Cation distributions and thermodynamic properties of binary spinel solid solutions

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Abstract

A general model is presented to enable the calculation of the cation distribution and thermodynamic properties of any binary solid solution between oxide spinels containing 2^+, 3^+ and 4^+ cations. The model includes the effect of disordering enthalpy which depends linearly on the degree of disorder. In addition there are important contributions to the thermodynamic properties from the size mismatch of the substituting cations, which may be accounted for adequately using the simplest possible approach, that of a strictly regular solution. The regular solution parameter, W, depends on the difference in volume of the substituting cations.

The model has been tested against the extensive literature data on spinel solutions; in the great majority of cases agreement with experimental observation is good. The model may be used to explain a diverse array of phenomena associated with the cation distribution in spinel solutions, to discriminate among conflicting experimental data, to extrapolate experimental data to other temperatures and pressures, and to predict the properties of unstudied systems.

Introduction

Double oxides with the spinel structure ("spinel" *sensu lato*) are some of the most studied substances in the solid state sciences, for among their number are found some of the most important magnetic materials and refractories, many semiconductors, pigments, etc. Spinels include the main ores of some elements, and often occur as by-products of metallurgical extraction processes. They are frequently encountered accessory minerals in the earth's crust; $MgAl_2O_4$-rich spinel is the characteristic mineral of the uppermost lherzolite facies of the mantle; and magnesium-rich silicate spinel is generally considered to be the dominant component of the lower part of the upper mantle. Iron-titanium spinels are important contributors to a rock's magnetism, and these and other iron-bearing spinels can provide estimates of a rock's equilibrium oxygen fugacity through such assemblages as ilmenite-spinel (Buddington and Lindsley, 1964). The exchange equilibrium involving Fe^{2+} and Mg^{2+} in olivine and spinel has often been proposed as a geothermometer.

The widespread occurrence of spinels is in part a result of the very large number of cations of different valencies that the structure can accommodate. Many interesting properties result not only from this, but also from the

ability of many of these cations to occur in both of the very dissimilar (tetrahedrally and octahedrally coordinated) sites in the structure. In a previous paper (O'Neill and Navrotsky, 1983) we presented a thermodynamic model to describe the cation distribution in simple spinels with stoichiometry AB_2O_4, where A and B are ions of either 2^+ and 3^+ charge or of 4^+ and 2^+ charge. Most complex spinels can be thought of as solid solutions between these "end-member" types, the thermodynamic properties as well as the cation arrangement of which are often known. Thus much progress may be made toward the understanding of the complex spinels if the mixing behavior of these end-members can be evaluated. In this paper we extend the previous model of O'Neill and Navrotsky to binary solutions (that is, solutions in which one cation is common to both end-members), and then evaluate the effectiveness of the model in reproducing and explaining much of the published data.

The three factors to be considered are cation distributions, electron exchange reactions, and size mismatch. That many ions are observed to occupy both sites of the spinel structure introduces an additional degree of freedom not available to solid solutions of simpler structures. The importance of such order–disorder phenomena to the thermodynamic properties of solid solutions is illustrated, for example, in such works as Navrotsky (1971) on orthopyroxenes, Navrotsky and Loucks (1977) on pyroxenes and carbonates, and Jacob and co-workers (Jacob and Alcock, 1977; Jacob and Fitzner, 1977; Petric et al., 1981) on spinels themselves.

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Electron exchange reactions are internal reactions, such as $Co^{2+} + Fe^{3+} \rightarrow Co^{3+} + Fe^{2+}$, which only involve the exchange of an electron. These reactions may take place between ions on either sublattice or between the octahedral and tetrahedral sites. Since in many cases they introduce another degree of freedom into the solid solution not available to the end members, such reactions often result in very large negative deviations from ideality, or even compound formation, e.g. the formation of $CuFeO_2 + 2Fe_2O_3$ from $CuFe_5O_8$ below ~1273 K (Yamaguchi and Shiraishi, 1969).

The effect of size is seen in many types of solid solution, including metals, organic compounds, and, as in this case, ionic substances. The nearer the molar volumes of the end-members are to each other, the nearer the solution approaches ideal behavior. In simple ionic substances the reasons for this are relatively well understood, either in terms of strain theory (Greenwood, 1979), or of lattice energy considerations (Urosov, 1975; Catlow et al., 1977).

In this paper we show that provided some simplifying assumptions are made, all of these factors may be treated in a quantitative way, thus enabling the calculation of the cation distribution in, and hence the thermodynamic properties of, *any* binary spinel solution.

The model

Cation distribution

Both the composition and the cation arrangement of a solution may be described using a set of parameters, for example, N, the mol fraction of one of the end-members, and various distribution parameters x, y, z, etc. As a specific example consider the system $MgAl_2O_4–NiAl_2O_4$, for which the appropriate parameters are presented below:

Ion	Tet	Oct	Sum
Ni	N–x	x	N
Mg	1–N–y	y	1–N
Al	x + y	2–x–y	2
Sum	1	2	3

The configurational entropy (S_c) of the solution is given by:

$$S_c = -R \sum_i b^s N_i^s \ln N_i^s \qquad (1)$$

where N_i^s is the fraction of the species i in site s, and b^s is the number of sites of type "s" per formula unit. Any change in the distribution of the cations will also be accompanied by a free energy change, ΔG (cation distribution), which we will define relative to a standard state of zero disorder (x, y, z, etc. and hence S_c all equal to zero). The free energy change of the system on disordering is therefore:

ΔG (c.d. = cation distribution)

$$= G(x,y,z) - G(0,0,0)$$

$$= \Delta G_D - TS_c \qquad (2)$$

where ΔG_D is the nonconfigurational contribution to the free energy of disordering and S_c is the configurational entropy.

At the equilibrium cation arrangement the free energy will be at a minimum with respect to any change in the disorder parameters $(x,y,z \ldots)$ so that:

$$\left(\frac{\partial \Delta G \text{ (c.d.)}}{\partial x}\right) T,P,y,z \cdots$$

$$= \left(\frac{\partial \Delta G \text{ (c.d.)}}{\partial y}\right) T,P,x,z \cdots = \cdots = 0 \qquad (3)$$

Thus in the case of our example, the $NiAl_2O_4–MgAl_2O_4$ solid solution, equation (3) gives:

$$-RT \ln \left[\frac{x(x + y)}{(N-x)}(2-x-y)\right] = \frac{\partial \Delta G_D}{\partial x} \qquad (4)$$

and

$$-RT \ln \left[\frac{y(x + y)}{(1-N-y)}(2-x-y)\right] = \frac{\partial \Delta G_D}{\partial y} \qquad (5)$$

which, if ΔG_D is known, may be solved at various values of N to determine the equilibrium cation distribution throughout the solid solution. The free energy of mixing at each point, N, is then:

$$\Delta G \text{ mix(c.d.)} = \Delta G(\text{c.d.}, N) - N \, \Delta G(\text{c.d.}, N = 1)$$

$$- (1 - N)\Delta G(\text{c.d.}, N = 0) \qquad (6)$$

It is the nature of the ΔG_D term in equation (2) that we consider to be the crux of the problem.

Previous attempts at modelling spinel solutions (e.g., Jacob and co-workers) have adopted the simplest possible assumption, namely that ΔG_D results from the difference in the site preference enthalpies of the constituent cations in the solutions; these site preference enthalpies are taken to be constant independent of temperature and the degree of disorder (Navrotsky and Kleppa, 1967).

However, we have previously argued the following points (O'Neill and Navrotsky, 1983). The enthalpy of cation disordering (ΔH_D) is *not* independent of the cation distribution in the spinel; rather, for end-member spinels of stoichiometry AB_2O_4, ΔH_D is expected from lattice energy considerations to take the form $\alpha x + \beta x^2$, where α and β are expected to be approximately equal in magnitude, but opposite in sign, and the distribution parameter, x, is defined as the fraction of the B-type ions of the formula unit in the tetrahedral site. For certain transition metal cations a non-configurational entropy contribution to the ΔG_D term is to be expected from crystal field

electronic effects. Other non-configurational entropy contributions (e.g., vibrational) are expected to be small to negligible.

For these reasons it is felt that the previous models have oversimplified the thermodynamics of cation distribution in spinel solutions. Nevertheless, the ultimate target of this approach is to provide a practical and usable model with which the cation distribution and hence the thermodynamic properties of spinel solutions may be calculated quantitatively. Thus as a compromise between meticulous exactitude and feasibility, the following simplifying assumptions are made in the extension of the O'Neill–Navrotsky model to solid solutions. (1) The nonconfigurational free energy of disordering, ΔG_D, may be split into formal enthalpy and entropy terms, called ΔH_D and ΔS_D respectively. Both are taken to be constants independent of temperature. (2) ΔH_D takes the non-linear form found for the end-member spinels ($\Delta H_D = \alpha x + \beta x^2$). (3) β is a constant for all 2-3 spinels, and a different constant for all 4-2 spinels, see below. (4) The α terms may be split up into "site preference enthalpies" in a manner exactly analogous to that proposed by Navrotsky and Kleppa (1967) for the linear model. Thus if we denote the "site preference enthalpy" of a 2^+ cation, A, as α_A, and that of a 3^+ cation, B, as α_B, then

$$\Delta H_D \ (AB_2O_4) = (\alpha_A - \alpha_B)x + \beta x^2 \qquad (7)$$

which may alternatively be written:

$$\Delta H_D \ (AB_2O_4) = \alpha_{A-B}x + \beta x^2 \qquad (8)$$

These site preference enthalpies are constants independent of the specific spinel considered, analogous to those of the Navrotsky–Kleppa systematic approach. (5) The only contributions to ΔS_D is from the crystal field electronic effect in certain transition metal cations. These entropies, labelled σ_A, etc., are calculated from the simple crystal field model (see O'Neill and Navrotsky (1983), Table 4), and are treated in the same manner as the site preference enthalpies. Thus

$$\Delta S_D = (\sigma_A - S_B)x = \sigma_{A-B}x \qquad (9)$$

(6) In complex spinel solutions the β term depends on the overall degree of inversion, that is the total number of "wrong" ions on the tetrahedral site. Thus to return to the example of the $NiAl_2O_4$–$MgAl_2O_4$ system,

$$\Delta H_D = x[\alpha_{Ni-Al} + \beta(x + y)] + y[\alpha_{Mg-Al} + \beta(x + y)] \qquad (10)$$

Hence

$$\frac{\partial \Delta G_D}{\partial x} = \alpha_{Ni-Al} - T\sigma_{Ni-Al} + 2\beta(x + y) \qquad (11)$$

and

$$\frac{\partial \Delta G_D}{\partial y} = \alpha_{Mg-Al} - T\sigma_{Mg-Al} + 2\beta(x + y) \qquad (12)$$

which may be substituted into equations (4) and (5). The solution of these two equations is made considerably easier by the assumption of constant β.

For end member spinels individual values of α and β may in theory be determined from the experimentally measured change of equilibrium cation distribution with temperature. Unfortunately, for the range of temperatures accessible experimentally, the amount by which x changes is usually less than 0.20, and so it is seldom possible to determine the β term accurately. Nevertheless, it was found (O'Neill and Navrotsky, 1983 Table 5) that a selection of 2-3 spinels gave values of β between about -15 to -25 kJ/mol. Thus the experimental data neither support nor contradict the assumption of constant β. Indeed, the variation in β between different spinels is comparable to that found for β from different studies on the same spinel. The data in the above mentioned table suggest an average value for β of about -20 kJ/mol; this has therefore been adopted as a constant for all 2-3 spinels.

Given $\beta = -20$ kJ/mol, and taking the theoretical values for the crystal field electronic entropy, values of α_{A-B} may then be found from the data of equilibrium cation distribution versus temperature for each spinel AB_2O_4. A set of best site preference enthalpies, α_A, α_B etc., are then extracted. Further details are given in Appendix 1.

Selecting reasonable alternative values of β, e.g., in the range -15 to -25 kJ/mol, would significantly improve neither the fit to the cation distribution data in the end-members nor the subsequent application of the model to spinel solutions.

Since 4-2 spinels show negligible changes in x with temperature (being either essentially completely normal or inverse), there is no experimental evidence for the appropriate value of β for this type of spinel. However, electrostatic lattice energy calculations (see O'Neill and Navrotsky (1983), table 3) predict β to be about 3 to 5 times larger for 4-2 than for 2-3 spinels. Since electrostatic calculations generally overestimate actual energy differences, we initially adopted a value of β for 4-2 spinels equal to three times that for 2-3 spinels, that is, -60 kJ/mol. Subsequently we found that such a value produces excellent results when applied to 4-2 spinel solutions and has therefore been retained.

The most noteworthy effect of the β term, since it is approximately of equal magnitude but opposite sign to the α term, is to produce a maximum in the curve of ΔH_D against x, and thus to oppose the trend of an end-member spinel towards the entropically advantageous random cation distribution with increasing temperature. For end-member spinels this effect is of minor importance, as the increase of ΔH_D towards the random distribution is usually small anyway, and for 4-2 spinels, where α and β are expected to be large, the effect is always negligible. However, in a solid solution between a normal and an inverse spinel, the average cation distribution must at

some composition cross the random one. In such circumstances the maximum in the ΔH_D may cause a region of immiscibility between a largely normal and a largely inverse spinel, provided that β is large enough compared to the $T\Delta S$ term. This is a very significant effect, not obtainable with simpler cation distribution models.

Electronic exchange reactions

Electronic exchange reactions may be treated in the same way as cation distribution. Again, the first step is to describe the solid solution in terms of a set of compositional and ordering parameters: for an example the reader is referred to the discussion of the $FeV_2O_4-Fe_3O_4$ system below.

Again, similar to equation (6), the contribution to the free energy of mixing from any electronic exchange reactions is given by

ΔG mix (electron exchange = e.e.)

$$= \Delta G \text{ (e.e., N)} - N\Delta G \text{ (e.e., N = 1)}$$

$$- (1 - N) \Delta G \text{ (e.e., N = 0)} \qquad (13)$$

In many cases ΔG(e.e., N = 0 or 1) is zero (i.e., there is no electronic exchange reaction possible in either end-member). Any electronic exchange reaction in the solid solution will then provide an extra degree of freedom in the solution that results in a lowering of the free energy of mixing, often quite substantial (by 20–50 kJ/mol) when the electronic transfer is very favorable, as in the reaction $Co^{3+} + Mn^{2+} \rightarrow Co^{2+} + Mn^{3+}$ (Navrotsky, 1969).

Size mismatch

The effect of size mismatch is taken into account using the simplest possible model, that of a strictly regular solution. The free energy of mixing from this source is therefore given by:

$$\Delta G \text{ (size mismatch = s.m.)} = WN(1 - N) \qquad (14)$$

where W is a constant independent of temperature. The values of W have been obtained *ad hoc* from solvi and activity-composition relations for cases in which the free energies of cation distribution and electronic exchange reactions have been determined independently. A particularly pleasing feature of the model is that a very simple correlation between W and the difference in the volumes of the substituting cations emerges from such cases, see below. This correlation may then be used to estimate W's for other systems.

Summary of the model

The total free energy of mixing, ΔG mix, comprises contributions from the three effects we have considered, so that ΔG mix = ΔG mix (c.d.) + ΔG mix (e.e.) + ΔG (s.m.). The activity of an end member of the solid solution

may then be calculated by appropriate differentiation of the free energy of mixing.

For the purposes of comparing calculated, experimental, and "ideal" activity–composition relations, it is necessary to remember that statistical "ideality" of solid solutions gives $a_i = N_i$ for the case of $N(AB_2O_4) - (1 - N) (A'B_2O_4)$ solid solutions, but gives $a_i = N_i^2$ for $N(AB_2O_4) - (1 - N) (AB'_2O_4)$ solutions because two cations per formula unit are being mixed in the latter.

Finally, the lattice constants of spinel solid solutions may be calculated using the radii and the method given in O'Neill and Navrotsky (1983).

Problems and precautions in comparing the model with experimental data

Rates of cation distribution reactions

Many of the measurements of the physical properties which depend on the cation distribution are made at room temperature on spinels quenched from high temperature. Since thermodynamic calculations based on such measurements assume that the high temperature distribution is preserved during the quench, it is of utmost importance to ascertain how far this assumption is justified.

Faller and Birchenall (1970) studied $MgFe_2O_4$ by powder X-ray diffraction, both in situ at high temperature, and on quenched samples. They found good agreement for the measured cation distribution between the two sets of experiments below $\sim$1273 K, but one sample quenched from 1523 K showed a significantly anomalous distribution, the value of which was similar to that found for the 1273 K sample. The implication was that the rate of quenching from this high temperature was not fast enough to completely prevent some re-equilibration. To confirm these fast rates Walters and Wirtz (1971) showed that full cation redistribution in $MgFe_2O_4$ could occur in 10–100 hours at temperatures as low as 723 K. Kozlowski and Zarek (1973) performed an extensive study on the rates of cation redistribution in $NiAl_2O_4-NiFe_2O_4$ solid solutions, using saturation magnetization measurements. For instance, specimens of slightly oxygen-rich (cation-deficient) spinels were quenched from 1473 K, and then annealed for varying lengths of time at 873, 973 and 1073 K. At 1073 K substantial reequilibration was found even after the shortest annealing time, which was 2 minutes. Complete reequilibration occurred after 75, 3 and 0.5 hours at 873, 973, and 1073 K respectively.

Only some general conclusions are warranted from such limited data since the rates of redistribution will depend on composition, cation distribution and stoichiometry, but it seems likely that such rates are sufficiently rapid to permit effective quenching, with normal techniques, only from below a certain temperature. On the above evidence, this temperature may be as low as 1373 K. It is likely that some of the discrepancies in reported measurements of cation distributions (see O'Neill and Navrotsky, 1983) occur because of differences in the effectiveness of the methods of quenching used. Although a complication for studies of cation distributions, this rapid equilibration at $T > \sim$1373 K suggests that internal equilibrium in the spinels has probably been achieved in experiments measuring properties, such as activity–composition relations, at high temperatures.

Rates of electron exchange, especially in systems containing Fe_3O_4

The examples above involved the transfer of different ions between the octahedral and tetrahedral sites. One would expect electron exchange reactions to proceed even more rapidly. Magnetite ($Fe^{2+}Fe_2^{3+}O_4$) is a good example. Wu and Mason (1981) have shown from the temperature variation of the thermopower that there is a reproducible and reversible change in cation distribution with temperature for this substance, yet numerous studies at room temperature of the electrical and magnetic properties of magnetite show no dependence on the thermal history of the sample (provided constant stoichiometry has been maintained). Likewise, the many determinations of the lattice parameter on differently quenched samples produce the same result within experimental error. It would appear that the rate of redistribution of Fe^{2+} and Fe^{3+} (involving only the transfer of an electron) between the octahedral and tetrahedral site in magnetite proceeds too fast for the high temperature equilibrium arrangement ever to be quenched.

Magnetite also provides some information on the rates of electron exchange between ions on the octahedral site. Mössbauer spectroscopy is unable to resolve Fe^{2+} and Fe^{3+} on the octahedral site at all temperatures down to the Verwey transition near 120 K. This implies that the rate of electron hopping is faster than the precession of the iron nucleus ($\sim 10^{-7}$ sec). This raises the question whether Fe^{2+} and Fe^{3+} can be considered as distinguishable species in a thermodynamic sense. The model developed here, which assumes distinguishable Fe^{2+} and Fe^{3+}, with the site preference energies discussed in Appendix 1, reproduces the cation distributions in Fe_3O_4, as determined at high temperature by Wu and Mason (1981) to within ±0.05 in x. Thus it appears to be an adequate description, though see the discussion of excess entropy in O'Neill and Navrotsky (1983).

Non-stoichiometry

Many spinels contain transition metal cations that are known to exist in the spinel structure in more than one oxidation state. Substantial differences in the site preference of such an element in its various oxidation states can lead to very large errors in the calculated cation distribution parameters if one ignores such influences. Consider the example of $MnAl_2O_4$. The free energy of the reaction:

$$3MnAl_2O_4 + 1/2\ O_2 \rightarrow Mn_3O_4 + 3Al_2O_3 \qquad (15)$$

may be estimated from data in the literature (Chou, 1978; Tretyakov and Schmalzried, 1965; Jacob and Fitzner, 1977) (~ 55.6 kJ/mol at 1373 K). Thus at equilibrium

$$\frac{\Delta G}{RT} = \ln\left[\frac{a_{Mn_3O_4} \cdot a_{Al_2O_3}^3}{a_{MnAl_2O_4}^3}\right] = 1/2 \ln fo_2 \qquad (16)$$

If the solution of Al_2O_3 in the spinel structure (as γ-Al_2O_3) is ignored (and this would move the equilibrium further towards the right) so that $a_{Al_2O_3} = 1$, and if the spinel solid solution is presumed to behave ideally, solution of equation (16) at the oxygen fugacity of air gives an equilibrium mol fraction of Mn_3O_4 of 0.05. The high excess octahedral crystal field stabilization energy of the Mn^{3+} cation would indicate that all Mn^{3+} cations occupy octahedral sites, giving a total cation distribution of:

	Tet	Oct	Sum
Mn^{2+}	1–x	x	1
Al	x	1.9–x	1.9
Mn^{3+}	0	0.1	0.1
Sum	1	2	3

Thus if the cation distribution is determined from the fraction of Mn cations in the octahedral site, the apparent degree of inversion will be 0.1 too high. This is a substantial difference, and will lead to significant errors in the derived thermodynamic parameters. Similar large errors are to be expected if at much lower oxygen fugacities, excess MnO is incorporated in the system.

Summary of problems

The factors discussed above are possible sources of uncertainty in the data discussed below. We have confined our examples either to systems in which measurements have been made at high temperatures (solvus determinations with some attempt at showing reversals, activity–composition relations) or to samples which have been quenched rapidly from temperatures generally below 1473 K. Nevertheless, possible unsuspected errors may exist in any one particular data set. Thus the overall success of the model must generally be judged by its ability to explain a variety of recurring phenomena and a large number of data rather than by the quality of fit to any one particular data set.

Application of the model

Classification of binary spinel solutions

Many of the properties of spinel solutions are related to the cation distribution and charges in the end-members. We have restricted ourselves to 2-3 and 4-2 spinels, each of which may be considered as having a cation distribution that is either largely normal or largely inverse (i.e., tending towards these extremes as $T \rightarrow 0$ K). There are therefore ten possible combinations of these end-members, some of which may be further divided on the basis of which cation in a formula unit AB_2O_4 is substituted across the solution. We have assigned an arbitrary Roman numeral to each type as shown in Table 1.

These types fall fairly naturally into five groups: (1) no significant change in cation distribution possible across the solution, as both end-members are spinels of the same type with the ions substituting on only one sublattice: types IA, IB, VA, VIIIA, XA; (2) end-members of the same type, but substitution in both sites: type VIIIB, XB; (3) end-members have same charges, different distributions: types IIIA, IIIB, VIIA, VIIB; (4) inverse 4-2 spinel and a 2-3 spinel: IV, IX; (5) normal 4-2 spinel and a 2-3 spinel: II, VI.

Application to specific systems

We shall now discuss the application of the model to some of the literature data.

Group I (IA, IB, VA, VB, VIIIA, XA). This, the simplest group, is composed of solid solutions in which both the charge distribution and the cation arrangement

Table 1. Site preference energies in spinels, of the form $\alpha_i = \alpha'_i + \sigma_i T$ (kJ/mol).

	2-3 Normal	4-2 Normal	2-3 Inverse	4-2 Inverse
2-3 Normal	I(A,B)	II	III(A,B)	IV
4-2 Normal		V(A,B)	VI	VII(A,B)
2-3 Inverse			VII(A,B)	IX
4-2 Inverse				X(A,B)

are similar in the two end-members, which consequently precludes the possibility of any significant change in cation ordering along the solid solution. The lattice parameters generally follow Vegard's Law if the radii of the two substituting cations are similar, e.g., $CoRh_2O_4$–$ZnRh_2O_4$ (Fiorani and Viticoli, 1980), or show small and regular positive deviations where the radii are significantly different, e.g., Mg_2TiO_4–Mg_2SnO_4 (Poix, 1965).

The solution to equations (4), (5) and (6) shows that the contribution to the free energy of mixing from the cation distribution (ΔG mix (c.d.)) is equivalent to statistically ideal mixing when the ΔG_D term is the same for both end-members (i.e., if both members have the same cation distribution). Experimentally measured activity–composition relations confirm this for the cases where the size mismatch of the substituting cations is small: thus the IA solutions.$CoAl_2O_4$–$MgAl_2O_4$ (Rosén and Muan, 1966) and $FeAl_2O_4$–$MgAl_2O_4$ (Engi, 1978) have $a = N$ (one site mixing), while for $CoCr_2O_4$–$MnCr_2O_4$ (Jacob and Fitzner, 1977) a slight but regular positive deviation is observed as would be expected for the significant size mismatch between the Co^{2+} and Mn^{2+} ions.

For both the IA and IB classes of spinel solutions, any difference in the cation distribution of the two end-members is expected (from equation (4) to (6)) to lead to small negative deviations from ideality in ΔG mix (c.d.). This is illustrated in Figure 1 where we have calculated at
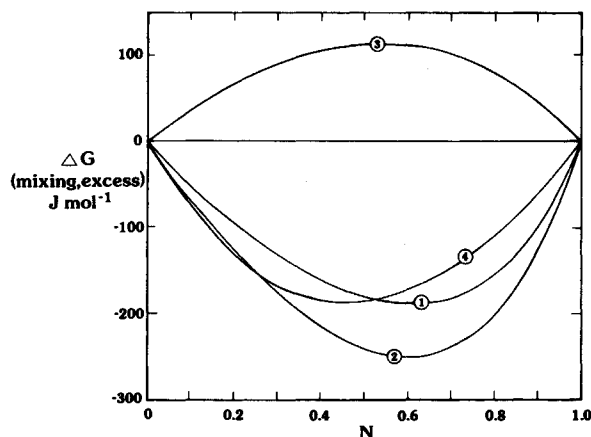

Fig. 1. Calculated excess free energy of mixing curves at 1373 K for some group 1 solutions—(1) $CoAl_2O_4$–$MnAl_2O_4$: $\alpha_{Co-Al} = 56$, $\alpha_{Mn-Al} = 81$, $\beta = 20$ (kJ/mol); (2) $CoAl_2O_4$–$MnAl_2O_4$: $\alpha_{Co-Al} = 50$, $\alpha_{Mn-Al} = 75$, $\beta = 0$; (3) $NiFe_2O_4$–Fe_3O_4: $\alpha_{Ni-Fe^{3+}} = -28 + 0.009T$; $\alpha_{Fe^{2+}-Fe^{3+}} = 16 + 0.0057T$, $\beta = -20$; (4) $NiFe_2O_4$–Fe_3O_4: $\alpha_{Ni-Fe^{3+}} = -60$, $\alpha_{Fe^{2+}-Fe^{3+}} = -10$, $\beta = 0$.

1373 K ΔG mix (c.d.) curves for the $CoAl_2O_4$–$MnAl_2O_4$ system, using both the model proposed above and, for comparison, the simple (linear) model as used by Jacob et al. (1977) ($\beta = 0$, the values of α correspondingly adjusted to describe the end-member cation distributions).

The actual measurements of activity–composition relations in $CoAl_2O_4$–$MnAl_2O_4$ (Jacob and Fitzner, 1977) do indeed show negative departures from ideality, whereas, as mentioned above, the analogous system $CoCr_2O_4$–$MnCr_2O_4$, in which, because of the very high octahedral site preference of Cr^{3+} both end-members have almost the perfectly normal distribution, shows small positive deviations. However, the extent of this departure is much more negative ($G^{ex} = -1.87$ kJ/mol at N = 0.5) than that predicted by either model; this discrepancy is further enhanced if the positive energy of mixing expected from the size mismatch of Co^{2+} and Mn^{2+} is included. We, however, add a caveat: the activity–composition relations in this study were determined from the composition of the spinel solid solution co-existing with CoO–MnO solid solutions, i.e., with excess MnO. Therefore there will be a significant amount of Mn_3O_4 formed in the spinel: this may be estimated from the reaction:

$$6MnO + O_2 \rightarrow 2Mn_3O_4 \qquad (17)$$

which gives

$$2 \ln a_{Mn_3O_4} = -\frac{\Delta G(17)}{RT} + \ln fo_2 + 6 \ln a_{MnO} \qquad (18)$$

Chou (1978) gives -11.678 for $\Delta G(17)/RT$ at 1373 K; therefore, at the oxygen partial pressure of the experiments (10^{-10} atm), $a_{Mn_3O_4}$ may be calculated to be 0.0034 in equilibrium with pure MnO which, assuming ideal two-site mixing ($a = N^2$), would yield a mol fraction of Mn^{3+} of 0.06 in the nomial $MnAl_2O_4$ end-member. This obviously diminishes across the solid solution but still remains appreciable. Since the compositions of the spinel solid solutions were determined by mass balance, such amounts of Mn^{3+} in the spinel would have a large effect on the calculated activity–composition relations.

The geologically important type IB solution $FeAl_2O_4$–$FeCr_2O_4$ is expected to show similar small negative deviations from ideality due to the cation distribution effect: this, however, is overwhelmed by the large effect from the size mismatch of the Al and Cr^{3+} cations. The experimental activity–composition data may be fitted to the model with $W = 28.0$ kJ/mol.

Naidu (1978) has measured the activities of two type IB solutions containing Co_3O_4, which is expected to be a completely normal spinel (Knop et al., 1968). Thus in Co_3O_4–$CoCr_2O_4$ there should be no contribution to the activities from the cation distribution, and indeed the experimental data show a small and symmetrical positive deviation from ideality as expected from the size mismatch of the Co^{3+} and Cr^{3+} cations ($W = 4.2$ kJ/mol). However, in Co_3O_4–$CoAl_2O_4$ the positive deviation is

observed to be both larger and with significant asymmetry, whereas we would expect it to be slightly smaller from the cation distribution effect and the close similarity of the Co^{3+} and Al^{3+} radii. This anomaly will be discussed more fully below.

Where the difference in size is very large, a solvus may develop in the system, as in $MnFe_2O_4$–$MnAl_2O_4$ (Ishida et al., 1977). It is therefore somewhat surprising to find that the heat of mixing for the mid-point compositions in the analogous $ZnFe_2O_4$–$ZnAl_2O_4$ system, as determined from high temperature solution calorimetry by Navrotsky and Kleppa (1968) is close to zero.

Thermodynamic studies have been undertaken on three type VIIIA solutions. Katayama et al., (1979) measured the activity of Fe_3O_4 in $NiFe_2O_4$–Fe_3O_4, using the reaction: $2Fe_3O_4 + 1/2 O_2 \rightarrow 3Fe_2O_3$. The results show nearly ideal behavior, except at the $NiFe_2O_4$-rich end, where significant positive deviations occur. This anomaly may be related to non-stoichiometry towards Fe_2O_3 along the series. Trinel-duFour et al. (1978) derived the activities of $NiFe_2O_4$–$MgFe_2O_4$ from the compositions of coexisting NiO–MgO solutions, assuming that the latter behaved ideally. Other work shows that NiO–MgO probably should be treated as having negative deviations from ideality (Davies and Navrotsky, 1981; Shirane, 1982; Evans and Muan, 1971a). If this is taken into account the positive deviations from ideality in the spinel solution found by Trinel-duFour et al. would be lessened.

$NiFe_2O_4$ is a nearly completely inverse spinel, whereas both $MgFe_2O_4$ and Fe_3O_4 show some randomization. The calculated excess free energy curve for the system $NiFe_2O_4$–Fe_3O_4 is shown in Figure 1, where it is compared for a similar curve generated from an appropriate set of site preference energies without the non-linear β term.

The system $CuFe_2O_4$–Fe_3O_4 (Katayama et al. 1980; Jacob et al. 1977) shows very large negative deviations from ideality. This is due to the electronic reaction: $Cu^{2+} + Fe^{2+} \rightarrow Cu^+ + Fe^{3+}$ which in this case may occur in both sites. As written, the free energy of the reaction is probably negative, since the midpoint composition in the solution decomposes to $CuFeO_2 + 2Fe_2O_3$ at about 1273 K (Yamaguchi and Shiraishi, 1969). Thus the solution is stabilized relative to the end-members both by the configurational entropy and the non-configurational free energy advantage of the electronic reaction. Since the magnitude of this free energy change is likely to be different for each site, we have not attempted a calculation.

Group 2 (VIIIB, XB). The difference between this group and the one previously discussed is that here the substitution occurs on both cation sites. Taking $MgGa_2O_4$–$MgFe_2O_4$ as the type example, the distribution parameters may be defined as:

	Tet	Oct	Sum
Mg	1−x−y	x+y	1
Fe³⁺	x	2N−x	2N
Ga	y	2−2N−y	2−2N
Sum	1	2	3

This gives the cation distribution equations:

$$-RT \ln \left[\frac{x(x + y)}{(1 - x - y)(2N - x)} \right] = \alpha_{Mg-Fe} + 2\beta(x + y)$$

(19)

and

$$-RT \ln \left[\frac{y(x + y)}{(1 - x - y)(2 - 2N - y)} \right] = \alpha_{Mg-Ga} + 2\beta(x + y)$$

(20)

Subtracting (20) from (19) gives:

$$-RT \ln \left[\frac{x(1 - 2N - y)}{y(2N - x)} \right] = \alpha_{Ga-Fe} \ 3+$$

(21)

Therefore the cation distributions are not strongly dependent on β, because this parameter affects only the distribution of the common ion.

Equation (21) is in excellent agreement with the cation distribution data on the system $MgGa_2O_4$–$MgFe_2O_4$ (Tellier, 1967), (taking α_{Ga-Fe} as 4.0 kJ/mol) in the range $N_{MgFe_2O_4} = 1$ to 0.7. The apparent discrepancy for degrees of substitution greater than this may be due to a breakdown of the Neél model for the saturation magnetization (from which the cation distributions are derived) rather than of the thermodynamic model.

Activities in systems of type VIIIB are predicted to show negative deviations from ideality, which may become very large if the difference in the site preference energies of the substituting cations is large. There will be some asymmetry, depending on the behavior of the common ion. We have not been able to find any examples of activity–composition relations of this type in the literature.

For type XB solutions the common ion (e.g., Ti,Sn) is confined to the octahedral site, and hence $x + y = 1$. There is therefore some advantage in redefining the distribution parameters x and y in terms of a single parameter, z, such that $x = N - z$ and $y = 1 + N + z$. This gives the arrangement, with the system Co_2TiO_4–Zn_2TiO_4 as an example:

	Tet	Oct	Sum
Ti	0	1	1
Co	N−z	N+z	2N
Zn	1−N+z	1−N−z	2−2N
Sum	1	2	3

which emphasizes the (theoretically) symmetric nature of these types of solutions. The cation distribution equation is:

$$-RT \ln \left[\frac{(N + z)(1 - N + z)}{(N - z)(1 - N - z)} \right] = \alpha_{Co-Zn}$$

(22)

Navrotsky and Kleppa (1968) have determined the excess enthalpy of mixing for the mid-point composition in this system as -9.6 kJ/mol. If it is assumed that this enthalpy is solely due to cation distribution, as seems very reasonable for ions of such similar size, then

$$z\alpha_{Co-Zn} = -9.6 \text{ kJ/mol} \qquad (23)$$

equations (22) and (23) may be solved simultaneously at $N = 0.5$. If we assume that the ordering in the spinel corresponds to the temperature at which the sample was prepared (1473 K), then α_{Co-Zn} is -32.8 kJ/mol and z = 0.292.

These values may then be used to calculate the cation distribution and hence the lattice constants throughout the solution. Calculated lattice constants for a distribution corresponding to 1323 K are compared to Figure 2 with the experimental data of Navrotsky and Muan (1970). Agreement is excellent, and the form of the lattice constant curve clearly reflects the cation distribution. Similar trends are shown by the $Mg_2TiO_4-Zn_2TiO_4$, $Co_2SnO_4-Zn_2SnO_4$ and $Mg_2SnO_4-Zn_2SnO_4$ systems (von Beckh et al., 1981; Poix, 1965).

The very large value of α_{Co-Zn} should lead to massive negative deviations from ideality. In contradiction, Navrotsky and Muan (1970) found exactly the opposite— massive positive deviations. However, negative deviations in excellent agreement with the prediction were found for $Co_2TiO_4-Mn_2TiO_4$ (Evans and Muan, 1971b). $Co_2TiO_4-Mg_2TiO_4$ is expected to be nearly ideal, and

indeed shows only very minor positive deviations, but with some slight asymmetry (Brezny and Muan, 1971). Both these latter systems may, therefore, be taken to agree with the model within experimental uncertainty. $Ni_2TiO_4-Mg_2TiO_4$ (Evans and Muan, 1971a) shows only slight negative deviations, but the data are limited. $Ni_2TiO_4-Zn_2TiO_4$ (Navrotsky and Muan, 1970) shows a complex sinusoidal deviation, where again large negative deviations are expected. The calculated lattice constants for this system do largely agree with those measured (see Fig. 2), even though the expected kink is not apparent from the data. Note that an experimental complication in the nickel titanate systems arises because the end-member Ni_2TiO_4 is not stable, but breaks down to $NiTiO_3$ plus NiO.

Group 3 (IIIA, IIIB, VIIA, VIIB). This group is composed of solutions in which the end-members have similarly charged cations, but with very different distributions. Consequently the cation distribution across the solution has more opportunity to vary, thus providing a sensitive test for the model. By far the largest number of studied examples come from the 2-3 spinel systems (i.e., IIIA and IIIB), and these will be discussed first.

Lattice constants for these solutions often show large and complex deviations from Vegard's Law. One of the most spectacular is that found in the system $FeCr_2O_4-Fe_3O_4$ (Fig. 3), which has been documented numerous times (e.g., Robbins et al., 1971). All investigations show the same trend, minor differences probably being due to varying degrees of nonstoichiometry. The lattice constants clearly reflect the change in the site preference energy of Fe^{3+} across the solution. Calculated curves are also shown in Figure 3, corresponding to the two extremes of quench rates which are equilibrium at room temperature and at preparation temperature.

The distribution parameters for this system may be written in the same way as for $MgFe_2O_4-MgGa_2O_4$ (see above), producing two equations similar to equations (19) and (20). The significant difference between these two systems is that in $Fe_3O_4-FeCr_2O_4$ the Cr^{3+}, because of its very large octahedral CFSE, remains essentially entirely on the octahedral site, allowing us to approximate the system with only one distribution parameter:

	Tet	Oct	Sum
Fe^{2+}	1–x	x	1
Fe^{3+}	x	2–2N–x	2–2N
Cr	0	2N	2N
Sum	1	2	3

so that:

$$-RT \ln \left[\frac{x^2}{(1-x)(2-2N-x)} \right] = \alpha_{Fe^{2+}-Fe^{3+}} + 2\beta x \qquad (24)$$

The maximum value of x is therefore 1 for n < 0.5, and $1 - N$ for N > 0.5. Thus as the composition of the system approaches the chromium end-member, the contribution
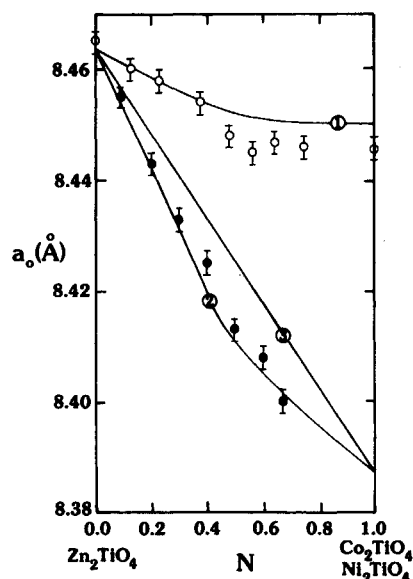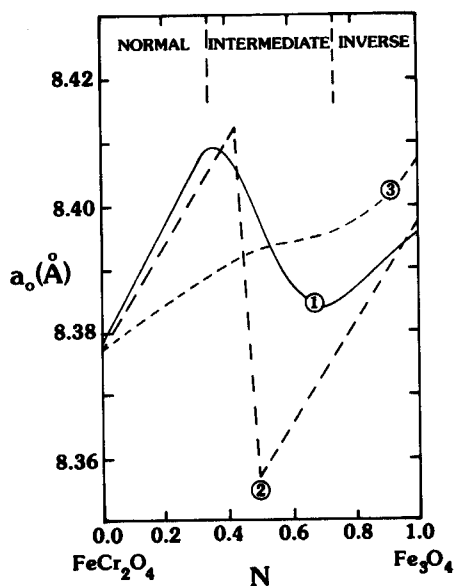

Fig. 2. Calculated lattice constant curves at 1323 K—(1) $Co_2TiO_4-Zn_2TiO_4$: $\alpha_{Co-Zn} = 33$ kJ/mol; (2) $Ni_2TiO_4-Zn_2TiO_4$: $\alpha_{Ni-Zn} = 81-0.009T$; (3) $Ni_2TiO_4-Zn_2TiO_4$: $\alpha_{Ni-Zn} = 0$ (random distribution). Points show literature data (Navrotsky and Muan, 1970; Beckh et al., 1981; Poix, 1965).

Fig. 3. Lattice constant curves for $FeCr_2O_4$–Fe_3O_4—(1) Experimental data (Robbins et al., 1971); (2) Calculated for equilibrium cation distribution at 300 K; (3) Calculated for equilibrium cation distribution at 1000 K.

Also shown in Figure 3 is the calculated lattice constant curve for Fe_3O_4–$FeCr_2O_4$ corresponding to an equilibrium temperature of 1000 K. Molar volume relations in this and other spinel systems are an important thermodynamic quality at high pressures, and are therefore of some practical significance to petrologists. To calculate excess volumes of mixing at high T and P from the measured lattice constants at room temperature would obviously be inappropriate. Note also that the large increase in the calculated lattice constant for Fe_3O_4 with temperature is reflected in the anomalously high coefficient of thermal expansion for this spinel (Skinner, 1966).

Calculated free energy of mixing curves for an idealized $FeCr_2O_4$–Fe_3O_4 system (no excess enthalpy from the size mismatch factor) are shown in Figure 5. At high temperatures these curves show negative deviations from ideality, but at lower temperatures they become positive and show the development of an asymmetric solvus between regions with a normal and an inverse distribution. The exact consolute temperature of the solvus and the degree of asymmetry are rather sensitive to the values of α and β. A model with $\beta = 0$ produces very large negative deviations and no solvus at any temperature. The effect of a small amount of disorder in the third cation (e.g., Al in Fe_3O_4–$FeAl_2O_4$) is to make the free energy of mixing slightly more negative.

These calculated curves may be compared to the experimentally determined activity–composition relations in three Fe_3O_4-containing systems of type IIIB. For $FeCr_2O_2$–Fe_3O_4 the most careful study is that of Katayama et al. (1977), who determined the activity of magnetite at 1500 K from reduction equilibria to wüstite at $N_{FeCr_2O_4} < 0.8$ and to iron at $N_{FeCr_2O_4} > 0.8$, taking into account both the oxygen non-stoichiometry and the chromium content of the wüstite phase. These measurements,

of the β term to the overall site preference energy of Fe^{3+} must diminish, and, as is observed, the site occupancy of Fe^{3+} changes from a preference for the tetrahedral site to one for the octahedral.

The effects of this change of site preference on the lattice parameters are enhanced in Fe_3O_4-containing systems since the cation distribution reaction is an electronic one. Thus, at least for Fe_3O_4-rich compositions, the cation distribution may reflect equilibrium at or near room temperature. However, the solution of equation (24) at $T = 300$ K fails to reproduce the intermediate region of random distribution seen in Figure 3 (and also in magnetic and Mössbauer studies (Robbins et al., 1971) the calculation showing instead a sudden transition (at about N = 0.55) between regions of normal and inverse distributions. Such an intermediate region is produced in the calculation if either a lower value for β is used, or if it is assumed that the cation distribution may be frozen in at somewhat higher temperatures.

The lattice constants in Fe_3O_4–FeV_2O_4 show an analogous trend (see Fig. 4). In Fe_3O_4–$FeAl_2O_4$ (Turnock and Eugster, 1962) the effect is not so obvious because there is a larger difference in the lattice constants of the two end-members. Furthermore, the disordering of Al needs to be included. An interesting consequence of the non-linear enthalpy model is that the calculated fraction of Al in the tetrahedral site remains appreciable right across the solution, as has been qualitatively confirmed by the Mössbauer measurements of Dehe et al. (1975).

At higher temperatures the cation distribution is expected to become more random throughout the solution.
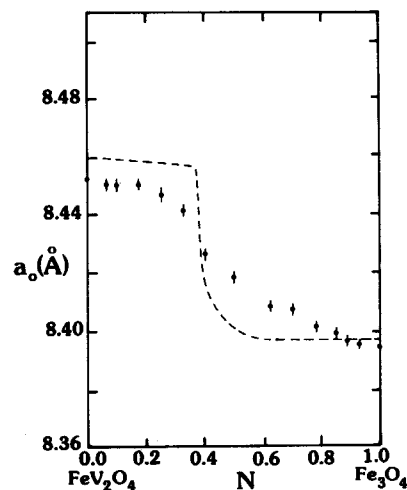

Fig. 4. Lattice constant curve for FeV_2O_4–Fe_3O_4 calculated for equilibrium cation distribution at 380 K. Experimental data from Wakihara et al. (1971).
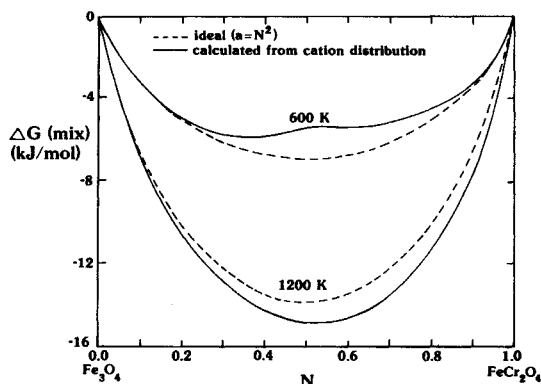
Fig. 5. Calculated free energy of mixing curves for $FeCr_2O_4$–Fe_3O_4 without any excess heat of mixing from the size mismatch of Fe^{3+} and Cr. At high temperatures the deviation from ideality (two site mixing) is negative; at low temperatures this deviation becomes positive, and a solvus develops between regions of normal and inverse spinel structures.

when compared to activities calculated from the cation distribution models given an excess enthalpy of mixing parameter $W = 20\pm2$ kJ/mol, due to size mismatch. Snethlage and Schröcke (1976) used the same method at 1273, 1368, and 1473 K, but ignored the Cr-content of the wüstite; this may be why their free energy of mixing curves show anomalous behavior in the region $N_{FeCr_2O_4} = 0.6$–0.8. When this is taken into account their measurements suggest $W = 12.5$ kJ/mol (with considerable scatter). Recent data by Petric and Jacob (1982a,b) are in reasonable agreement with this value of W, except for one point at $N_{Fe_3O_4} = 0.1$. The data of Schmahl and Dillenburg (1969) at 1173 K can neither be reconciled with the above three studies nor with the model.

The calculated solvus for this system with $W = 12.5$ kJ/mol is shown in Figure 6.

Activities in Fe_3O_4–$FeAl_2O_4$ have recently been measured by Petric et al. (1981) at 1573 K, and, as expected from the large differences in the lattice parameters, they show substantial positive deviations from ideality. When the measured activities are compared with activities calculated from the cation distribution model (see also Mason and Bowen, 1981), they give $W \approx 33$ kJ/mol. A slight increase in this value to $W = 36.5$ kJ/mol (well within the accuracy of Petric et al.'s data) gives a calculated solvus in perfect agreement with that determined by Turnock and Eugster (1962), as shown in Figure 6.

The system Fe_3O_4–FeV_2O_4 has also been studied by Katsura et al. (1975) at 1500 K using the same method as for Fe_3O_4–$FeCr_2O_4$. The activities show much larger negative deviations from ideality than are expected from the idealized cation distribution model. This is due to the electronic reaction:

$$Fe^{3+} + V^{3+} = Fe^{2+} + V^{4+} \qquad (25)$$
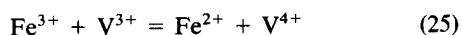
which can occur in the octahedral site of intermediate compositions.

Appropriate distribution parameters may be defined as:

	Tet	Oct	Sum
Fe^{2+}	1-x	x+z	1+z
Fe^{3+}	x	2-2N-x-z	2-2N-z
V^{3+}	0	2N-z	2N-z
V^{4+}	0	z	z
Sum	1	2	3

assuming all V^{3+} and V^{4+} ions are in octahedral sites. This gives the two equations:

$$-RT \ln \left[\frac{x(x + z)}{(1 - x)(2 - 2N - x - z)} \right]$$
$$= \alpha_{Fe^{2+}-Fe^{3+}} + 2\beta x \qquad (26)$$

and

$$-RT \ln \left[\frac{z(x + z)}{(2N - z)(2 - 2N - x - z)} \right]$$
$$= \frac{\partial \Delta G_{25}}{\partial z} \qquad (27)$$

ΔG_{25} is not known, but by considering the published thermodynamic data for the analogous reaction: $1/2\ Fe_2O_3 + 1/2\ V_2O_3 \rightarrow FeO + VO_2$, it may be "guestimated" to be close to zero. Calculated activities at 1500 K for this system with $\Delta G_{25} = 0$ are compared in Figure 7 with the experimental data. Agreement is fair, the calculated curve producing more asymmetric deviations from ideality. It is also instructive to consider the effects of other values of ΔG_{25}. If this quantity is very large and positive, the calculated activities will of course approach those of the Fe_3O_4–$FeCr_2O_4$ system with no size mismatch; progressively more negative values of ΔG_{25} give progressively larger negative deviations.
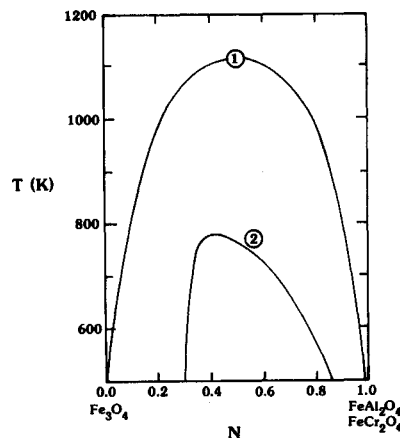

Fig. 6. Calculated for solvi for: $FeAl_2O_4$–Fe_3O_4 ($W = 36.5$ kJ/mol) and $FeCr_2O_4$–Fe_3O_4 ($W = 12.5$ kJ/mol).
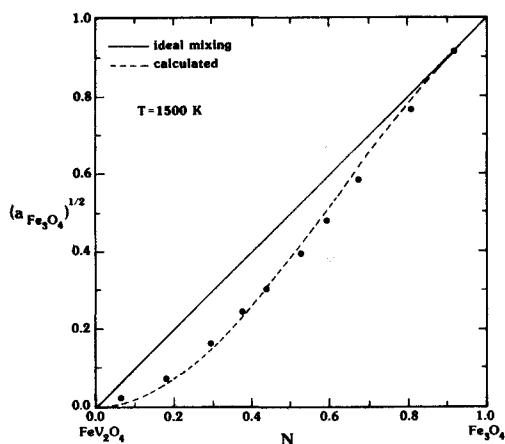
Fig. 7. Calculated activities of magnetite (Fe_3O_4) in the system Fe_3O_4–FeV_2O_4. Experimental points are from Katsura et al. (1975).

Since reaction (25) involves only the exchange of electrons between ions in the octahedral site, it is likely to proceed at a rate too fast to quench: thus, provided ΔG_{25} is positive at room temperature, negligible V^{4+} would be observed, in agreement with the conclusions of Wakihara et al. (1971) and Abe et al. (1974), (though there is some controversy in the matter, see Rogers et al. (1963) or Rossiter (1965)).

Activity–composition relations have also been determined in the type IIIA solutions $NiAl_2O_4$–$MgAl_2O_4$ at 1023–1423 K (Jacob and Alcock, 1977), and Fe_3O_4–$ZnFe_2O_4$ at 1123–1373 K (Benner and Kenworthy, 1966; Katayama et al., 1977; Tretyakov, 1967; Fitzner, 1979). $NiAl_2O_4$–$MgAl_2O_4$ shows large negative deviations from ideality (defined as a = N), which Jacob and Alcock demonstrated to be in excellent agreement with a cation distribution model with *no* non-linear enthalpy term (i.e., $\beta = 0$). The model with $\beta = -20$ kJ/mol produces calculated activities with a very slight positive deviation at these temperatures. Given the accuracy of the experimental data, this system seems to provide the most serious exception to our model.

Positive deviations have been found by the first two listed studies on Fe_3O_4–$ZnFe_2O_4$; the other two studies show negative deviations. Since all four investigations used very similar techniques, this discrepancy cannot be resolved directly. However, there is a geologic discriminant. Burke and Kieft (1972) have described a natural franklinite, with a composition very close to this synthetic join, from Långban, Sweden. The zinc-rich host contains exsolution lamellae of Fe_3O_4. This strongly suggests positive deviations from ideality, leading to unmixing in the spinels at metamorphic temperatures, perhaps at 600–1000 K. Calculated free energy of mixing curves are shown in Figure 8. Even without a size mismatch term, a very asymmetric solvus develops between regions of largely normal and inverse structures at low tempera-

tures. Thus the exsolution of Fe_3O_4 in this system is fully expected from the cation distribution model with the nonlinear β term, but cannot be explained without this term. However, nonstoichiometry may be a further complicating factor in the experimentally determined activity–composition relations of these systems.

We have been able to find only one example of type VIIA, namely Co_2GeO_4–Co_2TiO_4 (Romeijn, 1953). This system shows a large and very asymmetric miscibility gap even at 1673 K, the solubility of Co_2TiO_4 in Co_2GeO_4 being very low (~5 mol% Co_2TiO_4) but the solubility of Co_2GeO_4 in Co_2TiO_4 extending to about 55 mol% Co_2TiO_4. The measured lattice constants in this Co_2TiO_4-rich region suggest that Ge is substituting into the octahedral site. The principles involved in describing the cation distribution in this system should be identical to those for type IIIA, except that the β parameter is expected to be considerably larger. Let us assume, as discussed in section 2.1, that it is -60 kJ/mol. The appropriate α_{Co-Ge} parameter should be sufficiently large compared to this value so that the Co_2GeO_4 end-member has a normal distribution, and sufficiently small so that the site preference of Ge is reversed in the titanium-rich end of the solution. A value of $\alpha_{Co-Ge} = +90$ kJ/mol satisfies these criteria. The value for α_{Co-Ti} has little effect on the calculated solubilities and lattice parameters provided it is less than about 50 kJ/mol; we have adopted 20 kJ/mol. The free energy curve calculated for these distribution parameters at 1673 K is shown in Figure 9. It reproduces the observed miscibility gap very well.

The opportunity for finding systems of type VIIB is even more limited, as the tetravalent ions form end-member spinels that are either completely normal (Si, Ge) or completely inverse (Ti, Sn, V). The only possible exceptions are systems containing Zn_2GeO_4, which under most conditions has the phenacite structure. However, Syono et al. (1971) were able to prepare Zn_2GeO_4 with the spinel structure at 1873 K and 30 kbar. It has not been
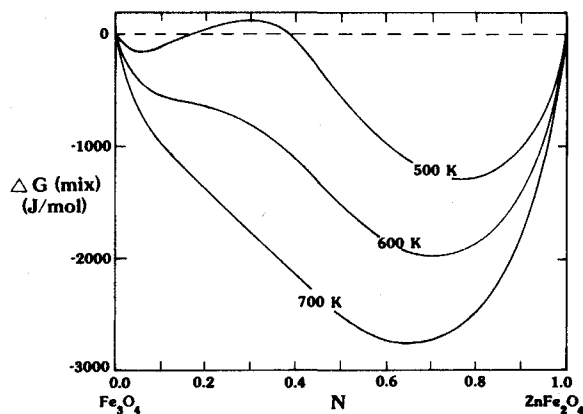

Fig. 8. Calculated free energy of mixing curves for the system $ZnFe_2O_4$–Fe_3O_4 showing development of very asymmetric solvus at low temperature, $W = 0$.
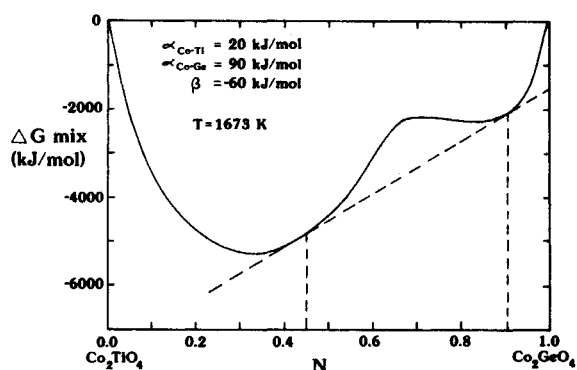
Fig. 9. Calculated free energy of mixing curve for Co_2TiO_4–Co_2GeO_4 at 1673 K.

proved to have a normal cation distribution, but the measured lattice constant is most consistent with this interpretation. The systems Co_2GeO_4–Zn_2GeO_4 and Ni_2GeO_4–Zn_2GeO_4 (Navrotsky, 1973) at 1323 K show the existence of single phase spinel near N = 0.50, which Reinen (1968) has shown to possess an inverse structure (octahedral germanium). This spinel field is separated by a large miscibility gap from the end-member spinels Co_2GeO_4 or Ni_2GeO_4, which both have a normal distribution, and from Zn_2GeO_4 by the transformation of the latter to the phenacite structure. Nevertheless, it appears that these two systems can be interpreted to have an asymmetric solvus very similar to that in the Co_2GeO_4–Co_2TiO_4 system, which would be explained in the same way (see Fig. 10). The solvus between the two spinels in the Co^{2+} system is smaller than that in the Ni^{2+} system; this follows from the smaller magnitude of α_{Co-Ge} than of α_{Ni-Ge} owing to the high contribution from the CFSE of Ni^{2+} to the latter.

Group 4 (IV and IX). This group is made up of the solutions between 2-3 and 4-2 inverse spinels. If it is assumed that the cation distribution in the latter is perfectly inverse (i.e., x = 1), then the charge distribution in this type of spinel is identical to that in a 2-3 normal spinel: 2+ in the tetrahedral site, and $2^+ + 4^+ = 2 \times 3^+$ in the two octahedral sites of the formula unit. This suggests that the mixing properties in this group may be treated using the same value of β as for the 2-3 spinels proper.

The cation distribution parameters (for, e.g., $MgFe_2O_4$–Mg_2TiO_4) may be defined as:

	Tet	Oct	Sum
Mg	1-x	N+x	1+N
Fe^{3+}	x	2-2N-x	2-2N
Ti	0	N	N
Sum	1	2	3

which gives the equation:

$$-RT \ln \left[\frac{x(N + x)}{(2 - 2N - x)(1 - x)} \right] = \alpha_{Mg-Fe^{3+}} + 2\beta x \quad (28)$$

The free energies of mixing and activities determined from equations (28) and (6) depend very strongly on the value of α, and hence on the cation distribution in the 2-3 spinel. In the limiting case where α is very large (i.e., the 2-3 spinel is nearly perfectly normal) the activities correspond to ideal two site mixing (a = N^2). As the cation distribution in the 2-3 end-member becomes more random, the deviations from ideality become increasingly positive, reaching a maximum at about the random distribution. A further increase in the cation distribution parameter, x, of the end-member 2-3 spinel toward the completely inverse case causes a decrease in the positive deviation from ideality. The calculated deviations are also extremely asymmetric.

The above calculations immediately explain, for example, why Tyson and Chang (1981) found complete miscibility in the system $ZnFe_2O_4$–Zn_2SnO_4 at 1333 K, but an extensive and asymmetric miscibility gap in the system $MgFe_2O_4$–Mg_2SnO_4 at the same temperature. $ZnFe_2O_4$ has an almost normal cation distribution, $MgFe_2O_4$ is random to inverse, and the tin spinels are inverse. Despite the asymmetry of the gap in $MgFe_2O_4$–Mg_2SnO_4, its extent can be perfectly reproduced from the cation distribution model assuming a symmetric excess enthalpy function to account for the size mismatch factor (W = 26.2 kJ/mol).

Solvi have been determined over a range of temperatures in the systems $FeAl_2O_4$–Fe_2TiO_4 and $MgAl_2O_4$–Mg_2TiO_4 (Muan et al., 1972). Again the asymmetry can be explained solely by the cation distribution, and the solvi reproduced using appropriate values of W (see Fig. 11).

Cation distributions have been determined experimentally in the system $MgFe_2O_4$–Mg_2TiO_4 at 1373 K (Tellier, 1967, de Grave et al., 1975). Figure 12 shows a plot of ln K vs. x (see equation (23)) for these data. The model is in excellent agreement down to $N_{MgFe_2O_4}$ = 0.4. At lower values of N the apparent discrepancy may be partly due
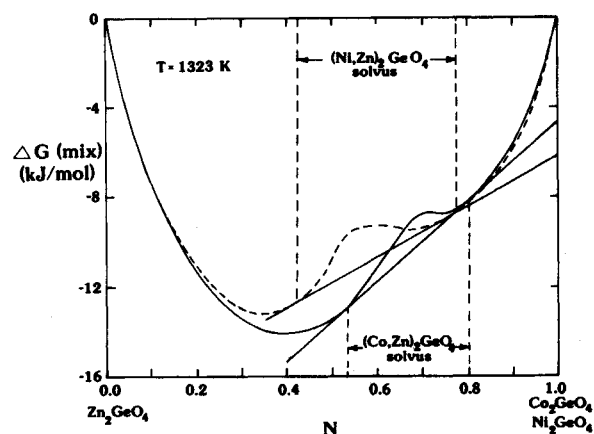

Fig. 10. Calculated free energy of mixing curves for Co_2GeO_4–Zn_2GeO_4 (solid curve) and Ni_2GeO_4–Zn_2GeO_4 (dashed curve) at 1323 K.
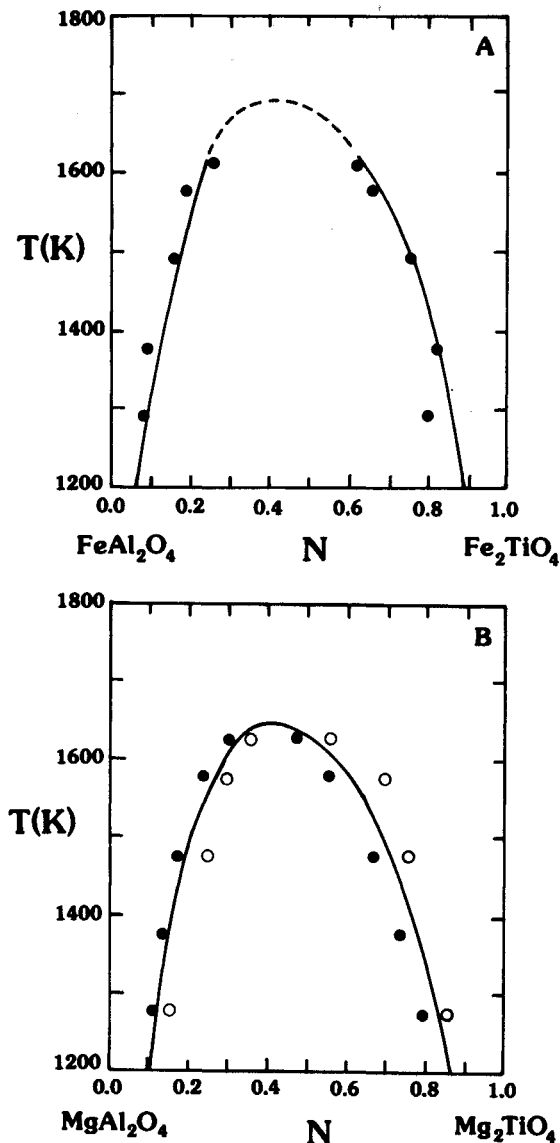
bution (and hence the magnetic properties) is temperature dependent. Obviously, the *equilibrium* cation distribution must depend on temperature. Since, if it is assumed that all Ti is fixed in the octahedral site, the cation distribution reaction, as in other Fe_3O_4-containing spinels, involves only an electron transfer between the tetrahedral and octahedral sites, and the question is whether the equilibrium distribution can be frozen in.

The saturation magnetization of the Fe_3O_4 end-member is always 4.0 Bohr magnetons, regardless of the temperature at which the sample has been prepared. This clearly indicates that the cation distribution is always representative of low temperature, and the equilibrium distribution (e.g., as determined by high T by Wu and Mason, 1981) can never be quenched. If this were to apply throughout the solid solution, then the properties of titanomagnetites would indeed be independent of the temperature of preparation. This point of view is supported by a recent study of Wechsler et al. (1981) who found no difference in structural parameters, determined by neutron diffraction, of several compositions along the Fe_3O_4-Fe_2TiO_4 join quenched from temperatures of 1203–1623 K or annealed at 1073 K. Earlier work which did suggest differences in samples quenched from different temperatures (Fujino, 1974; Bleil, 1976) may have been complicated by imperfect control of stoichiometry.

The lattice constants in this system (Lindsley, 1965; Fujino, 1974) show the same inflections corresponding to the site preference of Fe^{3+} as do $FeCr_2O_4$-Fe_3O_4 and

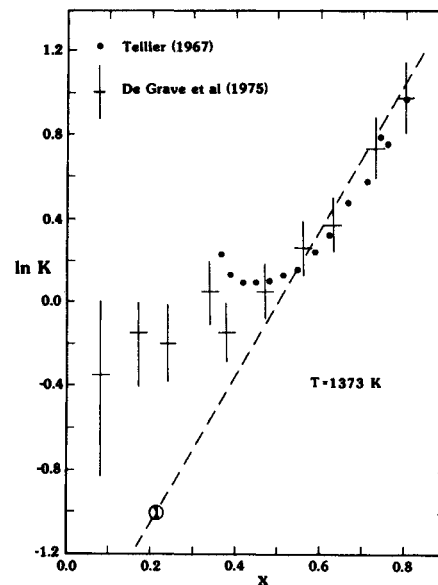Fig. 11. A. Calculated solvus for $FeAl_2O_4$-Fe_2TiO_4. $W = 53.5$ kJ/mol. Experimental data from Muan et al. (1972). B. Calculated solvus for $MgAl_2O_4$-Mg_2TiO_4. $W = 51$ kJ/mol. Experimental data from Muan et al. (1972) (dots) and Boden and Glasser (1973) (circles).

to a breakdown in the magnetic model used to determine the distribution of Fe^{3+} (cf., $MgGa_2O_4$-$MgFe_2O_4$). Also, any short range order in these 4-2 inverse spinels (see discussions in Preudhomme and Tarte (1980) and O'Neill and Navrotsky (1983) would introduce a complication not considered in this model.

The importance to petrology and rock magnetism of the titanomagnetite system Fe_3O_4-Fe_2TiO_4 has resulted in a plethora of experimental studies and some confusion about the interpretation of the data. The controversy centers around whether or not the observed cation distri-

Fig. 12. $\ln K = \ln \left[\dfrac{x(N + x)}{(1 - x)(2 - 2N - x)} \right]$ versus x for Mg_2TiO_4-$MgFe_2O_4$. The curve marked (1) is that calculated with $\alpha_{Mg-Fe^{3+}} = 20$, $\beta = -20$ kJ/mol.

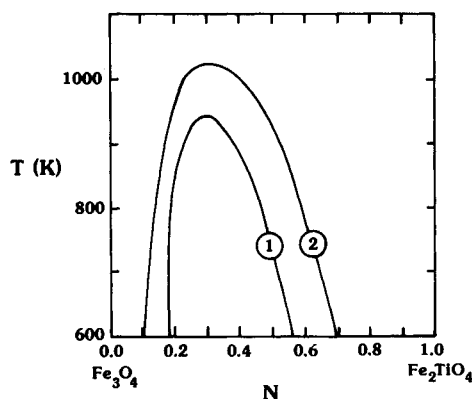Fig. 13. Calculated solvus for Fe_2TiO_4–Fe_3O_4, (1) $W = 0$, (2) $W = 9.2$ kJ/mol.

FeV_2O_4–Fe_3O_4, again with a large region of apparent random distribution for $0.2 < N < 0.8$.

Activity–composition relations have been determined by Katsura et al. (1975) from earlier experimental work. They may be fitted to the cation distribution model with an excess enthalpy parameter, $W = 9.2$ kJ/mol. This may then be used to calculate a solvus, shown in Figure 13. The calculated solvus is rather more extensive than that found experimentally by Vincent et al., (1957), Price (1981) or Lindsley (1981), the consolute point being about a hundred degrees too high, but the calculated solvus has very much the same degree of asymmetry as in the first mentioned study.

In the end-member 4-2 spinels the transition to long-range order of the 2^+ and 4^+ cations in the octahedral site occurs at ~773, 773–823, and 1043 K for Mg_2TiO_4, Zn_2TiO_4 and Mn_2TiO_4, respectively (Preudhomme and Tarte, 1980). Thus similar ordering would be expected in Fe_2TiO_4, perhaps near 873 K, although this, to our knowledge, has not been demonstrated, perhaps as a result of the difficulty in preparing and maintaining stoichiometric Fe_2TiO_4. Recently Wechsler et al. (1981) have reported diffuse scattering, suggestive of considerable short range order, in annealed titanomagnetites. Wechsler and Navrotsky (1982) argue on the basis of thermochemical evidence that Mg_2TiO_4 spinel appears to retain substantial short range order in the cubic phase at temperatures near 973 K, some 200 K higher than the transition temperature given by Preudhomme and Tarte (1980). However, recent work by Wechsler (pers. comm.) suggests that the actual transition temperature in Mg_2TiO_4 lies in the region 903–973 K. Short range and/or long range order would be expected to have an appreciable effect on the low temperature magnetic and thermodynamic properties of the solution, and may be the cause of some of the discrepancies noted above.

Group 5 (II, VI). This group contains the least studied types of solutions, those between normal 4-2 and 2-3 spinels. The treatment of this group is made difficult as

the assumption of a constant value for the non-linear enthalpy (β) term cannot be justified. Hence we have not attempted any quantitative calculations.

The only example of a type II solution that we were able to find is $CoAl_2O_4$–Co_2GeO_4. Furuhashi et al. (1973a) showed that there is a very asymmetric miscibility gap in this system. No solubility of $CoAl_2O_4$ could be detected in Co_2GeO_4 even up to 1673 K, whereas the solubility of Co_2GeO_4 in the aluminate-rich spinel was quite extensive, ranging from about $N_{Co_2GeO_4} = 0.45$ at 1373 K to 0.75 at 1673 K. The lattice constants show a linear increase with increasing substitution of Co_2GeO_4 into $CoAl_2O_4$ but do not extrapolate to the lattice constant of Co_2GeO_4.

Furuhashi et al. followed Romeijn (1953) in assuming that the germanium substitutes onto the tetrahedral site; however, the observed increase in oxygen parameter would be better explained if the germanium substitutes onto the octahedral site. Since the charge distribution in the aluminate rich spinel would then correspond to that in a 4-2 inverse spinel, the solution would be analogous to Co_2GeO_4–Co_2TiO_4, and this is consistent with the similarly asymmetric solvus.

By contrast the two type VI solutions which have been studied Fe_3O_4–Fe_2GeO_4 (Takayama et al., 1981) and $NiFe_2O_4$–Ni_2GeO_4 (Romeijn, 1953) both show complete miscibility, in the former case at least down to 1273 K. The lattice constants in the magnetite solution again show the sinusoidal form similar to other Fe_3O_4 systems, and by analogy with these we interpret this to mean that the site preference of Fe^{3+} also changes across the solution.

Generalizations and systematics

Size mismatch and the regular solution parameter

Davies and Navrotsky (1983) have shown that deviations from ideality in solid solutions could be systematized for a large variety of structure types through a correlation of the regular or subregular solution parameters with a volume mismatch term. For the regular solution approximation, W was linearly correlated with a parameter of the form

$$\Delta V = (V_2 - V_1)/0.5(V_2 + V_1) \qquad (29)$$

where V_1 and V_2 are the molar volumes of the smaller and larger components, respectively. However, in spinels the molar volume depends on the cation distribution (O'Neill and Navrotsky, 1983), the energetics of which have been taken into account in the solid solution model before the effects of size mismatch are considered. It therefore seems more appropriate to attempt to relate W to some volume term that is independent of cation distribution, e.g., the different in volumes of the substituting cation-oxygen pairs. By analogy with equation (29) an appropriate parameter may be defined as:

$$\Delta R = (R_2 - R_1)/0.5(R_2 + R_1) \qquad (30)$$

where

$$R_1 = (r_1 - O)^3 \text{ and } R_2 = (r_2 - O)^3. \qquad (31)$$

$r_1 - O$ being the sum of the cation radius (from O'Neill and Navrotsky, 1983) and the oxygen anion radius (1.4Å). Note that this formulation is equivalent to equation (29) for rocksalt structures.

Figure 14 shows a plot of the regular solution parameters determined in this study against ΔR for substituting 3^+ cations; also included are the data for solutions involving 4-2 inverse spinels, where the effective charge on the octahedral site of the 4-2 end-member is also 3^+ (in these cases the radii of the 4^+ and 2^+ ions have been averaged to calculate ΔR). A least squares regression, omitting the two anomalous Co_3O_4-containing spinels, gives:

$$W = 239.3 \, \Delta R + 0.3 \text{ (kJ mol}^{-1}), \qquad (32)$$

with a correlation coefficient of 0.930.

The clearly anomalous behavior of both of the Co_3O_4-containing solutions invited further investigation into this substance. The activity–composition measurements (Naidu, 1978) were carried out by direct measurement of the pressure of oxygen above the sample in the range 1222–1262 K. As yet unpublished work (O'Neill, in preparation) revealed a large change of slope of about 40 JK^{-1} in the temperature dependence of the reaction: $6Co + O_2 \rightarrow 2Co_3O_4$ (determined by E.M.F. measurements in the range 900–1200 K) at around 1100 K; below this temperature the slope was in excellent agreement with the literature data on the relevant standard entropies and heat capacities. Preliminary high temperature X-ray diffraction measurements up to 1173 K (R. J. Hill, personal communication) showed that Co_3O_4 retained the spinel structure,
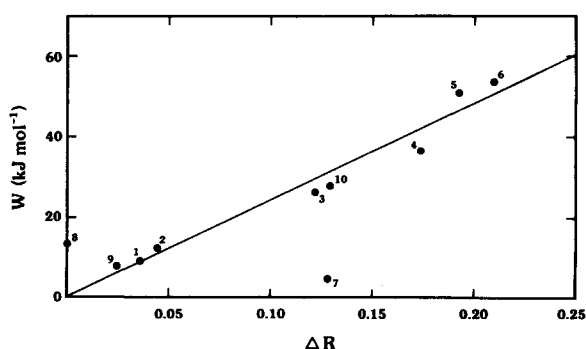

Fig. 14. Ad hoc derived values of W derived for mixing of 3^+ (or $2^+ + 4^+$) cations in spinels plotted against the volume mismatch term ΔR. W's in kJ per gram formula unit. (1) Fe_2TiO_4–Fe_3O_4, $W = 9.2$; (2) $FeCr_2O_4$–Fe_3O_4, $W = 12.5$; (3) Mg_2SnO_4–$MgFe_2O_4$, $W = 26.2$; (4) $FeAl_2O_4$–Fe_3O_4, $W = 36.5$; (5) Mg_2TiO_4–$MgAl_2O_4$, $W = 51$; (6) Fe_2TiO_4–$FeAl_2O_4$, $W = 53.5$; (7) Co_3O_4–$CoAl_2O_4$, $W = 13.5$ (a); (8) Co_3O_4–$CoCr_2O_4$, $W = 4.2$; (9) Fe_3O_4–Fe_2MoO_4, $W = 8.3$ (b); (10) $FeAl_2O_4$–$FeCr_2O_4$, $W = 28.0$; (a) A poor fit to an anomalously asymmetric solution (b) Katayama et al. (1977); all other references in text.

although there was an anomalously large increase in the lattice parameter between 1073 and 1173 K. The observed change in slope of ΔG is close to that expected from the change in electronic entropy of the Co^{3+} ion in going from the low to high spin states (9.13 JK^{-1} per g-atom: 36.5 JK^{-1} per $2Co_3O_4$, O'Neill and Navrotsky (1983)). If such a change does occur in Co_3O_4, then the low spin state cation radius assumed for Co^{3+} (0.53Å) is inappropriate. Shannon (1976) suggests a radius of 0.61Å for Co^{3+} in the high spin state, which, if used to calculate the ΔR parameter, would bring the two anomalous Co_3O_4 solutions into good agreement with the best fit line in Figure 14.

The correlation between W and ΔR enables the former to be estimated for unstudied solutions involving the substitution of 3^+ (or $2^+ + 4^+$) cations. A similar correlation cannot, as yet, be presented for solutions with substituting 2^+ cations due to lack of data. However, for many 2^+ substitutions the ΔR term is small enough for one to predict that W should be almost negligible.

Conclusions and some further applications

The present model, whose essential feature is a disorder-dependent disordering enthalpy, has been developed in an attempt to account for the observed solid solution properties of all oxide spinels. Such a generalization can hardly be expected to be completely accurate in every case, but we believe that it is sufficiently accurate to be useful in at least five capacities related to cation distribution and thermodynamic data for spinel solid solutions: (1) to provide an explanation for observed phenomena, (2) to discriminate among incompatible experimental data, (3) to extrapolate experimental data to other temperatures and pressures, (4) to predict the properties of unstudied systems, and (5) to provide a framework for the extrapolation of the data on binary systems into multicomponent systems.

Examples of some of these applications have already been treated. Some others will now be discussed briefly.

As an example of the way in which cation distribution can influence activity–composition relations, consider the systematics of solutions between Al and Fe^{3+}. The best studied is $FeAl_2O_4$–Fe_3O_4, the solvus of which has been determined by Turnock and Eugster (1962) by reversal experiments. In order to fit the cation distribution model to this data it is necessary to introduce an excess enthalpy of mixing, described by the regular solution parameter $W = 36.5$ kJ/mol. The correlation between W and the difference in volume of the substituting cations (see Fig. 14) found for solutions between different types of end-members suggests that analogous values of W may be used for other Al-Fe^{3+} solutions. Thus, we predict that the solution between the two type IB spinels $MnFe_2O_4$–$MnAl_2O_4$ should develop a solvus at temperatures below about 1073 K, although this particular case appears to be complicated by non-stoichiometry (Ishida et al., 1977) and possibly also by the electronic reaction: $Mn^{2+} +$

$Fe^{3+} = Mn^{3+} = Fe^{2+}$. A better example would be $ZnAl_2O_4$–$ZnFe_2O_4$ which is predicted to show a similar solvus. A somewhat different case would be $NiAl_2O_4$–$NiFe_2O_4$, where, in contrast to the three systems above, the large stabilizing effect of cation redistribution should suppress any solvus. This has not been proven, although Kozlowski and Zarek (1973) reported no unmixing in an extensive series of experiments down to 773 K.

A cation distribution model without the non-linear enthalpy (β) term would predict quite different relations. Thus the model proposed by Petric et al. (1981) for $FeAl_2O_4$–Fe_3O_4, should give, if the same excess enthalpy is added to the cation distribution model, unrealistically extensive solvi in the Mn or Zn analogue systems (consolute point at ~1973 K), and similarly for the Ni system.

There has been some controversy over the extent of the solvus in the $MgFe_2O_4$–$MgAl_2O_4$ system. Kwestroo (1959) found two spinels coexisting along the stoichiometric join even at 1673 K; Ulmer (1969) checked this result at 1573 K and also observed two spinels. Allen (1966) found a solvus only below 1273 K. Sharma et al. (1973) were able to homogenize the end-members at 1223 K and 7 kbar using hydrothermal techniques, but experiments at lower temperatures by these investigators were inconclusive. Given the similarity of the site preference of Mg to Fe^{2+}, we should expect the Mg system to behave very much like the Fe^{2+} system, thus supporting the work of Sharma et al.

Other controversial solvi have been reported by Cremer (1969) in the systems $FeAl_2O_4$–Fe_3O_4, $FeCr_2O_4$–Fe_3O_4 and $FeCr_2O_4$–$FeAl_2O_4$ with crests at ~1073, 1173 and 1223 K, respectively. The results in the first system are moderately similar to those of Turnock and Eugster (1962); however, those in the other two are incompatible with the work of Chassagneux and Rousset (1976), who were able to synthesize complete solutions at 973 K. We have already presented the expected solvus in $FeCr_2O_4$–Fe_3O_4 (Fig. 6); the solvus in the $FeAl_2O_4$–$FeCr_2O_4$ system may be calculated to be nearly symmetrical with the critical temperature at ~820 K. Evans and Frost (1975) noted complete solutions in magnesium-substituted natural analogues of these latter two systems at 773 to 973 K.

The very high pressures needed to stabilize Mg_2SiO_4 spinel makes the study of this geologically important mineral difficult. It is of some interest to know if this spinel can absorb some of the trivalent cations presumed to be present in the earth's mantle, such as Al, Cr, Fe^{3+}, etc., through solid solutions of the type Mg_2SiO_4–$MgAl_2O_4$ etc., as has been proposed by O'Hara (1969). Ma (1974) studied the $NiAl_2O_4$–Ni_2SiO_4 system as a possible analogue, but $NiAl_2O_4$ is an inverse spinel and therefore not completely analogous. Moreover, Ma found that, rather than forming a solid solution, this system formed a series of intermediate compounds with spinel-derivative "spinelloid" structures. This may be a phenomenon peculiar to nickel systems, as something similar has been observed by Colin (1968) in the $NiAl_2O_4$–Al_2O_3 system (albeit

possibly metastably). On the other hand, the presence of other aluminosilicate phases, especially garnet, in Mg- and Fe-containing systems, may account for the absence of spinelloids. In any case, the existence of these intermediate structures, rather than a continuous MAl_2O_4–M_2SiO_4 spinel solid solution suggests that relative instability of the latter.

Among those spinels that have been studied, the best analogues to silicates are provided by germanates, including the Co_2GeO_4-containing systems. Co^{2+} has a very similar site preference to Mg, and Co_2GeO_4, like Mg_2SiO_4 is a 4-2 normal spinel. As have been shown by Furuhashi et al. (1973a) the solubility of $CoAl_2O_4$ in Co_2GeO_4 is very small, despite the similarity in ionic radius of Ge^{4+} and Al^{3+}. These observations and the predictions of our model cause us to conclude that the solubilities of Al^{3+}, Fe^{3+}, and Cr^{3+} spinels in a silicate spinel phase would be even smaller because Si has both a larger tetrahedral site preference and a smaller radius than Ge.

There are few data on the mixing properties of the ternary and higher order spinel solid solutions. Exceptions are those of the type Co_3O_4–Mn_3O_4 (e.g., Navrotsky, 1969). Such solutions involve the *simultaneous* mixing of Co^{2+} and Mn^{2+} with Co^{3+} and Mn^{3+}, and therefore require for their full description some consideration of the reciprocal solid solution effect (Wood and Nicholls, 1978), and are thus beyond the scope of this paper. However, the model presented here provides an excellent basis from which to estimate the mixing properties of higher order solutions where the reciprocal effect does not apply. For example, it is of some interest to calculate the activity of Fe_3O_4 in complex spinel solid solutions, particularly by the system Fe_3O_4–$FeAl_2O_4$–$FeCr_2O_4$–Fe_2TiO_4. The distribution parameters in this system may be defined as:

	Tet	Oct	Sum
Fe^{2+}	$1-x-y$	$N_{Ti}+x+y$	$1+N_{Ti}$
Fe^{3+}	x	$2N_{Fe^{3+}-x}$	$2N_{Fe^{3+}}$
Al	y	$2N_{Al}-y$	$2N_{Al}$
Cr	0	$2N_{Cr}$	$2N_{Cr}$
Ti	0	N_{Ti}	N_{Ti}
Sum	1	2	3

if it is assumed that all Cr and Ti is confined to the octahedral site. Therefore at equilibrium there are two cation distribution equations:

$$RT \ln \left[\frac{x(N_{Ti} + x + y)}{(2N_{Fe^{3+}} - x)(1 - x - y)} \right]$$
$$= (\alpha_{Fe^{2+}-Fe^{3+}} - \sigma_{Fe^{2+}-Fe^{3+}})x + 2\beta(x + y) \quad (33)$$

and

$$RT \ln \left[\frac{y(N_{Ti} + x + y)}{2N_{Al}-y(1 - x - y)} \right]$$
$$= (\alpha_{Fe^{2+}-Al} - \sigma_{Fe^{2+}-Al})y + 2\beta(x + y) \quad (34)$$

calculated in the usual manner. ΔG mix (s.m.) can be obtained by the extension of the regular solution model into multicomponent systems. The appropriate W terms can be calculated and no electronic exchange reactions are likely to be important, and so the activity of Fe_3O_4 may be calculated.

Natural spinels do, however, have extensive substitution of Mg for Fe^{2+}. Since the site preference energy of Mg is close to that of Fe^{2+}, calculations can be extended to natural spinels in a fairly straightforward fashion. These points will be addressed in the future.

Acknowledgments

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Appendix 1

Systematic site preference energies in oxide spinels

The aim is to produce a systematic set of site preference energies for all the commonly occurring 2^+, 3^+ and 4^+ cations in oxide spinels within the limitations of the model. Thus, a priori, values of -20 and -60 kJ/mol for the non-linear part of the enthalpy of disordering (the β parameter) were assumed for 2-3 and 4-2 spinels, respectively. Three models for the electronic entropy (σ) of crystal field cations were then considered: (a) σ is negligible; (b) σ arises from degeneracy in both the octahedral and the tetrahedral sites; (c) σ arises from degeneracy in the tetrahedral site only. Given that the deviation from perfect symmetry in the octahedral site of the spinel structure is small, model (b) might seem to be the preferred option. However, model (c) gives the best empirical fit, and has therefore been adopted.

In practice, there is only a significant difference between (b) and (c) for Cu^{2+}, Co^{2+} and Fe^{2+}. There is also some independent evidence for this choice. Jacob and Valderraman (1977) discussed the entropy of formation of some 4-2 inverse spinels with reference to the reaction:

$$2BO + AO_2 \rightarrow AB_2O_4 \qquad (A1)$$
$$\text{rocksalt} \quad \text{rutile} \quad \text{inverse spinel}$$
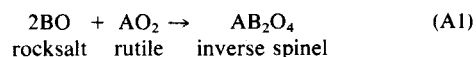
where A = Ti or Sn, and B = Mg, Zn or Co^{2+}. For the spherically symmetrical divalent cations, the entropy of reaction (A1) was: Mg$_2$TiO$_4$, 14.06; Mg$_2$SnO$_4$, 12.38±1.05 (e.m.f. method) or 15.23±3.76 (phase equilibrium); Zn$_2$TiO$_4$, 13.64±1.17 (all

in JK^{-1} mol^{-1}). This gives an average of 13.0 JK^{-1} mol^{-1}. For Co^{2+} the entropy change was: Co$_2$TiO$_4$, -0.63, Co$_2$SnO$_4$, -3.97, or an average of -2.3 JK^{-1} mol^{-1}. The difference in the entropy of formation between Co^{2+} and the non-transition metal ions is then 16 (±3) JK^{-1} mol^{-1}. The electronic contribution to Co^{2+} would be 9.13 JK^{-1} mol^{-1} for option (b) and 18.26 for option (c); the latter is obviously closer.

The assumed values of β and σ may then be used to obtain best fit values for the interchange enthalpies (α_{A-B}, etc.) from literature data on the equilibrium cation distribution at temperature for as many spinels as possible. Unfortunately for many spinels the data reported by different investigators are inconsistent, e.g., such well studied examples as FeAl$_2$O$_4$, CoAl$_2$O$_4$, NiAl$_2$O$_4$ and MgFe$_2$O$_4$, and in most cases there are no obvious criteria from which it is possible to decide which data (if any) are to be preferred. We have therefore adopted such data as are internally consistent with the model—admittedly a circular argument, but the only approach possible under the circumstances.

The next step is to divide the interchange enthalpies, α_{A-B}, etc. into site preference enthalpies, α_A, α_B, etc., where the latter are defined as:

$$\alpha_A - \alpha_B = \alpha_{A-B} \qquad (A2)$$

As the site preference enthalpies are obtained only as the difference of one from the other, it is necessary to designate some arbitrary point on the scale as zero; we have chosen the site preference enthalpy of Fe^{3+} (that is, $\alpha_{Fe^{3+}}$) as this zero point, as the Fe^{3+}-containing spinels are among the most studied and often show significant degrees of disorder, which is advantageous to the accurate estimation of interchange enthalpies. This is a different choice of zero than that made by Navrotsky and Kleppa (1967).

Cations with a very high octahedral crystal field stabilization energy (e.g., Cr^{3+}, Rh^{3+}, V^{3+}) show small to negligible amounts of disorder in any spinel even at the highest temperatures, and therefore there are no data from which to obtain site preference enthalpies. Accordingly these have been estimated from crystal field theory using the approximations explained in Dunitz and Orgel (1957). Δ_{tet} is assumed to be 4/9 Δ_{oct}. A few other site preference enthalpies have been estimated from solid solution effects and radius arguments (see O'Neill and Navrotsky, 1983).

The set of site preference energies so obtained is given in Table A1; these energies reproduce nearly all the data on measured cation distributions in end-member spinels to better than 0.05 in x except for CuAl$_2$O$_4$ (Cooley and Reed, 1972) and the Mn^{3+} spinels NiMn$_2$O$_4$ (Boucher et al., 1969) and MgMn$_2$O$_4$ (Radakrishnan and Biswas, 1976). However, these latter may be accounted for if it is assumed that the manganese in the tetrahedral site is produced by the electron reaction:

$$2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+} \qquad (A3)$$

Thermodynamic data in the literature for analogous reactions in oxides suggest ΔG (A3) is about 50±5 kJ mol^{-1}. (Note also that Mn^{3+} disproportionates in aqueous solution). Assuming that all Mn^{3+} and Mn^{4+} remains in the octahedral site, the cation distribution parameters may be defined as:

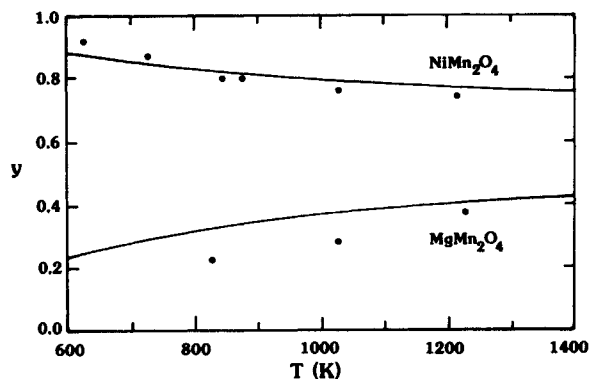|	Tet	Oct	Sum
Ni or Mg	1–y	y	1
Mn^{3+}	0	2–2x	2–2x
Mn^{4+}	0	x	x
Mn^{2+}	y	x–y	x
Sum	1	2	3

Fig. 15. Calculated (solid lines) and experimental (points) degree of inversion in manganite spinels. $NiMn_2O_4$ from Boucher et al. (1969); $MgMn_2O_4$ from Radhakrishnan and Biswas (1976).

From the above the following two equations are obtained:

$$-RT \ln \left[\frac{y^2}{(1-y)(x-y)} \right] = \alpha_{Mn^{2+}-Ni^{2+}} \text{ or } \alpha_{Mn^{2+}-Mg^{2+}} \quad (A4)$$

$$-RT \ln \left[\frac{x(x-y)}{(2-2x)^2} \right] = \Delta G_{A3} \quad (A5)$$

Calculated and experimentally observed values of y (the apparent degree of inversion) are shown in Figure 15. The calculation is very sensitive to ΔG_{A3}: a change of ± 5 kJ causes a change in y of the order of 0.05. Also $MgMn_2O_4$ is tetragonally distorted at these temperatures. Therefore agreement may be considered satisfactory.

This explanation for the disordering in nickel manganite in terms of disproportionation is supported by the value of the oxygen positional parameter of 0.263 found by Boucher et al. (1969) which would be energetically unfavorable from a lattice energy agrument for an inverse 2-3 spinel (see O'Neill and Navrotsky, 1983).

Table A1. Classification of spinel solutions according to the cation distributions and charges of the end-members

Cation	α'_i (kJ)	σ_i (JK^{-1})	Refs.	Comments
2+				
Cd	(70)	0		>Zn due to larger ionic radius
Co	20	0	1,2	
Cu	6	-9.13	3,4	Does not fit $CuAl_2O_4$
Fe	16	-5.76	5,6	
Mg	20	0	7,8,9	
Mn	45	0	10,11	
Ni	-28	-9.13	12,13	
Zn	53	0		From Co_2TiO_4-Zn_2TiO_4 heats of mixing
3+				
Al	-36	0	1,5,9, 10,12	
Co L.S.	(-375)	0		CFSE
Co H.S.	(-30)	-5.76		CFSE
Cr	(-160)	-9.13		CFSE
Fe	0	0	2,3,6,7 11,12	
Ga	-4	0		
Mn	(-95)	-9.13		CFSE
Rh	(-545)	0		CFSE
V	(-55)	0		CFSE
4+				
Ge	110	0		From observed miscibility gaps in germanium spinel solutions
Si	150	0	16,17,18	
Sn	(0)	0		<Ti due to larger radius
Ti	(50)	0		From Co_2GeO_4-Co_2TiO_4

Values in parentheses are order of magnitude estimates.
(1), $CoAl_2O_4$Furuhashi et al. (1973b); Schmalzried (1961); Greenwald et al. (1954); Pepe et al. (1976); (2), $CoFe_2O_4$Sawatsky et al. (1969); (3), $CuFe_2O_4$Néel (1950); Pauthenet and Bochirol (1951); Ohnishi and Tetranishi (1961); (4), $CuAl_2O_4$Cooley and Reed (1972); (5), $FeAl_2O_4$Gaballah et al. (1975); Yagnik and Mathur (1968); Chassagneux and Rousset (1976); Roth (1964); (6), Fe_3O_4Wu and Mason (1981); (7), $MgFe_2O_4$Kriesman and Harrison (1956); Epstein and Frankiewicz (1958); Tellier (1967); Pauthenet and Bochirol (1951); Mozzi and Paladino (1963); Faller and Birchenall (1970); (8), $MgGa_2O_4$Schmalzried (1961); Weidenborner et al. (1966); (9), $MgAl_2O_4$Schmocker et al. (1972); Schmocher and Waldner (1976); (10), $MnAl_2O_4$Roth (1964); (11), $MnFe_2O_4$Hastings and Corliss (1956); Yamanaka and Nakahira (1973); (12), $NiAl_2O_4$Schmalzried (1961); Cooley and Reed (1972); Datta and Roy (1967); Furuhashi et al. (1973); Porta et al. (1974); (13), $NiFe_2O_4$Robertson and Pointon (1966); (14), $CoGa_2O_4$Pepe et al. (1976); (15), $FeGa_2O_4$Ghose et al. (1977); (16), Co_2SiO_4Morimoto et al. (1974); (17), Fe_2SiO_4Yagi et al. (1974); (18), Ni_2SiO_4Yagi et al. (1974); Marumo et al. (1977).