JOURNAL OF SOLID STATE CHEMISTRY **20**, 79–88 (1977)

Activities and Their Relation to Cation Distribution in $NiAl_2O_4$–$MgAl_2O_4$ Spinel Solid Solutions

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Received May 29, 1976; in revised form August 27, 1976

The activity of $NiAl_2O_4$ in $NiAl_2O_4$–$MgAl_2O_4$ solid solutions has been measured by using a solid oxide galvanic cell of the type, Pt, Ni + $NiAl_2O_4$ + $Al_2O_3(\alpha)$/CaO–ZrO_2/Ni + $Ni_xMg_{1-x}Al_2O_4$ + $Al_2O_3(\alpha)$. Pt, in the temperature range 750–1150°C. The activities in the spinel solid solutions show negative deviations from Raoult's law. The cation distribution in the solid solutions has been calculated using site preference energies independent of composition for Ni^{2+}, Mg^{2+}, and Al^{3+} ions obtained from crystal field theory and measured cation disorder in pure $NiAl_2O_4$ and $MgAl_2O_4$, and assuming ideal mixing of cations on the tetrahedral and octahedral positions. The calculated values correctly predict the decrease in the fraction, α, of Ni^{2+} ions on tetrahedral sites for $1 > x > 0.25$, observed by Porta *et al.* [*J. Solid State Chem.* **11**, 135 (1974)] but do not support their tentative evidence for an increase in α for $x < 0.25$. The measured excess free energy of mixing can be completely accounted for by using either the calculated or the measured cation distributions. This suggests that the Madelung energy is approximately a linear function of composition in the solid solutions. The composition of NiO–MgO solid solutions in equilibrium with $NiAl_2O_4$–$MgAl_2O_4$ solid solutions has been calculated from the results and information available in literature.

Introduction

Recently, Porta et al. (*1*) reported values for the fraction, $\alpha = (N_{Ni^{2+}})/x$, of Ni^{2+} ions on tetrahedral sites for a number of compositions of the $Ni_xMg_{(1-x)}Al_2O_4$ solid solutions, using X-ray analysis, magnetic susceptibility, and reflectance spectroscopy, and assuming that $\beta = (N_{Mg^{2+}})/(1-x) = 1$. Addition of $MgAl_2O_4$ to $NiAl_2O_4$ decreased the value of α from 0.22 to 0.1 for $x = 0.25$, indicating that the fraction of Ni^{2+} ions on the octahedral sites in the solid solution is higher than in pure $NiAl_2O_4$. This effect was linked to an increase in *Dq*, the strength of the crystal field. Below $x = 0.25$ there was tentative evidence that α may increase (*1*). Calculations based on site preference energies for cations independent of composition (see following section and Fig. 1) are in accord with the measured values for $1 > x > 0.5$, but do not support the increase in α for $x < 0.25$. The calculations also indicate that β varies nonlinearly from 0.87 for $x = 0$ to 0.97 for $x = 1$, and the inversion parameter, $\lambda = (N_{Al^{3+}})/2$, which represents the fraction of trivalent cations on the tetrahedral sites, varies almost linearly with composition.

The availability of detailed structural information and the close similarity in the cationic radii of Mg^{2+} (0.72) and Ni^{2+} (0.70) for sixfold coordination on the Shannon–Prewitt scale make the $NiAl_2O_4$–$MgAl_2O_4$ system an ideal starting point for the study of the factors that determine the thermodynamic properties of solid solutions between normal and inverse spinels. Since the lattice parameters of the solid solutions do not deviate by more than 9×10^{-4} Å (*1*) from Vegard's law, and the lattice parameters of the end members differ by only 4×10^{-2} Å, strain or mismatch contributions to the free energy of mixing

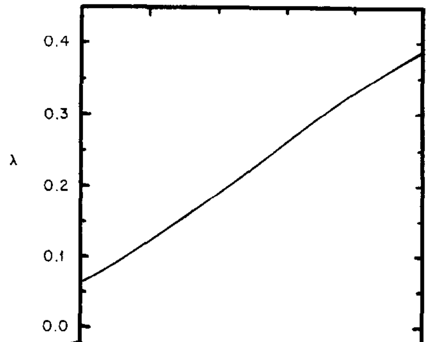

FIG. 1. Variation of α, β, and λ with composition of the spinel solid solution, $(\mathrm{Ni}_{x\alpha}\mathrm{Mg}_{(1-x)\beta}\mathrm{Al}_{2\lambda})$ $[\mathrm{Ni}_{x(1-\alpha)}$-$\mathrm{Mg}_{(1-x)(1-\beta)}\ \mathrm{Al}_{2(1-\lambda)}]\ O_4$, at 1000°C; ——, values calculated from site preference energies; $\overset{\top}{\underset{\bot}{\phi}}$, values obtained from the measurements of Porta et al. (*1*).

may be neglected. The valencies of the cations in the system are also unambiguously defined. Higher oxides of nickel are unstable below 1 atm oxygen pressure, so that in the spinel solid solutions containing $NiAl_2O_4$ in equilibrium with metallic nickel the concentration of Ni^{3+} ions may be expected to be negligibly small. It is interesting, therefore, to compare the measured activities with those calculated from cation disorder. No previous thermodynamic study of this system has been reported in literature.

The activity of $NiAl_2O_4$ in the solid solution can be obtained readily by emf measurements on the solid oxide galvanic cell,

$$\mathrm{Pt, Ni} + \mathrm{NiAl_2O_4} + \mathrm{Al_2O_3}(\alpha)/\mathrm{CaO\text{-}ZrO_2}/\mathrm{Ni} + \mathrm{Ni}_x\,\mathrm{Mg}_{(1-x)}\,\mathrm{Al_2O_4} + \mathrm{Al_2O_3}(\alpha), \mathrm{Pt}. \tag{1}$$

The electromotive force of the cell (E) in volts is related to the activity of $NiAl_2O_4$ in the solid solution by the relation,

$$RT\ln a_{\mathrm{NiAl_2O_4}} = -2FE = RT\ln\frac{a''_{\mathrm{NiO}}}{a'_{\mathrm{NiO}}} = RT\ln\left(\frac{pO_2''}{pO_2'}\right)^{1/2}, \tag{2}$$

where $F = 23{,}063$ cal V^{-1}; R is the gas constant; T is the temperature, in degrees Kelvin; a''_{NiO} and pO_2'' are the activity and oxygen partial pressure at the electrode containing the spinel solid solution; and a' and pO_2' are the corresponding values at the reference electrode containing pure $NiAl_2O_4$. The measurements have been restricted to temperatures below 1150°C, where the $(\alpha)Al_2O_3$-saturated $MgAl_2O_4$ reaches a content of 4 mole% excess Al_2O_3 (*2*).

Activities in the binary NiO–MgO solid solutions have been determined independently by three groups of researchers (*3*–*5*). The results of Hahn and Muan (*3*) (1100–1300°C) and Petot et al. (*4*) (840–1200°C) suggest that the solid solution is essentially ideal, while the measurements of Seetharaman and Abraham (*5*) indicate positive deviations from ideal behavior. Kubaschewski (*6*) has shown that the separation between liquidus and solidus temperatures for the NiO–MgO system is compatible with ideal mixing of the components. From the equilibrium constant for the reaction,

$$\mathrm{MgO} + \mathrm{NiAl_2O_4} \rightarrow \mathrm{NiO} + \mathrm{MgAl_2O_4}, \tag{3}$$

the directions of the conjugate lines between NiO–MgO solid solutions and $NiAl_2O_4$–$MgAl_2O_4$ solid solutions can be calculated, using activities in the spinel solid solution obtained in this study and information available in the literature on NiO–MgO solid solutions.

Calculation of Cation Distribution and Free Energy of Mixing

The cation distribution in $NiAl_2O_4$ has been measured by a number of investigators

(*1*, *7–10*) as a function of temperature. While there are some discrepancies in the reported temperature coefficients of the disorder parameter, the values obtained at high temperatures are in good agreement. Using a mean value of $\alpha = 0.21$ (for $x = 1$) and remembering that

$$2\lambda = 1 - x\alpha - (1 - x)\beta, \qquad (4)$$

the difference in the octahedral site preference energies of the two cations Ni^{2+} and Al^{3+} may be calculated using the relation (*11*),

$$H^{\text{oct}}_{Ni^{2+}} - H^{\text{oct}}_{Al^{3+}} = -RT\ln\frac{\lambda(1-\alpha)}{\alpha(1-\lambda)} = -2.0\ \text{kcal}, \qquad (5)$$

where $H^{\text{oct}}_{Ni^{2+}}$, etc., represent the octahedral site preference energies of the cations. This equation is based on ideal mixing of the cations on each of the cation sublattices. The difference in octahedral site preference energies is equal to the enthalpy change for the exchange reaction,

$$(Ni^{2+}) + [Al^{3+}] \rightarrow [Ni^{2+}] + (Al^{3+}) \qquad (6)$$

where ( ) denotes tetrahedral positions and [ ] denotes octahedral positions. Similarly, from the measured cation disorder in $MgAl_2O_4$ ($x = 0$), the difference in the octahedral site preference energies of Mg^{2+} and Al^{3+} ions is,

$$H^{\text{oct}}_{Mg^{2+}} - H^{\text{oct}}_{Al^{3+}} = -RT\ln\frac{\lambda(1-\beta)}{\beta(1-\lambda)} = 11.6\ \text{kcal}. \qquad (7)$$

Dunitz and Orgel (*12*) have tabulated the crystal field stabilization energies of transitional metal ions in the octahedral and tetrahedral sites. For the Ni^{2+} ion, the octahedral site preference energy is −20.6 kcal, so that Eqs. (5) and (7) suggest values for octahedral site preference of −18.6 kcal for the Al^{3+} ion and −7 kcal for the Mg^{2+} ion. The stabilization of nontransitional metal ions in the cation sites have different origins from those of transitional metal ions. Assuming orbital energy sums parallel total energies, Tossell (*13*) has given a qualitative explanation for the relative stability of the octahedral oxy-ions of Mg and Al over tetrahedral oxy-ions in terms of orbital binding energies obtained from X-ray emission spectra, optical spectra, and molecular orbital calculations. The empirical site preference energies for Mg^{2+} and Al^{3+} ions may also contain contributions from anion polarization. It has been shown earlier (*11*) that the cation distributions for a number of transitional metal aluminates calculated from site preference energies are in good agreement with X-ray and neutron diffraction measurements.

In the $NiAl_2O_4$–$MgAl_2O_4$ solid solution there are three different cations, Ni^{2+}, Mg^{2+}, and Al^{3+}, competing for the occupancy of the two types of cation positions. The values of α, β, and λ obtained by solving the three simultaneous equations [Eqs. (4), (5), and (7)] for various values of x using a digital computer are shown in Fig. 1, along with the values for α reported by Porta et al. (*1*). The calculated values of α are in good agreement with the measured values for $1 > x > 0.5$. Although there appear to be significant differences between calculated and measured values for $x < 0.25$, it should be noted that the actual concentration of Ni^{2+} ions in tetrahedral positions is small. For example, at $x = 0.1$, the measurements of Porta et al. (*1*) suggest 1.9 ionic% of Ni^{2+} on tetrahedral sites while the calculations indicate a value of 0.42 ionic %. Consequently, the values of β and λ are virtually unaffected by the discrepancy between the calculated and measured values of α.

The ideal cation mixing contribution to the total entropy of the spinel solid solution is given by

$$\Delta S^{\text{CM}} = -R\{\sum (N_j)\ln(N_j) + 2\sum [N_j]\ln[N_j]\}, \qquad (8)$$

where (N_j) denotes the ionic fraction of cation j on tetrahedral sites. For Ni^{2+} ion, $(N_{Ni^{2+}}) = x\alpha$ and $[N_{Ni^{2+}}] = x(1-\alpha)/2$, where α is the fraction of the total Ni^{2+} ions in the solid solution that occupy the tetrahedral sites. By definition, therefore,

$$\sum (N_j) = \sum [N_j] = 1.$$

This equation can also be written in terms of α, β, and λ as

$$\Delta S^{\mathrm{CM}} = -R\left[\{x\alpha \ln x\alpha + (1-x)\beta \ln (1-x)\beta + 2\lambda \ln 2\lambda\} + \left\{x(1-\alpha)\ln\frac{x(1-\alpha)}{2} + (1-x)(1-\beta)\ln\frac{(1-x)(1-\beta)}{2} + 2(1-\lambda)\ln(1-\lambda)\right\}\right]. \quad (9)$$

The entropy of mixing of the spinel solid solution may be obtained by subtracting from the cation mixing entropy of the solid solution the mole fraction weighted sum of the cation mixing entropy of the two pure component spinels;

$$\Delta S = \Delta S^{\mathrm{CM}} - x\Delta S^{\mathrm{CM}}_{\mathrm{NiAl_2O_4}} - (1-x)\Delta S^{\mathrm{CM}}_{\mathrm{MgAl_2O_4}}. \quad (10)$$

Similarly, the heat of mixing of the spinel solid solution due to cation rearrangement can be calculated from the site preference energies;

$$\Delta H = (\alpha - \alpha_{\mathrm{NiAl_2O_4}})\cdot x \cdot 20600 + (\beta - \beta_{\mathrm{MgAl_2O_4}})\cdot(1-x)\cdot 7000 + 2(\lambda - x\lambda_{\mathrm{NiAl_2O_4}} - (1-x)\lambda_{\mathrm{MgAl_2O_4}}) \cdot 18{,}600\ \mathrm{cal\cdot mole^{-1}}. \quad (11)$$

Equations (9) and (11) can be recast in terms of two independent variables rather than in terms of three separate but dependent variables α, β, and λ. The resulting equations, however, are more complex and the physical significance of the terms is obscure. The present form, it is believed, clearly displays the entropy and heat contributions arising from mixing on cation sites. The excess free energy of mixing of the spinel solid solution is then given by,

$$\Delta G^E = \Delta H - T\Delta S - RT[x \ln x + (1-x)\ln(1-x)]. \quad (12)$$

The calculated values for ΔH, ΔS, and ΔG^E, using the values for α, β, and λ at 1000°C shown in Fig. 1, are summarized in Table I. Since the cation distribution parameters (α, β, and λ) depend on temperature as well as composition, the enthalpy and entropy of mixing in this model will also show a small temperature dependence.

Experimental

Materials

Fine powders of Ni, NiO, MgO, and α-Al_2O_3 used in this study were supplied by Alfa Inorganics and were 99.99% pure. Nickel and magnesium aluminates and their solid solutions were prepared by heating pressed pellets containing appropriate amounts of the component oxides at 1300°C for 3 to 4 days in air. Although the pellets were contained in an alumina crucible, alumina saturation at 1300°C was restricted to a surface layer which was subsequently removed by polishing. The formation of the spinels was confirmed by X-ray diffraction analysis.

TABLE I

CALCULATED INTEGRAL ENTHALPY- ENTROPY, AND EXCESS FREE ENERGY OF MIXING IN THE SYSTEM $NiAl_2O_4$–$MgAl_2O_4$ AT 1000°C

x or $X_{\mathrm{NiAl_2O_4}}$	ΔH (cal·mole^{-1})	ΔS (cal·degree^{-1} mole^{-1})	ΔG^E 1000°C (cal·mole^{-1})
0.75	−391	1.115	−388
0.5	−671	1.31	−586
0.25	−698	0.96	−496
0.1	−458	0.51	−285

The composition of the spinel solid solutions obtained by chemical analysis for nickel using the dimethylglyoxime method (*1*) agreed with that calculated from the weights of the starting materials to within 2%. Calcia-stabilized zirconia tubes containing 15 mole% calcium oxide were supplied by the Zirconia Corporation of America. The argon used as the atmosphere for the emf runs was 99.99% pure and was dried and then deoxidized by passing through a column of titanium granules maintained at 900°C.

Apparatus and Procedure

The method of preparation of the electrodes was similar to that described earlier (*11*, *14*). Fine powders of the component metal and oxides were mixed in equimolar proportions, compacted into pellets, placed inside alumina crucibles, and sintered in evacuated quartz capsules at 1100°C. The apparatus and cell arrangements were identical to those used in an earlier study (*14*). The reversible emf of the cell 1 was measured using a Keithley digital voltmeter as a function of temperature in the range 750 to 1150°C for values of x equal to 0.1, 0.25, 0.4, 0.5, 0.65, and 0.75, respectively. The reversibility of the cell was checked by passing small currents through the cell in either direction. In each case, the emf was found to return to the original value. The time required to reach equilibrium (steady emf) varied from 16 to 24 hr depending on temperature. The emf was not dependent on the flow rate of the inert gas. Application of an ac ripple with an amplitude of 50 mV was found to shorten the time required for equilibration by approximately a factor of 2 (*11*). The cell emfs were monitored for 2 to 6 hr after the removal of the ac potential. Other studies (*22*) in our laboratories have shown that this "ac voltage activation technique" results in rapid attainment of equilibrium, since heats and entropies of formation of spinels so obtained are found to be in good agreement with independent calorimetric data. The phases present in the electrodes were established before and after the experiments by X-ray diffraction. These studies showed that no changes occurred in the electrodes during the experiments.

Results

The variation of the emf of cell 1 with temperature for various concentrations of $NiAl_2O_4$ in $MgAl_2O_4$ is shown in Fig. 2. For each composition of the spinel solid solution, the emf is a linear function of temperature. The equations for the temperature dependence of the emf obtained by least-mean-squares regression analysis are summarized in Table II. The activity of $NiAl_2O_4$ in the alumina-saturated spinel solid solution at 1000°C relative to alumina-saturated $NiAl_2O_4$ calculated from the emf using Eq. (2) is shown in Fig. 3. The activity of $MgAl_2O_4$ is derived using the Gibbs–Duhem relation,

$$\ln \gamma_{MgAl_2O_4} = \int_{x=0}^{x=x} -\frac{x}{(1-x)}\, d\log \gamma_{NiAl_2O_4}. \tag{13}$$

The activities of both components of the spinel solid solution exhibit moderately negative deviations from Raoult's law. The integral excess free energy of mixing of the spinel solid solution at 1000°C, given by

$$\Delta G^E = RT\left[x \ln \frac{a_{NiAl_2O_4}}{x} + (1-x)\ln \frac{a_{MgAl_2O_4}}{(1-x)}\right], \tag{14}$$

is plotted as a function of composition in Fig. 4. The minimum value for the excess free energy of mixing is −545 cal·mole^{-1}. Due to the small temperature range covered in this study, and the increasing solubility of α-Al_2O_3 in the spinel phase with increasing

TABLE II

THE TEMPERATURE DEPENDENCE OF THE emf OF CELL 1

x or $X_{NiAl_2O_4}$	E (mV)
0.75	4.5 + 0.011T
0.65	5.9 + 0.0173T
0.50	16.8 + 0.025T
0.40	17.04 + 0.039T
0.25	40.7 + 0.05T
0.10	58.2 + 0.089T

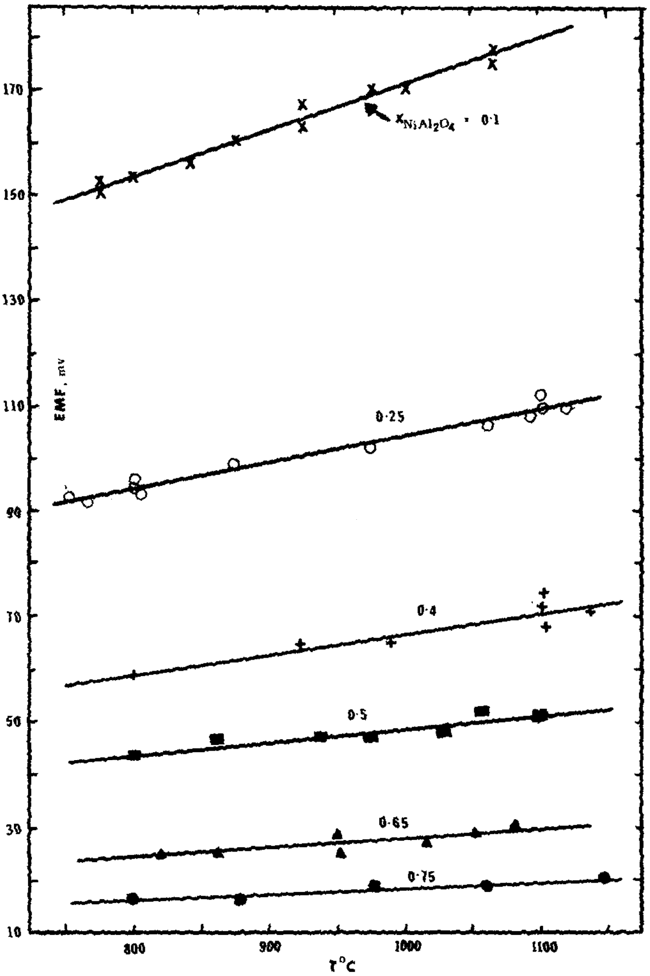

FIG. 2. The variation of the emf of cell 1 with temperature for various compositions of the spinel solid solution.

temperature, reliable values for partial and integral excess entropies and enthalpies of mixing cannot be obtained from the emf results for comparison with theoretical values.

Discussion

It can be seen from Fig. 4 that the measured excess free energy of mixing is in good accord with that calculated from the theoretical cation distribution, based on site preference energies (Fig. 1, Table II). The excess free energy can also be calculated based on the measured distribution of Ni^{2+} ions (I) between tetrahedral and octahedral positions and allowing the Mg^{2+} and Al^{3+} ions to fill the remaining positions in accordance with their site preference energies. The results of this calculation are also shown in Fig. 4. The two sets of calculated excess free energies agree almost exactly for $x > 0.5$, while for $x < 0.5$ they differ by 0 to 80 cal·mole^{-1}. While the measured excess free energy of mixing lies between the two sets of calculated values for $x < 0.4$, it indicates a greater support for the measured cation distribution than the theoretical one based on constant site preference energies. Although it has not been possible to separate the excess free energy into enthalpy and excess entropy terms with sufficient accuracy, the agreement between the measured and calculated cation

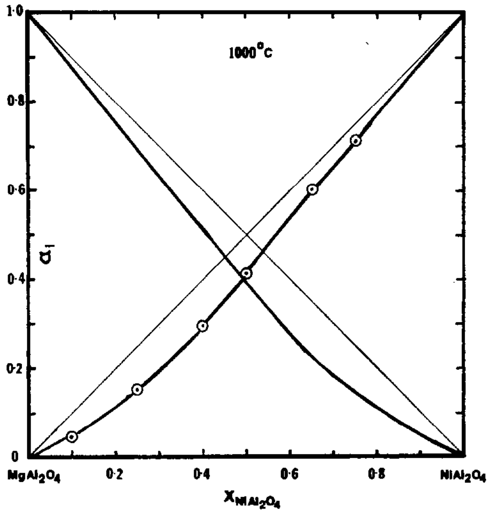

FIG. 3. Activities of components of the spinel solid solution at 1000°C.

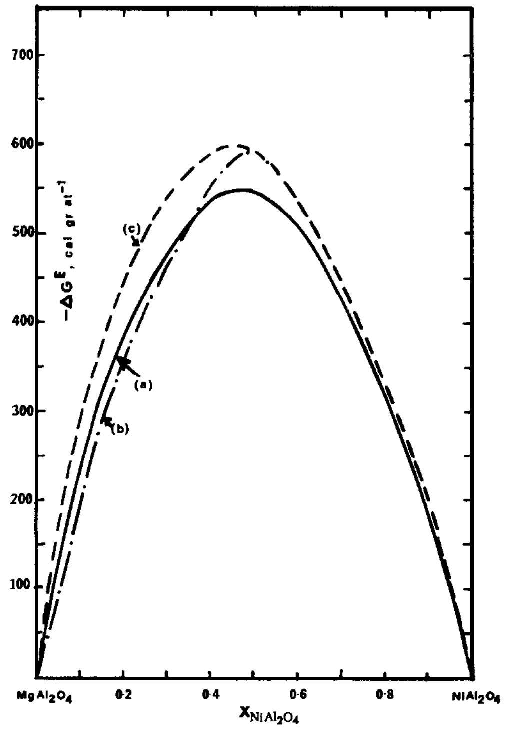

FIG. 4. The integral excess free energy of mixing of the $NiAl_2O_4$–$MgAl_2O_4$ solid solution at 1000°C (a) ——, measured values; (b) —·—, values calculated from the measured cation distribution (*1*); (c) – – –, values calculated from the theoretical cation distribution obtained from site preference energies.

distribution (Fig. 1) on the one hand, and the measured excess free energy and that calculated on the basis of cation distribution on the other hand, suggests that the Madelung contribution to the enthalpy or excess free energy of mixing is insignificant. Verwey et al. (*15*, *16*) have shown that the Madelung constant and the electrostatic stability of the spinel phase depends on the values for the oxygen parameter, u, and the average charge on the tetrahedral site, q_A. Gorter (*17*) has presented a graphical representation of the variation of the Madelung constant (M) with u and q_A. The curves giving the dependence of M on u for different values of q_A are very nearly straight lines. It can also be approximated that the slope of this line ($\Delta M/\Delta u$) varies linearly with q_A. The analytical expression for M,

$$M = 1522u - 430.8 + (172.2–488.2u)q_A + 2.61q_A^2 \tag{15}$$

is in agreement with the graphical representation of the Madelung constant (*17*). A slightly different equation has been proposed by Delorme (*18*);

$$M = 128.82 - 0.78\lambda + 10.5\lambda^2 - 1023\lambda\delta - 4970\lambda\delta^2 + 1000\delta - 8880\delta^2, \tag{16}$$

where λ is the fraction of trivalent ions on tetrahedral site and $\delta = u - 0.375$. Magnesium aluminate is characterized by a value of $u = 0.387$, while there is some discrepancy in the reported values for $NiAl_2O_4$. A value of 0.381 is given by Romeijn (*19*), while Wyckoff (*20*) suggests a value of 0.39. The accuracy in the determination of u is not very high, and there are no reported values of u for $NiAl_2O_4$–$MgAl_2O_4$ solid solutions. Since the inversion parameter λ varies linearly with composition, it is reasonable to assume that the oxygen parameter is also a linear function of composition. Then the value of u equal to 0.39 for $NiAl_2O_4$ suggested by Wyckoff (*20*) is more compatible with the linear variation of the Madelung constant with composition (or negligible Madelung contribution to the excess free energy) than the value of 0.381 (*19*) suggested by Romeijn and used by Porta et al. (*1*). It must be emphasized, however, that the quantitative calculation of lattice energies of spinels, especially when they contain transition metal ions, cannot be done with sufficient accuracy to allow the calculated enthalpy of mixing (of the order of 0.1 % of the total lattice energy) to be meaningful.

Navrotsky and Kleppa (*29*) have shown by calorimetric measurements at 700°C that the heat of mixing in the system $ZnFe_2O_4$–$ZnAl_2O_4$ at the equimolar composition is approximately zero (±250 cal). High-temperature X-ray diffraction measurements (*9*) indicate that the fraction of Zn^{2+} ion in tetrahedral sites of $ZnAl_2O_4$ is 0.96 at 905°C, the extent of cation disorder being roughly similar to that in $MgAl_2O_4$. Although $ZnFe_2O_4$ is a "normal" spinel at room temperature, the cation distribution at high temperatures may be expected to be close to that of the "random" distribution. From the point of view of the crystal field theory (*12*), the octahedral site preference energies of Zn^{2+} and Fe^{3+} ions are zero, the values being generally accurate to ±2.5 kcal. On the empirical scale of Navrotsky and Kleppa (*30*), based on measured cation distributions and calorimetric information, Fe^{3+} ion has an excess octahedral site preference over Zn^{2+} ion of 3.8(±1) kcal. A weighted mean value of 2.8 kcal for the octahedral preference of the Zn^{2+} ion, which could be inferred from these observations, corresponds to a value of 0.55(±0.15) for the fraction of Zn^{2+} on tetrahedral sites at 700°C. The $ZnFe_2O_4$–$ZnAl_2O_4$ system is therefore similar to the $NiAl_2O_4$–$MgAl_2O_4$ system in that one component of the solid solutions has the cation distribution close to that of the "normal" spinel, while the other component has a cation distribution close to that of the "random" spinel. However, in the case of the $ZnFe_2O_4$–$ZnAl_2O_4$ system, the divalent cation is common to both component spinels, while in the $NiAl_2O_4$–$MgAl_2O_4$ system the trivalent cation is common to both components of the solid solution.

The increase in α for $x < 0.25$ (Fig. 1) observed by Porta et al. (*1*) was attributed by them to the increasing predominance of the Madelung energy term over crystal and ligand field terms as x approached zero. This is in conflict with out conclusion that the Madelung contribution to the enthalpy of mixing is negligible. A small increase in α for $x < 0.25$ could arise from the increased Jahn–Teller entropy of the Ni^{2+} ion in the tetrahedral position. The $3d^8$ ion causes significant prolate Jahn–Teller distortion in tetrahedral sites, and when the spinel phase has cubic symmetry, the distortion must have random orientation. Recent measurements (*11*, *21*, *22*) on the thermodynamics of formation of 2:3 spinels indicate that the entropy of formation of cubic spinels from component oxides with rock-salt and corundum structures can be expressed as,

$$\Delta S_f = -1.75 + \Delta S^{\mathrm{CM}} + \Delta S_{\mathrm{rand}} (\pm 0.3) \quad \mathrm{cal \cdot degree^{-1}\, mole^{-1}}, \qquad (17)$$

where ΔS^{CM} is the entropy of cation mixing on the tetrahedral and octahedral sites, and $\Delta S_{\mathrm{rand}} = nR\ln 3$ (where n is the moles of the distorting cation on the interstitial site) is the entropy arising from the randomization of the orientation of orbital distortions. Because of the predominantly octahedral distribution of nickel ions in $NiAl_2O_4$ and its solid solutions with $MgAl_2O_4$, the Jahn–Teller entropy is $\leqslant 0.45$ cal·degree^{-1}mole^{-1} and its contribution to the entropy of mixing of the solid solutions is not very significant.

While the measurements of Porta et al. (*1*) and the calculations presented in this communication are in quantitative agreement regarding the decrease in the value of α between $x = 1$ and $x = 0.5$, this effect appears in our view to be a consequence of the entropy of mixing of the three cations on the two cation sublattices rather than the result of an increase in Dq for Ni^{2+} suggested by Porta et al. (*1*). It is interesting to note that the effects attributed by Porta et al. (*1*) to crystal field and Madelung energy contributions find an explanation in this study in terms of the entropy of ternary mixing and random orientation of Jahn–Teller distortions.

The directions of the conjugate lines between NiO–MgO solid solution with rock-salt structure and $NiAl_2O_4$–$MgAl_2O_4$ solid solution with spinel structure may be deduced from the results of this study. An evaluation of thermodynamic measurements on $MgAl_2O_4$ (*23–28*) suggests that the standard free energy of formation from component oxides, MgO and α-Al_2O_3, may be expressed as

$$\Delta G^\circ = -7000 - 0.7T(\pm 300)\,\text{cal}\cdot\text{mole}^{-1}. \tag{18}$$

The corresponding standard free energy of formation of $NiAl_2O_4$ is (*22*)

$$\Delta G^\circ = -1499 - 2.31T(\pm 150)\,\text{cal}\cdot\text{mole}^{-1}. \tag{19}$$

Therefore, for the exchange reaction (3), the standard free energy change at 1000°C is −3450 cal and the equilibrium constant is

$$K = 0.256 = \frac{a_{MgAl_2O_4}\cdot X_{NiO}}{a_{NiAl_2O_4}\cdot X_{MgO}} \tag{20}$$

since the NiO–MgO solid solution is ideal (*3*, *4*). For any chosen composition of the NiO–MgO solid solution, the ratio of activities in the coexisting spinel solid solution can be readily calculated. Since the range of nonstoichiometry is narrow at 1000°C, the activities of the components of the spinel solid solution obtained in the study along the α-Al_2O_3 saturated phase boundary may be assumed to be the same as along the NiO–MgO saturated boundary. The composition of the spinel solid solution in equilibrium with the rock-salt solid solution can therefore be calculated from the activity measurements reported in this communication. The results are shown in Fig. 5; the two phase mixtures being considered in equilibrium with metallic nickel, the conjugate lines are therefore paths of constant oxygen potential, which may be calculated from the standard free energy of formation of NiO and $NiAl_2O_4$ given by (*22*)

$$Ni + \tfrac{1}{2}O_2 \rightarrow NiO$$
$$\Delta G^\circ = -55{,}965 + 20.29T\,(\pm 100)\,\text{cal}, \tag{21}$$

$$Ni + \alpha - Al_2O_3 + \tfrac{1}{2}O_2 \rightarrow NiAl_2O_4$$
$$\Delta G^\circ = -57{,}464 + 17.98T(\pm 150)\,\text{cal}. \tag{22}$$

Acknowledgment

The authors are grateful to the National Research Council for financial support.

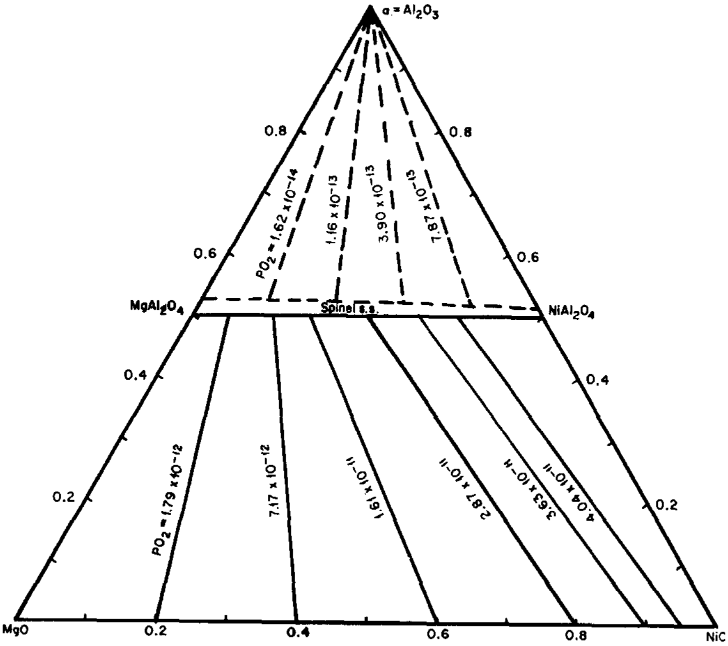

FIG. 5. Direction of conjugate lines in the system, NiO–MgO–$Al_2O_3(\alpha)$, at 1000°C. The oxygen partial pressures corresponding to three phase equilibria between metallic nickel and two oxide phases are also shown.

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