

## Cation-distribution energetics and heats of mixing in $\text{MgFe}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$ , $\text{ZnFe}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$ , and $\text{NiAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$ spinels: Study by high-temperature calorimetry

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### ABSTRACT

Enthalpies of mixing of spinels in the systems  $\text{MgFe}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$ , and  $\text{NiAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$ , determined by oxide-melt solution calorimetry at 973 K, can be described by regular solution parameters of 40.4, 20.1, and 40.1  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. These values contradict the systematics, based on cation size and cation distribution, proposed by O'Neill and Navrotsky (1984, *American Mineralogist*, 69, 733–755). Transposed-temperature-drop calorimetry (room temperature to 973 K) of samples quenched from different temperatures was used to obtain enthalpies of annealing associated with re-equilibration of cation distribution. These enthalpy data and independently measured cation-distribution data in the literature are consistent with the O'Neill and Navrotsky disordering model in which  $\Delta H = \alpha x + \beta x^2$ , where  $x$  is the degree of inversion. Values of  $\beta$  needed to fit the enthalpy data are in the range of  $-30$  to  $-35 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{NiAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$ , rather than near the average value of  $-20 \text{ kJ}\cdot\text{mol}^{-1}$  proposed for 2-3 spinels by O'Neill and Navrotsky. In the range 298–973 K, the system  $\text{MgAl}_2\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  shows a small negative excess heat capacity whereas  $\text{NiAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$  shows no excess heat capacity.

### INTRODUCTION

Spinel form a ubiquitous and compositionally variable group of compounds important in both materials science and mineralogy. Those of the 2-3 charge type  $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$ , can have cation distributions that are normal (A)[B<sub>2</sub>]<sub>4</sub>, inverse (B)[AB]<sub>4</sub>, or intermediate, with ( ) denoting tetrahedral and [ ] denoting octahedral coordination. Many pairs of 2-3 spinels form complete solid solutions that can be between two normal spinels (e.g.,  $\text{MgCr}_2\text{O}_4$ - $\text{ZnCr}_2\text{O}_4$  or  $\text{ZnCr}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$ ), between two mainly inverse spinels (e.g.,  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ ) or between a normal and an inverse spinel (e.g.,  $\text{FeCr}_2\text{O}_4$ - $\text{Fe}_3\text{O}_4$ ). Especially in the latter case, some spinel series, including  $\text{FeCr}_2\text{O}_4$ - $\text{Fe}_3\text{O}_4$ , show significantly nonlinear variation of lattice parameters with composition (Robbins et al., 1971), and a solvus may develop at low temperature (Katayama et al., 1980; O'Neill and Navrotsky, 1984). Qualitatively, such behavior can be related to two factors: (a) difference in lattice parameters or ionic sizes and (b) the variation in cation distribution across the solid-solution series. A quantitative model incorporating these two factors was proposed by O'Neill and Navrotsky (1983, 1984). It includes the size-difference term as a regular solution parameter whose magnitude depends on the difference in radii of ions being mixed. The cation distribution is modeled using interchange enthalpy terms (Navrotsky and Kleppa, 1967, 1968) that, in the present formalism, depend linearly on the degree of inversion,  $x$ . This model can predict heats, entropies, and free energies of mixing as well as asymmetric

miscibility gaps in normal-inverse spinel series at low temperatures. Most previous studies of the thermodynamics of spinel solid solutions have measured activities or free energies of mixing by gas-equilibration or electrochemical techniques. The results of such studies are in general agreement with the predictions of the model, though some discrepancies exist for specific systems (O'Neill and Navrotsky, 1984). However, the enthalpies and entropies of mixing, which would form the basis for a more stringent test of the model's quantitative predictions, are generally not sufficiently accurately established through the temperature dependence of activity data. The purpose of this work is to measure the enthalpies of mixing in several spinel solid solutions by high temperature oxide melt solution calorimetry (Navrotsky, 1977). In addition, transposed-temperature-drop (cold-to-hot) calorimetry has been used to measure the enthalpies associated with re-equilibration of cation distribution at 973 K of samples quenched from higher temperatures. The three systems chosen for study are  $\text{MgFe}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  (inverse-normal with mixing of trivalent ions),  $\text{ZnFe}_2\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$ - $\text{NiAl}_2\text{O}_4$  (normal-inverse with mixing of divalent ions). The thermochemical data are compared with values predicted from the model calculations.

### EXPERIMENTAL PROCEDURES

#### Synthesis and characterization

All spinels were synthesized from stoichiometric mixtures of dry reagent-grade oxides: MgO, NiO, ZnO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

Table 1. Enthalpies of solution of spinels in 2PbO·B<sub>2</sub>O<sub>3</sub> at 973 K

$y$	$\Delta H_{\text{sol}}$ (kJ·mol <sup>-1</sup> )
MgFe <sub>2</sub> O <sub>4</sub> -MgAl <sub>2</sub> O <sub>4</sub> , $y = X_{\text{MgAl}_2\text{O}_4}$	
0.0	80.76 ± 0.71 (7)*
0.2	69.70 ± 0.47 (5)
0.4	61.50 ± 0.67 (4)
0.6	59.95 ± 0.55 (5)
0.8	56.81 ± 0.33 (5)
1.0	59.81 ± 0.48 (5)**
ZnFe <sub>2</sub> O <sub>4</sub> -ZnAl <sub>2</sub> O <sub>4</sub> , $y = X_{\text{ZnAl}_2\text{O}_4}$	
0.0	94.60 ± 0.91 (5)
0.2	90.74 ± 0.55 (6)
0.4	89.12 ± 0.77 (6)
0.6	87.50 ± 0.66 (4)
0.8	91.79 ± 0.68 (5)
1.0	92.19 ± 1.02 (5)
NiAl <sub>2</sub> O <sub>4</sub> -ZnAl <sub>2</sub> O <sub>4</sub> , $y = X_{\text{ZnAl}_2\text{O}_4}$	
0.0	70.84 ± 0.50 (6)
0.2	70.04 ± 0.50 (5)
0.4	70.86 ± 0.76 (5)
0.6	73.24 ± 0.47 (5)
0.8	78.88 ± 0.79 (5)
1.0	92.19 ± 1.02 (5)

Note: Error is standard deviation of mean; number in ( ) is number of experiments.  
 \* Value for MgFe<sub>2</sub>O<sub>4</sub> prepared at higher  $T$  (1873 K) is 80.44 ± 1.06.  
 \*\* Value for MgAl<sub>2</sub>O<sub>4</sub> prepared at higher  $T$  (1873 K) is 61.07 ± 0.92.

Several grams of oxide mix were ground together and heated in Pt crucibles in air, generally at 1473 K, for periods of 2 to 4 d. They were checked for completeness of reaction by optical and X-ray examination. If necessary, they were subjected to additional grinding and heating cycles. All products used for calorimetry were found to be single-phase spinels by X-ray and optical examination. Selected samples, coarse-grained enough for standard mounting procedures, were checked for composition by electron-microprobe analysis. No significant deviations from nominal compositions were detected. Lattice parameters were determined using a Guinier film technique with Si as internal standard. They were consistent with reported values for the nominal compositions. Samples (100–200 mg) prepared by quenching from a given temperature (1273–1973 K) were hung in ~0.1-in.-diameter Pt foil tubes in a quench furnace, annealed for the desired time and then dropped into liquid N. The small samples reached temperatures below red heat (<~973 K) in less than 1 min.

### Calorimetry

The calorimeter and solution calorimetric techniques have been described previously (Navrotsky, 1977; Navrotsky et al., 1980). About 30 g of molten lead borate, 2PbO·B<sub>2</sub>O<sub>3</sub>, held at 973 K in a Pt crucible in the calorimeter, was the solvent. Into it was dissolved a 20–50-mg sample of spinel held in a Pt sample cup with a Pt foil bottom which, through small perforations, allowed easy access of flux. The entire assembly was equilibrated at 973 K in the calorimeter for several hours or overnight before the heat of solution was measured. This ensured thermal equilibrium and a steady baseline signal. It also usually allowed the cation distribution in the spinel to reach equilibrium at 973 K (see below). The heat effect measured in each run was 20–40 J; the molar heats of solution were 50–100 kJ·mol<sup>-1</sup>. The reproduc-

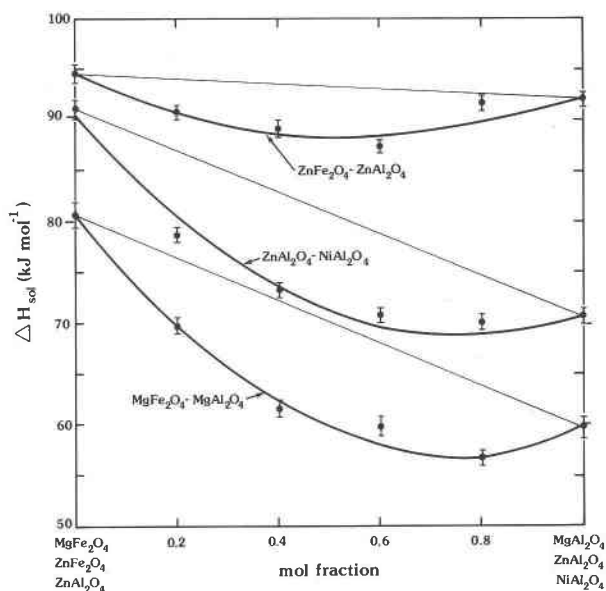


Fig. 1. Enthalpies of solution of spinel solid solutions in molten 2PbO·B<sub>2</sub>O<sub>3</sub> at 973 K. Error bars are one standard deviation of the mean. Heavy curves are given by Eqs. 1–3; light lines represent ideal mixing.

ibility (standard deviation of the mean of four to eight experiments) was ±0.5 to ±1.0 kJ·mol<sup>-1</sup>.

Samples quenched from  $T > 973$  K generally have cation distributions characteristic of those higher temperatures (see below). To find the enthalpy released when these anneal rapidly to the 973-K distribution, transposed-temperature-drop (cold-to-hot) calorimetry was performed. About 30 mg of sample quenched from high temperature was encapsulated in thin (0.0005 in.) Pt foil and dropped from room temperature into the calorimeter at 973 K (with no solvent present). The capsule was retrieved and then dropped a second and sometimes a third time. The first drop gave the heat content  $H_T - H_{298}$  of the Pt and of the spinel and any heat released when the cation distribution relaxed. Subsequent drops gave heat-content terms only. The Pt capsule contributed less than 30% of the total heat effect. The difference between the first and subsequent drops gave the enthalpy difference associated with the change in cation distribution. The heat effects measured were 20–40 J, corresponding to molar heat contents,  $H_T - H_{298}$  of 100–125 kJ·mol<sup>-1</sup>. Typical standard deviations of the mean (4–7 experiments) are ±0.3 to ±0.7 kJ·mol<sup>-1</sup>.

### ENTHALPIES OF SOLUTION AND OF MIXING

The calorimetric data for MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>-NiAl<sub>2</sub>O<sub>4</sub> are shown in Table 1 and Figure 1. The heats of solution of solid solutions deviate to less positive values than those of a mechanical mixture of endmembers, indicating positive heats of mixing for all three systems. Least-squares fits to the data give the following ( $\Delta H$  in kJ·mol<sup>-2</sup>). For MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, with  $y =$  mole fraction MgAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{\text{sol}} = 80.5(\pm 0.9) - 61.1(\pm 4.3)y + 40.4(\pm 4.1)y^2. \quad (1)$$

Table 2. Calculated and observed regular solution parameters for spinel solid solutions

System	1	2	3	4	5	6	7
MgFe <sub>2</sub> O <sub>4</sub> -MgAl <sub>2</sub> O <sub>4</sub>	8.360	8.086	1.885	1.790	0.155	37.4	40.4
ZnFe <sub>2</sub> O <sub>4</sub> -ZnAl <sub>2</sub> O <sub>4</sub>	8.416	8.086	1.885	1.790	0.155	37.4	20.1
NiAl <sub>2</sub> O <sub>4</sub> -ZnAl <sub>2</sub> O <sub>4</sub>	8.046	8.086	1.965	1.980	0.022	5.8	40.1

Note: Columns are as follows: (1)  $a_0$  = lattice parameter of first component (in ångströms). (2)  $a_0$  = lattice parameter of second component (in ångströms). (3)  $r_{1-O}$  = octahedral M-O distance of cation being mixed, first component (in ångströms); from O'Neill and Navrotsky (1983). (4)  $r_{2-O}$  = octahedral M-O distance of cation being mixed, second component (in ångströms); from O'Neill and Navrotsky (1983). (5)  $\Delta R = [(r_{1-O} - r_{2-O})/0.5(r_{1-O} + r_{2-O})]^2$ . (6)  $W_{calc} = 239.3\Delta R + 0.3$  (in kJ·mol<sup>-1</sup>), from O'Neill and Navrotsky (1983); this term accounts for size mismatch. (7)  $W_{obs}$ .

For ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>, with  $y$  = mole fraction ZnAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{sol} = 94.4(\pm 1.0) - 21.6(\pm 4.9)y + 20.1(\pm 4.7)y^2. \quad (2)$$

For NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>, with  $y$  = mole fraction ZnAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{sol} = 71.7(\pm 1.3) - 20.7(\pm 5.9)y + 40.1(\pm 8.7)y^2. \quad (3)$$

Fits using polynomials with higher terms are not warranted statistically. Equations 1-3 imply regular solution behavior with the following heats of mixing (in kJ·mol<sup>-1</sup>):

For MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{mix} = (40.4 \pm 4.1)y(1 - y). \quad (4)$$

For ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{mix} = (20.1 \pm 4.7)y(1 - y). \quad (5)$$

For NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>,

$$\Delta H_{mix} = (40.1 \pm 8.7)y(1 - y). \quad (6)$$

The striking observation is that ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub> has a heat of mixing half that of the other two systems. Indeed Navrotsky and Kleppa (1968) reported an essentially zero heat of mixing for the ZnFeAlO<sub>4</sub> ( $y = 0.5$ ) composition. These new data represent a refinement of that earlier value. No previous calorimetric data on heats of mixing in the other two systems are available.

The major source of a positive heat of mixing is lattice strain arising from cation-size mismatch. For oxide solid solutions, such effects have been quantified empirically by Davies and Navrotsky (1983) and by O'Neill and Navrotsky (1984). The former use a bulk-volume difference as a correlating parameter; the latter a bond-length mismatch. The O'Neill and Navrotsky correlation was developed specifically for spinels. Its predictions are shown in Table 2. It predicts similar heats of mixing ( $W \sim 37$  kJ) for MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> and for ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>, with a much smaller effect (because of much more similar lattice parameters and bond lengths) for NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>. The experimental data, instead, show similar values ( $W \sim 40$  kJ) for MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub> and a much smaller value ( $W \sim 20$  kJ) for ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>. The cation redistribution in solid solutions between a normal and an inverse spinel is pre-

dicted to contribute a negative term to the heat of mixing (O'Neill and Navrotsky, 1984). For the systems MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub> this would decrease the predicted heat of mixing and make it slightly asymmetric, but the correction, calculated using the site-preference energies in O'Neill and Navrotsky (1984) would be on the order of 10-20% of the observed heat of mixing. For ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>, where both endmembers are essentially normal spinels, no contribution from cation redistribution is expected. Thus, the observed heats of mixing clearly do not follow the predicted trends, and specific effects, particular to each solid solution and at present not understood, seem to dominate the heat of mixing. The O'Neill and Navrotsky (1984) regular solution parameters were determined from activity and phase-equilibrium data, rather than from experimental heats of mixing in solid solutions, since the latter are generally unavailable. Thus the correlations they give strictly represent excess free energies rather than enthalpies. It is possible that enthalpy and entropy effects partially compensate each other, leading to more regular systematics in the excess free energies than in the enthalpies and entropies of mixing taken separately.

#### HEAT CONTENTS AND ENTHALPIES OF CATION REDISTRIBUTION

The results of transposed-temperature-drop calorimetry are shown in Table 3. For all samples quenched from temperatures above 1000 K there is a significant difference between the enthalpy observed on the first and second drops from room temperature to 973 K. To interpret these differences completely, one needs information on the rates of re-equalization of cation distribution, both in the calorimeter at 973 K and during the quench from high temperature after annealing. This understanding is unfortunately quite incomplete, but several lines of evidence exist. In a study of Mg titanates, Wechsler and Navrotsky (1984) found that the pseudobrookite MgTi<sub>2</sub>O<sub>5</sub> equilibrates its lattice parameters (and hence probably its cation distribution) in days below 873 K, in less than an hour at 973 K, and in minutes or less above 1473 K. The inverse spinel Mg<sub>2</sub>TiO<sub>4</sub> was found, in the same study, to lose long-range order on octahedral sites in several minutes at 973 K. Recent NMR studies by Wood et al. (1986) on MgAl<sub>2</sub>O<sub>4</sub>

Table 3. Transposed-temperature-drop calorimetric data

Composition	$T_{\text{quench}}$ (K)	$H_{973} - H_{293}$ (kJ·mol <sup>-1</sup> )		$\Delta H_{\text{anneal}}$
		First drop	Second drop	
MgFe <sub>2</sub> O <sub>4</sub>	1473	117.9 ± 0.3 (5)	123.3 ± 0.4 (6)	-5.5 ± 0.5
	1873	107.3 ± 1.0 (4)	124.0 ± 0.6 (4)	-16.7 ± 1.2
	1873*	113.2 ± 0.3 (4)	119.8 ± 0.2 (6)	-6.6 ± 0.4
MgAl <sub>2</sub> O <sub>4</sub>	1473	106.4 ± 0.6 (3)	107.5 ± 0.2 (4)	-1.1 ± 0.7
	1873*	104.5 ± 0.6 (3)	105.2 ± 0.6 (4)	-0.7 ± 0.8
Mg(Fe <sub>0.8</sub> Al <sub>0.2</sub> ) <sub>2</sub> O <sub>4</sub>	1473	111.8 ± 0.7 (4)	117.5 ± 0.5 (4)	-5.7 ± 0.9
Mg(Fe <sub>0.6</sub> Al <sub>0.4</sub> ) <sub>2</sub> O <sub>4</sub>	1473	111.4 ± 0.5 (4)	113.3 ± 0.8 (3)	-1.9 ± 0.9
NiAl <sub>2</sub> O <sub>4</sub>	1973	103.4 ± 0.4 (6)	106.7 ± 0.4 (6)	-3.3 ± 0.6
	1773	103.3 ± 0.3 (5)	105.8 ± 0.5 (6)	-2.5 ± 0.6
	1673	100.8 ± 0.2 (6)	105.6 ± 0.5 (7)	-4.8 ± 0.5
	1673**	101.9 ± 0.7 (5)	106.6 ± 0.6 (5)	-4.7 ± 0.9
	1473	101.2 ± 0.4 (6)	105.0 ± 0.4 (6)	-3.8 ± 0.6
	1473†	102.8 ± 0.4 (6)	106.2 ± 0.4 (6)	-3.4 ± 0.6
	1273	103.4 ± 0.3 (4)	106.1 ± 0.3 (6)	-2.7 ± 0.4
Ni <sub>0.8</sub> Zn <sub>0.2</sub> Al <sub>2</sub> O <sub>4</sub>	1473	101.9 ± 0.3 (6)	105.0 ± 0.3 (4)	-3.1 ± 0.4
	1673	100.7 ± 0.3 (6)	106.2 ± 0.3 (5)	-5.5 ± 0.4
Ni <sub>0.6</sub> Zn <sub>0.4</sub> Al <sub>2</sub> O <sub>4</sub>	1473	97.8 ± 0.3 (6)	104.7 ± 0.3 (6)	-6.9 ± 0.4
	1673	97.7 ± 0.3 (4)	104.7 ± 0.3 (4)	-7.0 ± 0.4
Ni <sub>0.4</sub> Zn <sub>0.6</sub> Al <sub>2</sub> O <sub>4</sub>	1473	102.9 ± 0.2 (3)	105.3 ± 0.4 (3)	-2.6 ± 0.4
	1673	100.5 ± 0.3 (4)	106.1 ± 0.3 (4)	-5.6 ± 0.4
Ni <sub>0.2</sub> Zn <sub>0.8</sub> Al <sub>2</sub> O <sub>4</sub>	1473	101.9 ± 0.7 (4)	103.8 ± 0.4 (4)	-2.0 ± 0.8
	1673	98.5 ± 0.7 (4)	104.4 ± 0.7 (4)	-5.9 ± 1.0

Note: Error is standard deviation of mean, number in ( ) is number of experiments.

\* Sample synthesized previously by nominally similar methods but at 1873 K instead of 1473 K as for other samples. Anneal and quench temperatures as indicated.

\*\* Sample first annealed at 1273 K, then at 1673 K.

† Sample in Al<sub>2</sub>O<sub>3</sub> crucible rather than Pt crucible.

reveal that the cation distribution changes in hours to minutes at 973–1173 K and that further change above 1173 K is probably unquenchable. Solution calorimetry on NiAl<sub>2</sub>O<sub>4</sub> at 973 K quenched from various temperatures in the range 1000–1723 K yielded identical heats of solution (Navrotsky, unpub. data), suggesting that the different spinels re-equilibrated to very similar structural states during 3–12 h in the calorimeter prior to dissolution. These observations plus the general reproducibility of the transposed-temperature-drop data suggest that, in general, when a spinel sample is dropped into a calorimeter at 973 K, it re-equilibrates its cation distribution to or near the 973 K value during the course of the 30–60-min calorimetric experiment. The data also suggest that difficulty in completely quenching high-temperature cation distributions by normal sample-drop methods will be encountered above about 1473 K. The drop-calorimetric data will be interpreted with these points in mind.

## ENERGETICS OF CATION-DISTRIBUTION EQUILIBRIA

### NiAl<sub>2</sub>O<sub>4</sub>

The enthalpies of annealing (difference between first and second drop experiment) are plotted versus quench temperature in Figure 2A. In all cases, energy is released on equilibration at 973 K, presumably because of a readjustment of cation distribution. The magnitude of this energy increases with annealing temperature in the range 1273–1673 K, but, rather surprisingly, the samples quenched from 1773 and 1973 K release less energy than

those from 1673 K. These data are reproducible for several quench runs from the same temperature. The anneal from 1673 K gives similar enthalpy values for three sets of sample preparation conditions in air: NiAl<sub>2</sub>O<sub>4</sub> powder in a Pt capsule, NiAl<sub>2</sub>O<sub>4</sub> powder in a small Al<sub>2</sub>O<sub>3</sub> crucible, and a NiAl<sub>2</sub>O<sub>4</sub> pressed pellet suspended by a Pt wire. Thus, chemical effects (possible Ni loss to Pt, excess Al<sub>2</sub>O<sub>3</sub>) are probably not complicating the data. A possible explanation for the seemingly anomalous behavior above 1673 K is seen in the lattice parameters (see Fig. 2B). The sample from 1873 K appears to have a lattice parameter smaller than that of the samples from 1473 and 1673 K, although the large standard deviation on the measured lattice parameters ( $\pm 0.003$  to  $\pm 0.005$  Å) makes this conclusion speculative rather than definite. The measured enthalpies of annealing appear to vary linearly with the lattice parameters. Since  $a_0$  is expected to decrease with increasing  $x$  for NiAl<sub>2</sub>O<sub>4</sub> and for 2-3 spinels in general (Schmalzried, 1961; O'Neill and Navrotsky, 1983), the data suggest that the sample from 1873 K (and probably the one from 1773 K) has a larger value of  $x$  (is more inverse and therefore less disordered) than the sample from 1673 K. A possible reason for this may lie in the quenching kinetics; the samples quenched from higher temperature may spend a slightly longer time above  $\sim 1473$  K where cation equilibration may be quite rapid, which would lead to somewhat more cation reordering during the quench. A much more detailed study, including accurate lattice-parameter measurements and better control of quenching conditions, is needed to clarify this point. For the present discussion,

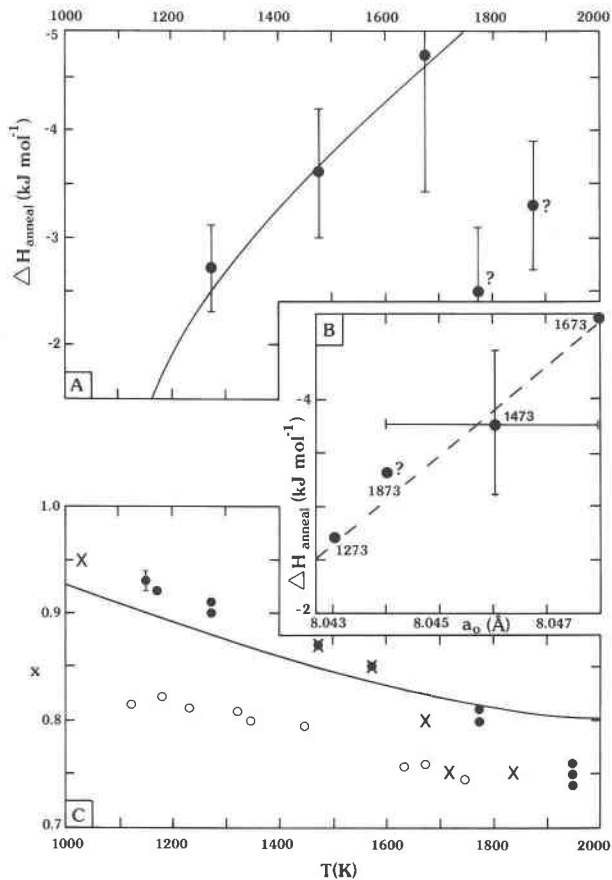


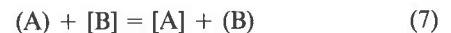
Fig. 2. (A) Enthalpy of annealing (enthalpy released during first drop) of NiAl<sub>2</sub>O<sub>4</sub> quenched from various temperatures (this study). Individual error bars in  $\Delta H_{\text{anneal}}$  shown; error in  $T$  is about size of symbol. (B) Lattice parameters of NiAl<sub>2</sub>O<sub>4</sub> quenched from various temperatures (this study). Typical error bars shown on one point. (C) Degree of inversion ( $x$ ) of NiAl<sub>2</sub>O<sub>4</sub> quenched from various temperatures. Filled circles represent data of Datta and Roy (1967); open circles, Schmalzried (1961); crosses, Cooley and Reed (1972). Typical error bars shown on one point.

the points above 1673 K (marked with question marks in Fig. 2) will be excluded from consideration in fitting models to the data.

The cation distribution of NiAl<sub>2</sub>O<sub>4</sub> as a function of quench temperature has been reported in three separate studies by X-ray diffraction methods (Schmalzried, 1961; Datta and Roy, 1967; Cooley and Reed, 1972). The results (see Fig. 2C) show considerable scatter. Schmalzried (1961), in particular, suggested that NiAl<sub>2</sub>O<sub>4</sub> does not approach a totally inverse structure at low  $T$  but begins to develop a superstructure with  $x \approx 0.81$ . This effect has not been seen in the other studies, which suggest  $x > 0.9$  for  $T < 1300$  K. Cooley and Reed's study takes into account that the oxygen parameter,  $u$ , does not have its ideal value, but their calculation does not let  $u$  and  $a_0$  vary with degree of disorder, though such variation is generally expected (Schmalzried, 1961; O'Neill and Navrotsky, 1983). Indeed, Cooley and Reed's lattice parameter,  $a_0 = 8.053$  Å,

is considerably larger than the values of 8.043 to 8.048 Å found in this work and other previous studies (Schmalzried, 1961; Datta and Roy, 1967). Datta and Roy (1967) recognized the variation of  $a_0$  and  $u$  with  $x$  but suggest that this has only a very small effect on calculated X-ray intensities. In addition, all the calculations involve assumptions about thermal parameters (Debye-Waller factors). Finally, the problems of quenching mentioned above (quench rates presumably will depend on the mass of the sample) may be a complication. Thus it is difficult to evaluate the absolute uncertainties (as opposed to statistical uncertainties of approximately  $\pm 0.01$ ) in  $x$ , or to decide which, if any, data set is the most reliable. Rather, the three data sets define a probable range of variation of  $x$  with  $T$ , with the Datta and Roy and Cooley and Reed data in good agreement and the Schmalzried data considerably different, especially at lower temperature.

One can then ask whether a cation-disordering model can be devised that is consistent with both the observed enthalpies (Fig. 2A) and the observed cation distributions (Fig. 2C). First, one can test the simple equilibrium model of Navrotsky and Kleppa (1967). For equilibrium in a spinel AB<sub>2</sub>O<sub>4</sub>,



and

$$\begin{aligned} \Delta G^0 &= -RT \ln K \\ &= -RT \ln x^2(1-x)^{-1}(2-x)^{-1} \approx \Delta H_{\text{int}}, \end{aligned} \quad (8)$$

where  $x$  is the fraction of tetrahedral sites occupied by B ions and  $\Delta H_{\text{int}}$  is an interchange energy independent of the degree of disorder.

If one takes the distribution at  $T = 1473$  K and  $x = 0.87$  as representative of the midrange of the available data of Datta and Roy (1967) and Cooley and Reed (1972), then  $\Delta G^0 \approx \Delta H_{\text{int}}^0 = -20.1$  kJ, the negative sign consistent with an inverse structural state at low temperature. The enthalpy of annealing is

$$\Delta H_{\text{anneal}} = \Delta H_{\text{int}}(x_{973} - x_T) \quad (9)$$

with  $x$  calculated from Equation 8 above. The results are shown as the first entry in Table 4. Comparing these with the experimental results (last entry in Table 4 and Figs. 2A and 2C), one sees that the calculated cation distribution does not disorder rapidly enough with increasing temperature and that the annealing enthalpies are underestimated in magnitude by a factor of two. In other words, the observed change in cation distribution and its accompanying energetics occurs more sharply (in a more cooperative fashion) with temperature than predicted by the simple equilibrium model. The choice of other values for  $\Delta H_{\text{int}}$  does not change these conclusions. Furthermore the calorimetric data, if they have systematic errors, would tend to underestimate the magnitude of the disordering enthalpy, either because the high-temperature distribution is not fully quenched (as surmised for points above 1673 K) or because re-equilibration may not occur completely at 973 K in the calorimeter during a drop exper-

iment. These effects would worsen the fit of the simple equilibrium model.

O'Neill and Navrotsky (1983) modified the simple equilibrium model to include a term, justifiable in terms of lattice energy, which makes the interchange enthalpy depend on the degree of inversion. Thus,

$$\Delta G^0 = \alpha + \beta x = -RT \ln x^2(1-x)^{-1}(2-x)^{-1}. \quad (10)$$

They further suggested (O'Neill and Navrotsky, 1984) that  $\beta$  is approximately constant for a given spinel charge type and that for 2-3 spinels,  $\beta = -20 \text{ kJ}\cdot\text{mol}^{-1}$ . In that case,  $\alpha$  retains the meaning of an interchange free energy or enthalpy. Furthermore, for spinels with transition metals containing partially filled  $d$  shells, the distribution of electrons among the split  $e_g$  and  $t_{2g}$  orbitals is different for octahedral and tetrahedral coordination, leading to a change in electronic entropy. On the basis of these considerations, O'Neill and Navrotsky gave expressions for the octahedral site-preference free energies of a series of cations. These values are a "best fit" to a large number of cation-distribution data. O'Neill and Navrotsky (1984) listed a series of such site-preference terms,  $\alpha_i$  (Table A1, which is inadvertently mistitled). For (Al) = [Al],  $\alpha_i = -36 \text{ kJ}$  and for (Ni) = [Ni],  $\alpha_i = -28 - 0.00913T$  (also in kilojoules), with the temperature-dependent term reflecting the electronic entropy (O'Neill and Navrotsky, 1984). Thus, for the exchange reaction (Ni) + [Al] = [Ni] + (Al), the free energy (in kilojoules) of the interchange reaction is the difference between  $\alpha_i$  for Ni and for Al,  $\Delta G_{\text{int}} = 8 - 0.00913T - 20x$ . Similarly,  $\Delta H_{\text{int}} = 8 - 20x$ . Using these expressions in Equation 10, the results of the second entry in Table 4 are obtained. These calculations do not fit the experimental data well; the spinel is calculated to remain far too inverse with increasing temperature (largely because of the electronic entropy term), and the magnitude of the enthalpy of annealing is underestimated by more than a factor of two.

The electronic entropy term is calculated assuming degeneracy among the  $t_{2g}$  and among the  $e_g$  orbitals. Since the octahedral and tetrahedral sites in a spinel are somewhat distorted for all but the ideal value of the oxygen positional parameter corresponding to perfect cubic close packing, this assumption is not strictly valid, and further  $d$ -orbital splittings occur. The electronic entropy term may be considerably reduced in magnitude or eliminated altogether. If so, the "best fit" site-preference terms would give a different value to the site-preference energy of  $\text{Ni}^{2+}$  and to the interchange enthalpy. One can then ask whether there are values of  $\alpha$  and  $\beta$  (treated as enthalpy terms independent of  $T$ ) consistent with the calorimetric and site-occupancy data. First, consider the case with  $\beta = -20 \text{ kJ}$ , O'Neill and Navrotsky's suggested average value for 2-3 spinels. Two cases,  $\alpha = -2$  and  $\alpha = +2 \text{ kJ}$ , are shown in Table 4; many others were tried with similar or worse results. The case with  $\alpha = -2$  slightly overestimates  $x$  at high temperature, that with  $\alpha = +2$  underestimates  $x$  at low temperature. Both cases (and all others tried,  $\alpha = -10$

Table 4. Calculated and experimental cation-distribution parameters and enthalpies of annealing for  $\text{NiAl}_2\text{O}_4$

Model	$T$ (K)	$x$	$\Delta H_{\text{anneal}}$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Simple equilibrium $\Delta H_{\text{int}} = -20.1 \text{ kJ}$	973	0.935	0.0
	1273	0.892	-0.8
	1473	0.870	-1.3
	1673	0.845	-1.8
O'Neill and Navrotsky $\alpha = 8 - 0.00913T$ , $\beta = -20 \text{ kJ}$	973	0.930	0.0
	1273	0.905	-0.6
	1473	0.895	-0.9
	1673	0.880	-1.3
O'Neill and Navrotsky $\alpha = -2, \beta = -20 \text{ kJ}$	973	0.936	0.0
	1273	0.890	-1.7
	1473	0.865	-2.7
	1673	0.841	-3.6
O'Neill and Navrotsky $\alpha = +2, \beta = -20 \text{ kJ}$	973	0.885	0.0
	1273	0.835	-1.9
	1473	0.811	-2.3
	1673	0.793	-2.8
O'Neill and Navrotsky $\alpha = +6, \beta = -26 \text{ kJ}$	973	0.914	0.0
	1273	0.861	-2.1
	1473	0.834	-3.2
	1673	0.812	-4.0
O'Neill and Navrotsky $\alpha = +6, \beta = -28 \text{ kJ}$	973	0.932	0.0
	1273	0.881	-2.3
	1473	0.852	-3.5
	1673	0.829	-4.5
O'Neill and Navrotsky $\alpha = +8, \beta = -30 \text{ kJ}$	973	0.930	0.0
	1273	0.870	-2.5
	1473	0.849	-3.7
	1673	0.826	-4.6
Experimental results	973	>0.95*	0.0
	1273	0.91	$-2.7 \pm 0.4$
	1473	0.87	$-3.6 \pm 0.6$
	1673	0.80	$-4.7 \pm 0.8$

\* Average of Datta and Roy (1967) and Cooley and Reed (1972) data.

to +10 kJ) underestimate the magnitude of the annealing enthalpy by 50–100%.

Decreasing the magnitude of  $\beta$  worsens the fit; increasing it is an improvement. Three cases are listed in Table 4 ( $\alpha = +6, \beta = -26$ ;  $\alpha = +6, \beta = -28$ ;  $\alpha = +8, \beta = -30 \text{ kJ}$ ), and the last, which shows the best agreement with the enthalpy data, is shown in Figures 2A and 2C. The uncertainties in the experimental data do not allow a meaningful regression to find statistically "best-fit" values of  $\alpha$  and  $\beta$ , but the above calculations and about 20 others tried suggest that values of  $\alpha$  in the range +6 to +9 kJ and  $\beta$  in the range -28 to -30 kJ offer reasonable fits both to the cation distributions (excluding Schmalzried's data, which do not have  $x \rightarrow 1$  or 0 at low  $T$  and hence cannot be predicted by the present approach) and to the enthalpies of annealing. Thus the overall formalism of the O'Neill and Navrotsky equations (without an electronic entropy term) appears substantiated by the data, though the most appropriate parameters are best determined by the individual data set, and  $\beta$  appears to be closer to -30 than to -20 kJ.

### $\text{MgAl}_2\text{O}_4$

Cation distributions of equilibrated quenched synthetic  $\text{MgAl}_2\text{O}_4$  samples have been determined recently by high-

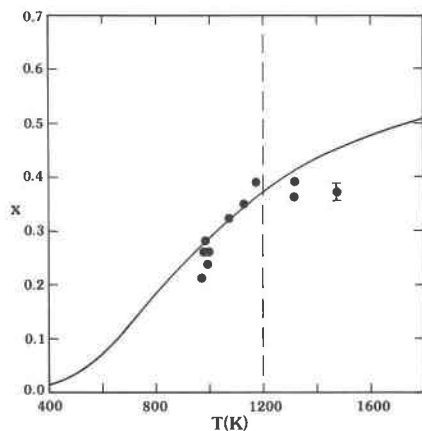


Fig. 3. Values of inversion parameter,  $x$ , as a function of  $T$  from NMR data of Wood et al. (1986). Solid curve represents values calculated using the O'Neill and Navrotsky model with  $\alpha = 31$ ,  $\beta = -30$  kJ. Vertical dashed line at 1200 K suggests that above this temperature, complete quenching does not occur. Typical error bars shown on one point.

resolution  $^{27}\text{Al}$  NMR spectroscopy (Wood et al., 1986). The results are shown in Figure 3. Equilibrium can be attained, reversed, and quenched at 973–1173 K, with  $\bar{x}$  ranging from 0.25 to 0.39. Samples quenched from higher temperatures have values of  $\bar{x}$  similar to those of samples quenched from 1173 K, suggesting that cation re-equilibration is very rapid above 1173 K. The data on enthalpy of annealing (see Table 2) support this idea; samples quenched from 1473 and 1873 K show very similar enthalpy releases (approximately  $-1$  kJ·mol $^{-1}$ ) on their first drop experiments, suggesting they represent similar structural states. The observed values of  $\bar{x}$  at 973–1173 K can be fitted by the O'Neill and Navrotsky model with  $\alpha = 31$  ( $\pm 1$ ) kJ, and  $\beta = -30$  ( $\pm 2$ ) kJ. Values of  $\beta$  near  $-20$  kJ definitely make  $\bar{x}$  vary too slowly with  $T$ , and values of  $\beta$  more negative than  $-32$  kJ make  $\bar{x}$  too large ( $>0.4$ ) at 973 K. The value of  $\alpha$  has to be larger in magnitude than  $\beta$  so that the normal spinel is the stable low-temperature configuration.

If the two samples in the drop experiments have cation distributions representative of these near 1200 K, which upon the drop re-equilibrate to values representative of 973 K, then the model would predict

$$\begin{aligned} \Delta H_{\text{anneal}} &= 0.27(31 - 0.27 \times 30) \\ &\quad - 0.375(31 - 0.375 \times 30) \\ &= -1.2 \text{ kJ.} \end{aligned} \quad (11)$$

The two experimental values are  $-1.1 \pm 0.7$  and  $-0.7 \pm 0.8$  kJ, certainly in the range predicted. As noted by Wood et al. (1986), a very small enthalpy is associated with annealing the most disordered distribution that can be quenched to produce a distribution representative of temperatures near 1000 K.

Navrotsky and Kleppa (1967) found a difference of  $\sim 4.0$  ( $\pm 0.4$ ) kJ·mol $^{-1}$  between the heat of solution of natural spinel (from alluvial gravels in Sri Lanka), and the same

samples annealed at temperatures of 1273 to 1573 K. Changes in the electron paramagnetic resonance (e.p.r.) spectrum of Cr impurities in similar natural spinels have been reported by Hafner and Laves (1961) and Schmocker and Waldner (1976). These changes have been interpreted in terms of cation disordering. The variation of  $\bar{x}$  with  $T$  is slightly different for different samples (Schmocker and Waldner, 1976). The kinetics of disordering may be sensitive to impurity content and/or grain-boundary defect, and crystal-size effects. It is conceivable, though less likely, that the thermodynamics of disordering may be strongly affected by impurities. If the difference between natural and synthetic samples is due to kinetic rather than to thermodynamic reasons, one can compare the Navrotsky and Kleppa (1967) disordering enthalpy to the predictions of the O'Neill and Navrotsky (1984) model with  $\alpha = 31$ ,  $\beta = -30$  kJ. If one assumes that the kinetics of order-disorder are far slower for the natural than for the synthetic samples, then the difference in heat of solution represents the difference in enthalpy between the initial low temperature where, over geologic time, the spinel cation distribution was "frozen in" at the temperature of  $\sim 1200$  K, above which the distribution cannot be quenched. Tight constraints cannot be placed on the first temperature. It is probably above room temperature and below 673 K, for argument's sake, a temperature of 600 K, with  $\bar{x} = 0.075$  from the model, is chosen. Then

$$\begin{aligned} \Delta H_{\text{anneal}} &= 0.375(31 - 0.375 \times 30) \\ &\quad - 0.075(31 - 0.075 \times 30) \\ &= 5.2 \text{ kJ.} \end{aligned} \quad (12)$$

This is in qualitative agreement with the experimental value of 4.0 kJ reported by Navrotsky and Kleppa (1967). Assuming a still-lower freeze-in temperature would lead to a larger value for  $\Delta H_{\text{anneal}}$ . In view of all the uncertainties regarding equilibration, such agreement can only be taken as a general indication that the O'Neill and Navrotsky model, with parameters chosen to fit the NMR data, appears to not be contradicted by the observed energetics of both natural and synthetic samples.

Wood et al. (1986) also suggested that the entropy of disordering, constrained by phase equilibria, is considerably smaller than the full configurational entropy, because of either short-range order in the spinel or a large negative nonconfigurational excess entropy of disordering. Such a term does not appear necessary for fitting the cation-distribution and enthalpy data, since the O'Neill and Navrotsky model basically assumes random mixing on each sublattice. However, the NMR and calorimetric data do not characterize the variation of  $\bar{x}$  and  $H$  with  $T$  accurately over a large enough range of temperature to completely rule out excess-entropy terms.

#### ZnAl $_2$ O $_4$

Preliminary experiments (not listed in Table 3) were done on ZnAl $_2$ O $_4$  quenched from 1473 and 1673 K and dropped into a calorimeter at 1073 K. No significant difference in enthalpy was seen in first and second drops.

$\text{ZnAl}_2\text{O}_4$  is generally assumed to be a completely normal spinel, though Cooley and Reed (1972) reported  $\bar{x} = 0.04$  and 0.06 for samples quenched from 1178 and 1470 K respectively. This would correspond to values of  $-RT \ln K$  of  $\sim 70$  kJ, in fair agreement with the 89 kJ calculated from the site-preference energies listed by O'Neill and Navrotsky (1984). In any case, a very small amount of order-disorder in  $\text{ZnAl}_2\text{O}_4$  would have only a very minor effect on its thermodynamic properties. The kinetics of any such order-disorder process are unknown.

### $\text{MgFe}_2\text{O}_4$

A sample quenched from 1473 K gave an enthalpy of annealing of  $-5.5$  kJ; one quenched from 1873 K gave a value of  $-16.7$  kJ, surprisingly large in magnitude. A differently prepared sample, also quenched from 1873 K, gave  $-6.6$  kJ (see Table 3). Values of cation-distribution parameters (Kriessman and Harrison, 1956; Mozzi and Paladino, 1963; Epstein and Frackiewicz, 1958; Tellier, 1967; Pauthenet and Bochirol, 1951) obtained from saturation magnetization measurements all agree that  $\text{MgFe}_2\text{O}_4$  has  $\bar{x} \approx 0.9$  at low  $T$  and  $\bar{x} \approx 0.7$  at high  $T$ , but the details of the variation of  $\bar{x}$  with  $T$  vary from study to study. Mozzi and Paladino (1963) suggested that the degree of nonstoichiometry may have a significant effect on the cation-distribution parameters. Such effects (slight reduction of  $\text{MgFe}_2\text{O}_4$  to a  $\text{MgFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$  solid solution at high  $T$  even in air and possible re-oxidation in the calorimeter at 973 K, as well as creation of possible point defects) may also affect the transposed-temperature-drop calorimetry. Thus the calorimetric results must be considered very tentative.

Epstein and Frackiewicz (1958) analyzed their data using a formalism similar to the O'Neill and Navrotsky model. Their parameters, in the present nomenclature, are  $\alpha = 16$  kJ,  $\beta = -35$  kJ. Using the values given by Epstein and Frackiewicz (1958), one obtains annealing enthalpies at 973 K of  $-3.9$  and  $-4.7$  kJ  $\cdot \text{mol}^{-1}$  for samples quenched from 1473 and 1873 K, respectively. Little is known about the kinetics of cation redistribution, though Epstein and Frackiewicz (1958) reported that samples quenched from 1373 K ( $\bar{x} = 0.74$ ) reach values of  $\bar{x} = 0.82$  at 873 K in  $\sim 7$  h and equilibrium values of  $\bar{x} = 0.83$  in  $\sim 12$  h. Presumably at 973 K, equilibration is substantially faster. Considering all these uncertainties, one must consider annealing enthalpies of  $-5$  to  $-7$  kJ to be reasonably consistent with the model parameters ( $\alpha = 16$ ,  $\beta = -35$  kJ), though the other enthalpy value ( $-16.7$  kJ for a sample quenched from 1873 K) is clearly anomalous. Because of oxidation-reduction and nonstoichiometry, " $\text{MgFe}_2\text{O}_4$ " is not a very suitable material for the study of cation-distribution energetics as distinct from these other possible phenomena.

### Solid solutions

Results of transposed-temperature-drop experiments of  $\text{MgAl}_2\text{O}_4\text{-MgFe}_2\text{O}_4$  solid solutions quenched from 1473 K and  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  quenched from 1473 and 1673

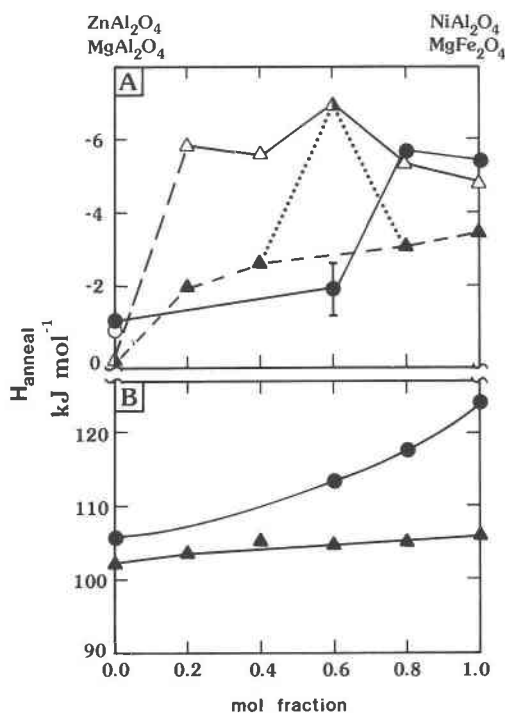


Fig. 4. (A) Enthalpy of annealing (enthalpy released during first drop) for various compositions. Filled circles represent  $\text{MgAl}_2\text{O}_4\text{-MgFe}_2\text{O}_4$  quenched from 1473 K. Filled triangles represent  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  quenched from 1473 K; open triangles represent  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$  quenched from 1673 K. Lines simply connect points. (B) Heat content,  $H_{973} - H_{298}$ , of annealed solid solutions (results of second drop). Filled circles represent  $\text{MgAl}_2\text{O}_4\text{-MgFe}_2\text{O}_4$ ; filled triangles represent  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$ . Curves are visual fits.

K are shown in Figure 4. Figure 4A shows the annealing enthalpy released on the first drop. Figure 4B shows the heat content  $H_{973} - H_{298}$  of samples equilibrated at 973 K. For  $\text{ZnAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$ , the annealing enthalpy is systematically larger in magnitude at 1673 than 1473 K. For each temperature, the annealing enthalpy stays fairly constant from  $\text{NiAl}_2\text{O}_4$  to  $\text{Zn}_{0.8}\text{Ni}_{0.2}\text{Al}_2\text{O}_4$  and then drops to values near zero at  $\text{ZnAl}_2\text{O}_4$ . For  $\text{MgFe}_2\text{O}_4\text{-MgAl}_2\text{O}_4$ , the annealing enthalpy for samples quenched from 1473 K has similar values (approximately  $-5.5$  kJ) for  $\text{MgFe}_2\text{O}_4$  and  $\text{MgFe}_{1.6}\text{Al}_{0.4}\text{O}_4$  and similar, but much smaller magnitude values (approximately  $-1$  to  $-2$  kJ) for  $\text{MgAl}_2\text{O}_4$  and  $\text{MgAl}_{0.8}\text{Fe}_{1.2}\text{O}_4$ . The statistical uncertainties in the annealing enthalpies are  $\pm 0.4$  to  $\pm 0.8$  kJ; the total uncertainties, when one considers possible compositional errors, quench-rate variations, nonstoichiometry, and other possible chemical factors, are probably on the order of  $\pm 1$  to  $\pm 1.5$  kJ. Because of these uncertainties and because very little is known about the rates of cation equilibration at intermediate compositions, one is not justified in fitting these enthalpy values by various cation-distribution models. However, the data indicate qualitatively that the re-equilibration at 973 K of cation distributions occurs



rapidly enough to have a measurable enthalpy in a drop-calorimetric experiment of 30–60 min.

The heat contents,  $H_{973} - H_{298}$ , of annealed samples (see Table 3) generally are in good agreement with literature values for the endmembers. Those values (Kelley, 1960)—124.1 kJ·mol<sup>-1</sup> for MgFe<sub>2</sub>O<sub>4</sub>, 105.6 kJ·mol<sup>-1</sup> for MgAl<sub>2</sub>O<sub>4</sub>, 108.5 kJ·mol<sup>-1</sup> for NiAl<sub>2</sub>O<sub>4</sub>, and 105.9 kJ·mol<sup>-1</sup> for ZnAl<sub>2</sub>O<sub>4</sub>—were obtained by drop calorimetry to room temperature of a sample equilibrated at 973 K. If such samples retain their 973-K cation distribution, both conventional drop calorimetry of samples from 973 K and the second transposed-temperature-drop experiments to 973 K measure only the integral of the vibrational heat capacity and not any further change in  $x$ . The agreement of measurements by these two methods supports this interpretation.

For NiAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>,  $H_{973} - H_{298}$  values are similar (103 and 107 kJ·mol<sup>-1</sup>), and intermediate compositions fall close to a straight line between the two endmembers (see Fig. 4B), indicating little or no excess vibrational heat capacity in the solid solutions. This is to be expected given the similar masses of Ni and Zn and the similar lattice parameters of NiAl<sub>2</sub>O<sub>4</sub> (8.046 Å) and ZnAl<sub>2</sub>O<sub>4</sub> (8.086 Å). On the other hand, the heat contents of MgAl<sub>2</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> differ significantly (106 and 124 kJ·mol<sup>-1</sup>, respectively). The two intermediate compositions measured (mole fraction MgFe<sub>2</sub>O<sub>4</sub> = 0.6 and 0.8) indicate a negative deviation from the straight line joining the endmembers, suggesting a negative excess heat content on the order of -3 kJ·mol<sup>-1</sup> or a negative excess heat capacity of approximately -4 J·K<sup>-1</sup>·mol<sup>-1</sup>. The difference in mass between Al and Fe and the large differences in lattice parameters (8.360 Å for the MgFe<sub>2</sub>O<sub>4</sub> and 8.086 Å for MgAl<sub>2</sub>O<sub>4</sub>) may affect the vibrational density of states enough to produce this difference. As noted above, however, the enthalpies of mixing in these two solid-solution series (MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, and NiAl<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>) are surprisingly similar ( $W = 40$  kJ·mol<sup>-1</sup>).

### CONCLUSIONS

1. The solid-solution series MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>-ZnAl<sub>2</sub>O<sub>4</sub>, and ZnAl<sub>2</sub>O<sub>4</sub>-NiAl<sub>2</sub>O<sub>4</sub> show positive enthalpies of mixing at 973 K, with regular solution parameters of 40.4, 20.1, and 40.1 kJ·mol<sup>-1</sup>. These values do not follow systematic trends predicted from differences in lattice parameters and changes in cation distributions.

2. The solid-solution series ZnAl<sub>2</sub>O<sub>4</sub>-NiAl<sub>2</sub>O<sub>4</sub> has essentially no excess heat capacity in the range 298–973 K, whereas MgAl<sub>2</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> has a negative excess heat capacity averaging -4 J·K<sup>-1</sup>·mol<sup>-1</sup> in that range.

3. Changes in cation distribution have measurable effects on the enthalpies of spinels. Because cation distributions in synthetic spinels appear to equilibrate rapidly at 973 K, these differences are measurable by transposed-temperature-drop calorimetry but not, generally, by high-temperature solution calorimetry.

4. For NiAl<sub>2</sub>O<sub>4</sub>, the measured enthalpies of annealing and observed cation distributions are consistent with the

O'Neill and Navrotsky (1983, 1984) model in which  $\Delta H (x = 0 \rightarrow x = x) = \alpha x + \beta x^2$  ( $\alpha = 8$  kJ,  $\beta = -30$  kJ) but not with the simple equilibrium model of Navrotsky and Kleppa (1967) in which  $\Delta H (x = 0 \rightarrow x = x) = \alpha x$ . Samples quenched from above 1700 K probably do not retain all their high-temperature disorder.

5. For MgAl<sub>2</sub>O<sub>4</sub>, the enthalpies of annealing and recently measured cation distributions are consistent with  $\alpha = 31$  kJ,  $\beta = -30$  kJ, but not with the simple equilibrium model. The solution calorimetric results of Navrotsky and Kleppa (1967) on natural MgAl<sub>2</sub>O<sub>4</sub> samples are also consistent with this model if one assumes the kinetics of cation redistribution are much slower for the natural samples. For synthetic MgAl<sub>2</sub>O<sub>4</sub>, disorder from above ~1200 K cannot be fully preserved on quench.

6. The results for MgFe<sub>2</sub>O<sub>4</sub> may be complicated by oxidation-reduction but are generally consistent with the O'Neill and Navrotsky model with  $\alpha = 16$  kJ,  $\beta = -35$  kJ.

7. ZnAl<sub>2</sub>O<sub>4</sub> shows no measurable enthalpy effects related to possible disordering.

8. Enthalpies related to changes in cation distribution are measurable for solid solutions as well, but their interpretation is complicated by a lack of kinetic data.

9. One concludes, therefore, that the O'Neill and Navrotsky (1983) model (with  $\beta$  closer to -30 to -35 kJ for 2-3 spinels than to the -20 kJ initially proposed) can account for both the variation in cation distribution with temperature and the enthalpy of annealing observed in transposed-temperature-drop experiments. The systematics developed using that model (O'Neill and Navrotsky, 1984) do not correctly predict the heats of mixing in 2-3 spinel solid solutions, however.

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