotsky (1983) produced on  $\alpha$  and  $\beta$  of +17(6) and -18(3) kJ/mol, respectively. The open and filled squares represent material that was initially more ordered and disordered, respectively.

1963), the presence of metastable alumina-rich nickel-aluminum-oxide phases (Lejus, 1964; Eppler, 1982; Basoul and Gilles, 1985), and the formation of an Ni-Pt alloy or variation in the oxidation state of Ni. Single-crystal (in situ) structural determinations may shed some light on these observed differences in the  $a$  cell edge above 1200 °C.

The degree of inversion decreases from 800 to 1200 °C but remains constant between 1200 and 1500 °C (Fig. 4). The decrease in the degree of inversion with quench temperature increase is consistent with previous X-ray powder diffraction studies, which show that the cation distribution becomes more random with increased quench temperature (Table 1). These results are also consistent with the optical transmission spectroscopy work of Becker and Rau (1987).

Attempts have been made to model quantitatively the change in the degree of inversion of nickel aluminate spinel with quench temperature (Navrotsky and Kleppa, 1967; O'Neill and Navrotsky, 1983, 1984; Navrotsky, 1986; Mocala and Navrotsky, 1989). The simple quadratic model, initially formulated by O'Neill and Navrotsky (1983), relates the interchange enthalpy to the degree of inversion through the relationship

$$\Delta H_{\text{int}} = \alpha + 2\beta x = -RT \ln \frac{x^2}{(1-x)(2-x)} \quad (3)$$

where  $\alpha$  and  $\beta$  are the inversion parameters and  $x$  is the degree of inversion of the spinel. The value of  $\beta$  has been found to vary with charge; in 2-3 spinels it is -20 kJ/mol (O'Neill and Navrotsky, 1983). Previously determined values of  $\alpha$  and  $\beta$  for nickel aluminate spinel are +8 and -15 kJ/mol (Navrotsky, 1986) and +8 and -20 kJ/mol (O'Neill and Navrotsky, 1984). Application of Equation 3 to our results for nickel aluminate spinel sug-

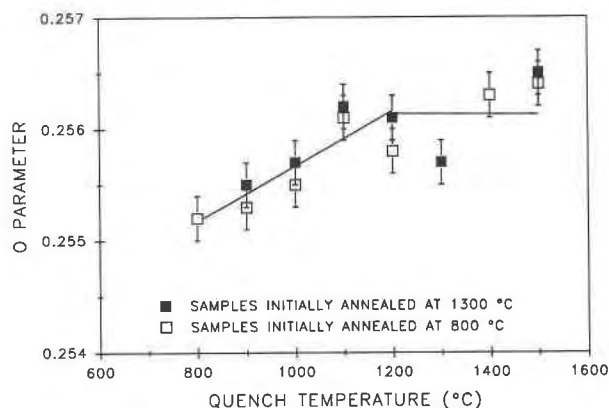


Fig. 6. Observed O positional parameter as a function of quench temperature.

gests a best fit for  $\alpha$  and  $\beta$  of +17(6) and -18(3) kJ/mol, respectively (Fig. 5).

The O positional parameter ( $u$ ) in this study increased slightly with increasing quench temperature until reaching a plateau at 1200 °C (Fig. 6). Similar O positional parameters were noted by Romeijn (1953), Greenwald et al. (1954), Schmalzried (1961), Datta and Roy (1967), Cooley and Reed (1972), Furuhashi et al. (1973), Porta et al. (1974), Otero Arean et al. (1983), Otero Arean and Diez Vinuela (1985), and Mocala and Navrotsky (1989). The increase of O positional parameter with temperature is consistent with increased Ni occupancy of the tetrahedral site as the cation distribution becomes more random.

The atomic thermal parameters vary little for the material studied. The O thermal parameter is approximately twice that of both the tetrahedral and octahedral thermal parameters (Tables 3A, 3B) and is similar in value to that determined by Cooley and Reed (1972).

Smaller  $a$  cell edges and larger degrees of inversion are associated with decreased quench temperatures (Figs. 3, 4). The negative slope observed in the  $a$  cell edge vs. degree of inversion graph (Fig. 7A) suggests that, as the quench temperatures increase, the nickel aluminate spinel structure expands. Mocala and Navrotsky (1989) observed a similar trend but with greater  $a$  cell edge variation. Structural expansion in nickel aluminate spinel also can be observed in Figure 7B, where the  $a$  cell edge increases with an increase of O positional parameter. Figure 7C shows the tendency toward a more random spinel structure, although the variation is not as large as that observed by Mocala and Navrotsky (1989). The observed structural variations are due to displacement of the Al atom from the tetrahedral site as the spinel becomes more random at elevated temperatures.

### CONCLUSIONS

For samples quenched from temperatures below 1200 °C, all studies on the structural variation of nickel aluminate spinel are consistent. Above 1200 °C, our results are consistent with the studies of Porta and coworkers

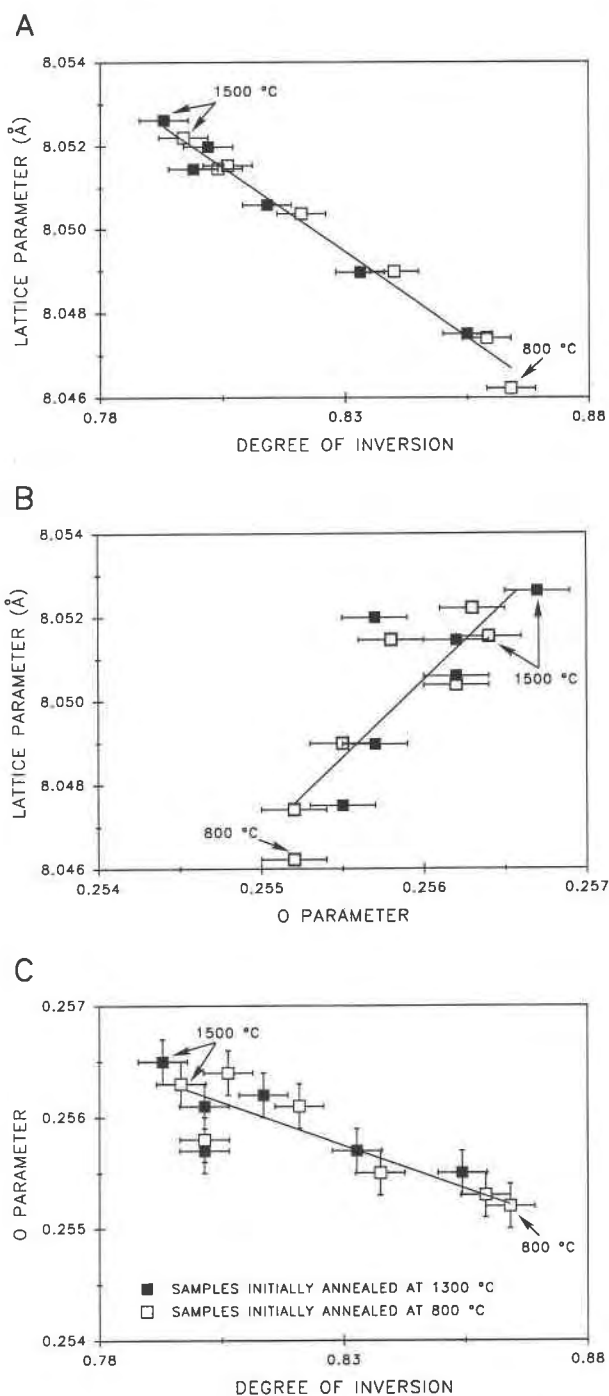


Fig. 7. The relationship between (A) the  $a$  cell edge and the degree of inversion, (B) the  $a$  cell edge and the O positional parameter, (C) the O positional parameter and the degree of inversion.

(Porta et al., 1974; Pepe et al., 1976; Porta et al., 1978). We were unable to reproduce the decrease in the  $a$  cell edge with quench temperature above 1200 °C observed by Mocala and Navrotsky (1989).

As the temperature of equilibration increases, the

structure becomes less inverse. The changes in structural parameters determined by Rietveld refinement are consistent with this change in the degree of inversion. Above 1200 °C, the plateaus in the *a* cell edge, degree of inversion, and O positional parameter are due to sample re-equilibration during the liquid-N<sub>2</sub> quench.

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