American Mineralogist, Volume 68, pages 181–194, 1983

Simple spinels: crystallographic parameters, cation radii, lattice energies, and cation distribution

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Abstract

Electrostatic lattice energy calculations and consideration of the structure of the spinel group of minerals show that the size of a cation is important in determining its site preference. In oxide spinels containing 2^+ and 3^+ ions (2–3 spinels) there is a tendency for the larger ion to prefer the tetrahedral site; the reverse holds for 2–4 spinels. A set of cation radii optimized to best fit spinel lattice parameters is presented. Based on lattice energy calculations, the enthalpy change accompanying cation disordering is not a linear function of the degree of cation disorder, but a quadratic, with the two parameters approximately equal in magnitude and opposite in sign. Most published data on the change of cation arrangement with temperature fit a thermodynamic model with this non-linear change in enthalpy, but those for Fe_3O_4 may require an additional non-configurational entropy as well, and the data for $MgAl_2O_4$ cannot be described adequately by any simple model.

Introduction

The oxide spinels comprise a large group of ternary compounds, significant not only as naturally occurring minerals, but also in many branches of solid state science. Despite their deceptively simple structure, many spinels exhibit complex disordering phenomena involving the two cation sites, which have important consequences both for their thermochemical and for their physical properties. Recently, there have been a number of studies of spinel solid solutions, (Porta *et al.*, 1974; Jacob and Alcock, 1977; Mason and Bowen, 1981) which have emphasized the necessity of understanding the cation distribution in these more complex systems.

A quantitative treatment of the thermodynamics of cation distribution in simple spinels was given some time ago (Navrotsky and Kleppa, 1967). In this paper we present a modification to this model, necessitated by some new insights into the energetics of the process, and by some new, more precise data on experimentally determined cation distributions. In a subsequent paper we will apply this new model to explain some features of the thermodynamic and structural properties of spinel solid solutions.

Structure

An understanding of the structure of the spinel group is fundamental to any theory of cation distribution, and so a brief description of the salient details will be given here. More complete reviews are available elsewhere, (Blasse, 1964; Hill *et al.*, 1979). The spinel unit cell is face-centered cubic, and contains 32 anions. The space group is $Fd3m$ (O_h^7, number 227 in the International Tables) with the cations occupying the special positions 8a and 16d. The anions occupy the general positions 32e, which require an additional parameter, generally designated u and known in oxide spinels as the oxygen parameter, for their complete description. If the origin of the unit cell is taken at the center of symmetry, then u lies between about 0.24 (for the silicate spinels) and 0.275. For a value of u equal to 0.250 the anions form an exactly cubic close packed array, and define a regular tetrahedral coordination polyhedron about the 8a sites (point symmetry $\bar{4}3m$) and a regular octahedron about the 16d sites ($m3m$). The octahedral cation–anion distance (bond length) in this case is 1.155 times larger than the tetrahedral bond length. As u increases, the oxygens displace along a [111] direction, causing the tetrahedral site to enlarge at the expense of the octahedral, while the symmetry of the latter degenerates to $\bar{3}m$. However, all six octahedral bond distances remain

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0003–004X/83/0102–0181$02.00

the same. Taking a to be the length of a unit cell, the cation to anion distances, R, are given by:

$$R_{tet} = a\sqrt{3(u - 1/8)} \qquad (1)$$

$$R_{oct} = a(3u^2 - 2u + 3/8)^{1/2} \qquad (2)$$

Thus the octahedral and tetrahedral bond lengths can be used to determine the two structural parameters, *a* and u.

A majority of simple oxide spinels have the stoichiometry AB_2O_4, with the cations A and B having the formal charges required by the condition for electrical neutrality:

$$Q_A + 2Q_B + 4Q_O = 0 \qquad (3)$$

where Q_A and Q_B are the charges on the A and B cations, and Q_O that on the anions (−2 for oxide spinels). Commonly, A = 2 and B = 3, (defining a 2–3 spinel) or A = 4 and B = 2 defining a 4–2 spinel). A perfectly *normal* spinel is one in which the single A cation of the formula unit occupies the tetrahedral site, and the two B cations the two equivalent octahedral sites. If we designate the parentheses ( ) and [ ] to denote these two types of sites, then this distribution may be written $(A)[B_2]O_4$. However, as Barth and Posnjak (1932) first suggested for $MgAl_2O_4$ the alternative distribution $(B)[AB]O_4$ is also possible, and this arrangement is referred to as being perfectly *inverse*. In fact all distributions falling between these two extremes may be realized, and to describe this situation it is convenient to define an additional parameter, x, the degree of inversion, which is the fraction of tetrahedral sites occupied by B ions. Thus x may vary between 0 for the perfectly normal case and 1 for the perfectly inverse case. Of special note is the completely random arrangment, $(A_{1/3}B_{2/3})[A_{2/3}B_{4/3}]O_4$. In general, any two ions A and B will have different sizes, so that a change in x will result in a corresponding adjustment of the two structural parameters *a* and u. This observation, which is supported by the few studies that have been undertaken on the matter, (see, for example, Tellier (1967) on $MgFe_2O_4$) will provide the basis for our treatment of cation distribution.

Thermodynamics of cation distribution

A thermodynamic treatment of cation distributions in simple spinels was presented some years ago by Callen *et al.* (1956), and is also summarized in Navrotsky and Kleppa (1967). We shall present a brief review here.

The configurational entropy of a substance is given, assuming completely random mixing of ions on each site by:

$$S_C = -R\Sigma b^s N_i^s \ln N_i^s \qquad (4)$$

where N_i^s is the fraction of species i in site s, and b^s is the number of sites of type "s" per formula unit. For an AB_2O_4 spinel this may be evaluated as:

$$S_C = -R[x \ln x + (1 - x) \ln (1 - x) + x \ln (x/2) + (2 - x) \ln (1 - x/2)] \qquad (5)$$

Thus at x = 0, $S_C = 0$. The configurational entropy then rises sharply to a maximum at the random arrangement of x = 2/3, and then decreases to a value of $2R \ln 2$ for an inverse spinel (x = 1). Here it is convenient to define as our standard state the perfectly normal spinel at the temperature and pressure of interest. If we write the changes in enthalpy and volume on disordering as ΔH_D and ΔV_D, and the change in the nonconfigurational entropy as ΔS_D then the change in free energy on disordering, ΔG_D, is:

$$\Delta G_D = \Delta U_D - T(\Delta S_C + \Delta S_D) + P\Delta V_D \qquad (6)$$

where ΔU_D is the internal energy change, ΔV_D the volume change, and *P* and *T* are pressure and temperature.

At equilibrium

$$\partial \Delta G_D/\partial x = 0 \qquad (7)$$

Substituting Equations (5) and (6) into Equation (7) and carrying out the differentiation where possible, we obtain:

$$\ln [x^2(1 - x)^{-1}(2 - x)^{-1}] = -(RT)^{-1}(\partial \Delta U_D/\partial x) + R^{-1}(\partial \Delta S_D/\partial x) - P(RT)^{-1}(\partial \Delta V_D/\partial x) \qquad (8)$$

As will be demonstrated later, ΔV_D is generally sufficiently small so that the last term in the above will be negligible at low or moderate pressures.

Navrotsky and Kleppa (1967) have shown that the term inside the logarithm on the left hand side of Equation (8) is equivalent to an equilibrium constant, *K*, for the interchange reaction:

$$(A) + [B] = (B) + [A] \qquad (9)$$

thus:

$$K = \frac{[A](B)}{(A)[B]} = \frac{x^2}{(1 - x)(2 - x)} \qquad (10)$$

A plot of ln *K* versus x is shown in Figure 1, and may be used to illustrate two points. First, for 0.2 <

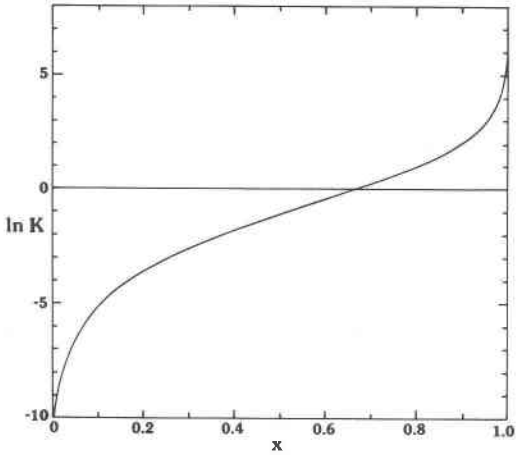

Fig. 1. The logarithm of the equilibrium constant (K) for the site exchange reaction in spinels as a function of the degree of inversion, x.

$x < 0.8$ this function is nearly linear (with a slope of about 7.7). Therefore, provided that the right hand side of Equation (8) takes a reasonably simple form for its dependence on x, and has a slope less than the above value, there will be a unique solution for x. Conversely if the right hand side of Equation (8) has a steeper slope, there will be (typically) three apparent solutions, two of which will generally be metastable with respect to the third.

Second, as $T \to \infty$, the enthalpy terms on the right hand side of Equation (8) become negligible, and x approaches a value determined by the non-configurational entropy term, ΔS_D. As will be noted later, the majority of experimental studies of the temperature dependence of the cation distribution in spinels show that x tends towards the random distribution ($x=2/3$) at very high temperatures, thus implying the ΔS_D is usually small or even negligible. (However, it is to be expected that in those spinels containing crystal field ions, there will be a small but definite electronic contribution to ΔS_D.) The values of $x = 2/3$ then provides a useful point at which to divide spinels with intermediate cation distributions, into those that are "largely normal" ($x \to 0$ as $T \to 0K$) and those that are "largely inverse" ($x \to 1$ as $T \to 0K$).

If for the moment, we assume the ΔS_D is indeed small, the question then reduces to what the form and magnitude of ΔU_D and ΔV_D are likely to be.

The change in internal energy on disordering

Dunitz and Orgel (1957) and, independently, McClure (1957) showed that a number of the observed cation distributions in spinels could be explained by crystal field theory. A transition metal ion will generally have a crystal field stabilization energy (CFSE) in octahedral coordination in excess of that in tetrahedral coordination, and so, in this model, ΔU_D is given by the difference in this excess CFSE between the two ions involved, and will be a simple linear function of x, *i.e.*, $\partial(\Delta U_D)/\partial x = \Delta\text{CFSE(A)} - \Delta\text{CFSE(B)}$. In fact, in about half of the cases where this model is applicable, it does not predict the observed cation distribution correctly (see Glidewell (1976) for a fairly comprehensive tabulation on this point). Furthermore, many of the ions that occur commonly in the spinel structure do not have any CFSE, and therefore, in cases where both ions are of this type, the model has nothing at all to say about which ion prefers which site. It is possible to conceive of *ad hoc* extensions to this model. For example, in the case of zinc spinels one could postulate an excess energetic stabilization for the zinc ion in the tetrahedral site, derived from its formation of sp^3-type covalent bonds, which would explain why all 2–3 zinc spinels are normal. But this approach could not be extended to many other cations, including those in the type mineral of the group, $MgAl_2O_4$, in which the apparent preference of Al over Mg for the octahedral site may seem somewhat surprising to mineralogists who are familiar with the opposite site preferences in such silicates as pyroxenes and amphiboles. (It was just this that led Barth and Posnjak (1932) to originally propose the inverse arrangement.)

A somewhat different empirical approach was used by Navrotsky and Kleppa (1967). Using Equation (8), they assumed that ΔS_D was negligible, and that ΔU_D was proportional to the degree of disorder, x and to the difference in the "site preference energies", assumed constant for all spinels, of the two ions involved. Values for these site preference energies were derived from a small number of observed cation distributions at known temperature, and could then be applied to predict cation distributions in other, less well-studied, spinels. The cation interchange energies calculated from this set of site preference energies was encouragingly similar to one obtained by Miller (1959) from a more theoretical treatment.

At this point we note that the precision with which it is possible to measure x as a function of temperature for a single stoichiometric spinel is seldom sufficient, and the total range of x seldom large enough, to justify the taking of a more complicated form for the right hand side of Equation (8). However, the variation to be expected in x from one end of a solid solution series to the other can be much larger, especially when the two end members have widely different cation distribution and so the model used becomes of much more consequence when dealing with solid solutions than with simple spinels. We therefore propose to take a closer look at the form of ΔU_D than a simple theory for the energetics of the cation distribution might suggest.

Both Dunitz and Orgel and McClure dismissed the change in lattice energy with cation distribution as being relatively unimportant. However, Glidewell (1976) has shown that in many instances the change in the electrostatic part of the lattice energy with disordering is likely to be of much greater magnitude than any CFSE. For a crystal composed of point charge ions the internal energy, U, is given by:

$$U = U_E + U_R + U_V \tag{11}$$

where U_E is the electrostatic energy that accompanies the movement of the constituent ions of the crystal from an infinite separation to their observed positions in the crystal lattice, and depends only on the geometry of the lattice, and may thus be evaluated fairly straightforwardly. U_R, as written, is an amalgam of other, non-coulombic, terms, including dipole–dipole and higher order "Van der Waal's" attractions, and a repulsion term which is usually given an inverse power or exponential form. The sum of these terms is opposite in sign to, and typically about 10–20% of, U_E. U_V is the vibrational energy, which for the sake of argument, we shall take as being given by a simple Debye model (*i.e.*, the harmonic approximation). This implies that U_V is independent of a, u and also x (and, of course, gives $\Delta S_D = 0$). At 0K, ΔU_D, in this model, is then given by the difference in lattice energy between x at the value of interest, and x = 0 (our standard state). At finite temperature, the ΔU_V term will be assumed negligible in accord with the above approximation.

The electrostatic term is both the largest and the most tractable, and will be considered first. It may be expanded into the form:

$$U_E = \frac{Ne^2 M}{4\pi\varepsilon_0 a} = 1389\,\frac{M}{a}\ \text{kJ mol}^{-1} \tag{12}$$

where M is the Madelung constant, which in this case will be a function of the charges on each ion, and also of the oxygen parameter, u. Values of M for completely normal and inverse spinels were first computed for different values of u by Verwey *et al.* (1948). Subsequent calculations by Hermans *et al.* (1974) and Thompson and Grimes (1977) have revealed some errors in this earlier work, but agreement between the latter two works is excellent. We have chosen the formulation offered by Thompson and Grimes as it allows for the calculation of M for intermediate cation distributions. Here M is given by:

$$M = \alpha_1 Q_O^2 + \alpha_2 Q_O Q_T + \alpha_3 Q_T^2 + \alpha_4 Q_O Q_{AN} + \alpha_5 Q_{AN}^2 + \alpha_6 Q_T Q_{AN} \tag{13}$$

where Q_O, Q_T and Q_{AN} are the average charges on the tetrahedral, octahedral and anion sites; α_1, α_2 and α_3 are constants; and α_4, α_5 and α_6 are, to a good approximation, quadratic functions of u. Note that α_1 to α_6 are not uniquely determined parameters, but depend on the method of summation. However, all such sets of parameters are related by the condition of electrostatic neutrality in the crystal (Equation 3) and produce the same value of M.

In Figure 2 we have plotted M against u for the extreme cases of a completely normal 2–3 spinel, an inverse 2–3 spinel, and a normal 4–2 spinel. Since an inverse 4–2 spinel has the same average charges in each site as a normal 2–3 spinel, it will also have the same Madelung constant. The cross-over point for the normal and inverse curves for a 2–3 spinel is at u = 0.2555. For values of u less than this, the electrostatic energy would favor the inverse distribution, and vice versa. The corresponding cross-

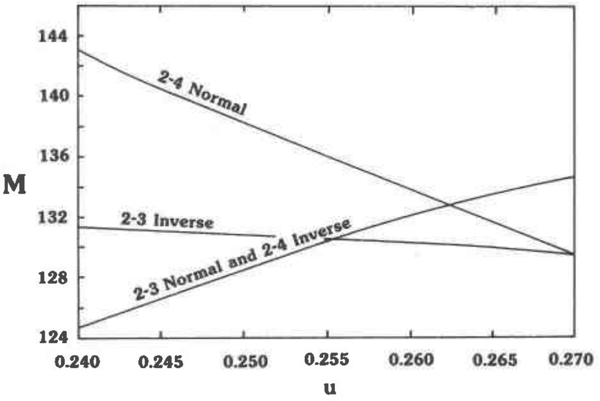

Fig. 2. Madelung constant (M) versus the crystallographic oxygen parameter (u) for normal and inverse 2–3 spinels and normal 4–2 spinels. Inverse 4–2 spinels have the same charge distribution and therefore the same Madelung constant as normal 2–3 spinels.

over point for a 4–2 spinel is at u = 0.2625 (which also is the value for u at which the tetrahedral and the octahedral bond lengths are equal). Table 1 shows the observed values of u and the known cation distribution for a number of spinels. Nearly all the 2–3 and most of the 4–2 spinels conform to the expectation of this model, but there are a few notable exceptions, *e.g.*, Zn_2TiO_4, which will be discussed later.

That many spinels show an oxygen parameter appropriate to their cation distribution does not prove that the electrostatic energy controls this cation distribution: for, as stated earlier, u, and to a lesser extent, *a*, may be expected to vary with the cation distribution.

Both *a* and u are uniquely determined by a combination of the octahedral and tetrahedral bond lengths (Equations (1) and (2)). In their recent study of spinel systematics, Hill *et al.* (1979) showed that, by using Shannon's (1976) ionic radii, 96.9% of the variation in *a* in a sample of 149 oxide spinels could be accounted for. This remarkably good statistical correlation led Hill *et al.* to state that up to 40% of the published u parameters, which were not so well accounted for, may be in error. In view of the far greater difficulties in determining u as compared to a, this may well be the case.

Table 1. Oxygen parameters and cation distributions for some spinels. Data from Tabulation of Hill *et al.* (1979). Normal 2–3 spinels are expected to have an oxygen parameter greater than 0.2555, inverse 2–3 spinels less than this; for 4–2 spinels the corresponding point is at u = 0.2625. In the table N means x < 2/3, I means x > 2/3.

Spinel	u	Cation Distribution
$MgAl_2O_4$	0.2624	N
$ZnGa_2O_4$	0.2617	N
$MgFe_2O_4$	0.2615	N
$ZnFe_2O_4$	0.2615	N
$MgCr_2O_4$	0.2612	N
$NiCr_2O_4$	0.260	N
MgV_2O_4	0.2598	N
$NiFe_2O_4$	0.2573	I
$MgFe_2O_4$	0.257	I
$NiAl_2O_4$	0.256	I
Fe_3O_4	0.2548	I
$MgGa_2O_4$	0.254	I
Fe_2SiO_4	0.2409	N
Co_2SiO_4	0.2423	N
Ni_2SiO_4	0.2439	N
Mg_2GeO_4	0.2508	N
Zn_2TiO_4	0.255	I
MgV_2O_4	0.261	I
Fe_2TiO_4	0.265	I
Zn_2SnO_4	0.265	I

Table 2. Effective ionic radii in the oxide spinels. The radius for the O^{2-} ion is assumed to be 1.38Å (Shannon, 1976).

Cation	Tetrahedral Coordination		Octahedral Coordination		Ratio (tet/oct) This work
	Radius (Å)		Radius (Å)		
	This work	Shannon	This work	Shannon	
2+ Cd	0.78	0.78	-	0.95	0.821
Co	0.58	0.58	0.72	0.745	0.806
Fe	0.615	0.63	0.74	0.78	0.831
Mg	0.585	0.57	0.715	0.72	0.824
Mn	0.655	0.66	0.80	0.83	0.819
Ni	0.565	0.55	0.69	0.69	0.819
Zn	0.58	0.60	0.73	0.74	0.795
3+ Al	0.39	0.39	0.53	0.535	0.736
Co	0.45	-	0.53	0.545*	-
Cr	-	-	0.615	0.615	-
Fe	0.485	0.49	0.645	0.645	0.760
Ga	0.47	0.47	0.615	0.62	0.764
Rh	-	-	0.68	0.665	-
V	-	-	0.645	0.64	-
4+ Ge	0.38	0.39	0.52	0.53	0.731
Si	0.275	0.26	-	0.40	0.675
Sn	-	0.55	0.745	0.69	0.738
Ti	-	0.42	0.60	0.605	0.700
V	-	-	0.55	0.58	-

*Low spin state

If one assumes that R_{oct} and R_{tet} are determined completely by a spinel's composition, site occupancy, and the ionic radii, one can compute directly the variation of *a* and u, and hence of the electrostatic energy, with the degree of disorder, x, for any spinel.

Interionic distances in oxide spinels

Shannon's ionic radii (Shannon and Prewitt, 1969; Shannon, 1976) were derived from a large number of different structures, rather than confined to spinels only, and therefore it is not surprising that Hill *et al.*'s tabulation contains certain systematic differences between the observed and the calculated values of *a* and u. Accordingly, we have refined Shannon's radii specifically for the spinel structure, so as to eliminate these anomalies. The results are listed in Table 2. We have used Shannon's value of 1.38Å for O^{2-} in tetrahedral coordination for easy comparison. Our data base was largely similar to that of Hill *et al.*, but we used only those spinels in which the oxidation states of the cations are unambiguously known, and for which the cation distribution was close to either the normal or the inverse extreme. Less weight was given to the value of u than to *a*, particularly for some of the older structural determinations, in which the accuracy in evaluating u was not high. For the inverse spinels, some assumption needs to be made for averaging the radii of the two different ions in the same site. We decided on the simplest approach (like Hill *et al.*), and assumed that these distances could be averaged in a simple linear fashion, so that:

$$R_{tet} = R_{tet,A}(1 - x) + R_{tet,B}(x) \tag{14}$$

$$R_{oct} = R_{oct,A}(0.5\,x) + R_{oct,B}(1 - 0.5x) \tag{15}$$

The radii were then obtained by a process of adjustment (in steps of 0.005Å) until the optimum fit (as judged from histograms such as that shown in Fig. 3) was achieved. This histogram shows the difference (Δa) between the calculated and the experimentally determined values of *a*. From Equations (1) and (2) it may be estimated that a variation of 0.005Å in bond length will cause an uncertainty in *a* of about 0.01Å (and in u of ~0.001). Over 75% of the spinels fall within these limits. Much of the remaining variation comes from the silicate and germanate spinels.

These radii have a number of applications. First, they may be used to identify some of the anomalies in the literature, which may be simply due to incorrect measurements, or, more significantly, accurate measurements on poorly characterized samples. Many spinels contain cations that occur in more than one oxidation state, and others have a tendency to form defect structures with cation vacancies, particularly at high temperatures (Schmalzried, 1961). A combination of these two factors may easily produce substantial variations in lattice parameters in a spinel of nominally fixed composition with different conditions of preparation. These variations cannot be ascribed to cation disordering. For example, $NiFe_2O_4$ has been shown by Robertson and Pointon (1966) to have an almost completely inverse cation distribution over a wide range of temperatures. Yet Subramanyan and Khare (1979) found that the measured value of *a* increases with the temperature of sintering in air, which was inferred to be caused by oxygen loss from the sample and the accompanying formation of some Fe^{2+}. In this case the calculated value for *a* from this work may be compared with values reported in the literature to enable one to distinguish between stoichiometric and nonstoichiometric samples. Similarly, the calculated values of *a* and u may be used to disriminate between various alternative arrangments that could be postulated for cation distribution and oxidation state. This will be particularly useful in describing spinel solid solutions. For example, consider a spinel with the formula $CoFe_2O_4$. There are four possible extremes of cation and valence arrangements, as shown below, which, together with their calculated values of *a* and u are:

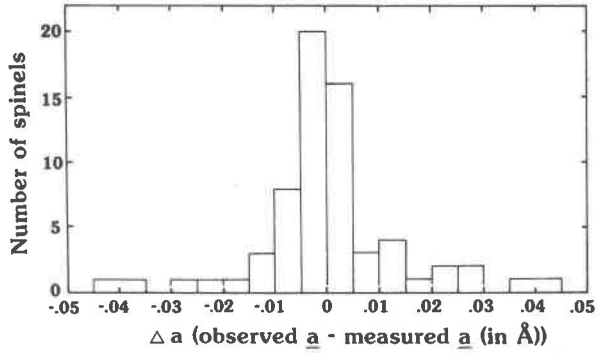

Fig. 3. Histogram showing the differences between the measured lattice constant (*a*) and that calculated from the ionic radii of Table 2 for 66 simple oxide spinels. The measured values are from the tabulation of Hill *et al.* (1979).

	a(Å)	u
1. $(Co^{2+})[Fe_2{}^{3+}]O_4$	8.4091	0.2596
2. $(Fe^{3+})[Co^{2+}Fe^{3+}]O_4$	8.3702	0.2536
3. $(Co^{3+})[Fe^{2+}Fe^{3+}]O_4$	8.3439	0.2516
4. $(Fe^{2+})[Co^{3+}Fe^{3+}]O_4$	8.3004	0.2638

Blasse (1964) lists measured values of $a = 8.35$ and $u = 0.256$. A more accurate determination of *a* is given by Roiter and Paladino (1962) as 8.382±0.001Å for $CoFe_2O_4$ prepared at high temperatures. These values are nearest to option 2 above, tending toward option 1. Sawatzky *et al.* (1969) have in fact shown by Mössbauer spectroscopy and magnetic measurements that the cation arrangement in $CoFe_2O_4$ is nearest to the second option, with a temperature-dependent degree of disorder toward the first. For an actual high temperature arrangement of $(Co^{2+}_{0.3}Fe^{3+}_{0.7})[Co^{2+}_{0.7}Fe^{3+}_{1.3}]O_4$, calculated values of *a* and u are 8.3826Å and 0.2554 respectively, in excellent agreement with the observed values.

Second, the change of *a* with x gives the volume change of the spinel on disordering (ΔV_D), and hence the dependence of x on pressure (see Equation (8)). There have been relatively few studies in which both *a* and x have both been measured for a spinel equilibrated at different temperatures. An exception is magnesium ferrite, (which, as a complication, also tends to be slightly nonstoichiometric) and in Figure 4 the calculated values of a are shown as a function of x, together with the experimental data obtained by Tellier (1967) on "$MgFe_2O_4$," and by Mozzi and Paladino (1963) on $Mg_{1.06}Fe_{1.94}O_{3.97}$. The former used saturation magnetization measurements to determine x, the latter a combination of this technique and X-ray diffraction. The data of Allen (1966) also show the same trend, but with considerably more scatter.

The slight decrease in lattice parameter with increasing degree of inversion seen in magnesium ferrite is generally to be expected for 2–3 spinels, with cations of sizes similar to Mg^{2+} and Fe^{3+}. For a 4–2 spinel such as Mg_2SiO_4, a calculation using the radii of Table 2 shows that an increase in x from 0 to 0.1 causes an *increase* in the molar volume of about 0.4%.

This point is of particular importance in Mg_2SiO_4, which may be an abundant mineral in the lower part of the upper mantle. Navrotsky (1977) has shown that the small amounts of cation disordering which might occur in this spinel at the very high temperatures (2000K and above) of this region may have an important influence on the slopes of the phase equilibrium boundaries defining the stability field of Mg_2SiO_4 spinel. The predicted increase in molar volume with disordering, although small, will tend to decrease any tendency toward disordering at pressures of several hundred kilobars.

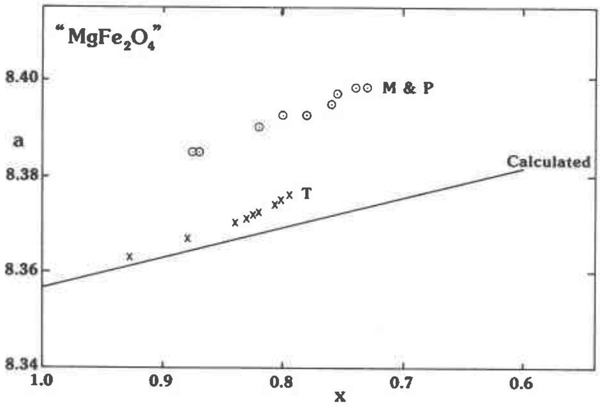

Fig. 4. Calculated lattice constant (*a*) for $MgFe_2O_4$ as a function of the degree of inversion (x). Shown also are the experimental data of Tellier (1967) (crosses labelled T) and Mozzi and Paladino (1963) (circles labelled M and P) on "$Mg_{1.06}Fe_{1.94}O_{3.97}$." Note that the effect of impurity Fe^{2+} ions would be to increase *a*.

Finally, as both *a* and u can be calculated as a function of x, the change in the electrostatic part of the lattice energy with x may be evaluated accurately.

The change in enthalpy on disordering: revised model

The constant ionic radii of the previous section predict that *a* and u are linear functions of x. Substituting this into Equations (12) and (13), together with the appropriate expressions for the average charges on each site, shows that the electrostatic contribution to the lattice energy will have a *quadratic* dependence on x, which we may write in the form:

$$\Delta U_E = \alpha_E x + \beta_E x^2 \qquad (16)$$

This quadratic dependence was also recognized empirically by Kriessman and Harrison (1956) who tried to justify it in terms of electrostatic energies but did not consider the simultaneous variation of *a* and u with x.

In order to demonstrate the behavior of this electrostatic term, we have calculated the coefficients α_E and β_E for a number of specific spinel structures, as given in Table 3. A number of points worthy of further discussion arise:

Table 3. Calculated values for the change in the electrostatic energy on disordering given in the form $\Delta U_E = \alpha_E x + \beta_E x^2$, $\Delta U_E = U_E\ (x = 0) - U_E\ (x = 1)$. Units are kJ/mol.

	α_E	β_E	ΔU_E
$MgAl_2O_4$	1667	-1320	347
$MgGa_2O_4$	1093	-903	181
$MgFe_2O_4$	861	-806	56
$MgIn_2O_4$	-181	-181	-361
$NiFe_2O_4$	750	-736	14
$MgFe_2O_4$	861	-806	56
$ZnFe_2O_4$	958	-820	125
Fe_3O_4	1042	-931	111
$MnFe_2O_4$	1361	-1111	250
$CdFe_2O_4$	1903	-1528	375
Mg_2SiO_4	6417	-4764	1653
Mg_2GeO_4	4792	-3500	1278
Mg_2TiO_4	4417	-3042	1375
Mg_2SnO_4	2861	-1806	1056
Ni_2GeO_4	4639	-3403	1250
Mg_2GeO_4	4792	-3500	1278
Zn_2GeO_4	4792	-3514	1278
Fe_2GeO_4	5070	-3736	1333
Mn_2GeO_4	5459	-4042	1417

(1) ΔU_E is very large and would swamp any CFSE term. Even at temperatures near 2000K, ΔU_E is about two orders of magnitude larger than the product TS_C, the contribution to the free energy of disordering from the configurational entropy.

(2) ΔU_E is consistently larger for 4–2 than for 2–3 spinels. This implies that, all other things being equal, 2–3 spinels are more likely to show intermediate cation distributions. Most 4–2 spinels observed are in fact either completely normal or completely inverse.

(3) The term in x^2 (β_E) is approximately equal in magnitude, and opposite in sign, to that in x (α_E).

(4) Both terms increase with the difference in the radii of the two ions.

(5) $MgIn_2O_4$ is the only example given for which ΔU_E is negative at $x = 1$, and hence the only example for which the electrostatic energy would favor the inverse arrangement.This conclusion is quite different from that reached by Glidewell (1976) in his consideration of the relative effects of the electrostatic versus CFSE terms. The difference arises because Glidewell did not take into account the change of *a* and u with x.

(6) In the 2–3 spinels there is a tendency for the electrostatic energy to favor putting the *larger* ion into the tetrahedral site (*e.g.*, compare the observed cation distributions in the series MgB_2O_4 where the radius of the B ion increases in the order Al < Ga < Fe < In, and the series AFe_2O_4, where the radius of the A ion increases in the order Ni < Mg ≃ Zn < Fe^{2+} < Mn < Cd). In the 4–2 spinels, the effect acts oppositely, so as to favor placing the *smaller* ion in the tetrahedral site.

There is considerable support for these generalizations in real spinels. Thus in the aluminates, only $NiAl_2O_4$ and $CuAl_2O_4$ are observed to be largely inverse (although CFSE would also favor this) and the ferrites $MnFe_2O_4$ and $CdFe_2O_4$ are indeed normal (although the formation of tetrahedrally symmetric sp^3 type covalent bonds would again favor this in the latter case, as in $ZnFe_2O_4$). Perhaps the most startling and emphatic illustration of this tendency is provided by de Sitter *et al.* (1977) in a study of Ca-substituted magnetites. They showed by Mössbauer spectroscopy that all of the very large Ca^{2+} ion resided in the tetrahedral site. Ca^{2+} is normally found in eight-fold coordination, and indeed Shannon (1976) does not even list a value for its ionic radius in tetrahedral coordination. That in 2–3 spinels, the larger ion should seem to prefer to assume tetrahedral coordination is an interesting and somewhat unexpected result. The variable u parameter removes the geometric constraint which, in close-packed structures, would cause small ions to prefer tetrahedral coordination. In the 4–2 spinels, when the tetravalent ion is small, the spinel is always found to be normal (*e.g.*, the silicates and germanates, except Zn_2GeO_4) and when the tetravalent ion is large, the spinel is inverse (*e.g.*, the titanates and stannates).

The electrostatic energy is, of course, only one part of the total lattice energy and since ΔU_E is an order of magnitude larger than what one might reasonably expect for ΔU_D calculated from observed intermediate and inverse cation distributions, it is pertinent to investigate the effect of the short-range force terms (U_R in Equation 11). The most significant of these are the repulsion terms between nearest neighbor cations and anions, which are usually assumed to take the exponential form, $D\exp(-R/\rho)$, or the inverse power form, DR^{-n}, where R is the interionic separation, ρ or n are "hardness" parameters, and D a factor with the units of energy. Using the former, this gives U_R' (where the ′ denotes that only nearest-neighbor repulsions are being considered) as:

$$\begin{aligned} U_R' = {} & 4D_A(1 - x) \exp(-R_T/\rho_A) \\ & + 4D_B \times \exp(-R_T/\rho_B) + 6D_A \times \exp(-R_O/\rho_A) \\ & + 6D_B(2 - x) \exp(-R_O/\rho_B) \end{aligned} \tag{17}$$

where the subscripts A and B refer to the ions in the formula until AB_2O_4, and the distances R_T and R_O are the simpler linear functions of x given by Equations (14) and (15). Thus this term, too, depends mainly on the differences in the radii of the two ions. By differentiating U_R' with respect to x, it may easily be shown that to a very good approximation, $\Delta U_R'$ also takes a quadratic form in its dependence on x, which we may write:

$$\Delta U_R' = \alpha_R' x + \beta_R' x^2 \tag{18}$$

The ρ quantities may in theory be evaluated from such sources as the equilibrium interionic distances in, and compressibilities of constituent binary oxides. Unfortunately all the required data are not available. Nevertheless, by assuming physically reasonable values for ρ_A and ρ_B (*e.g.*, this hardness parameter may be taken as 0.35Å for both A and B by analogy with alkali halides, (Tosi, 1964) and divalent metal oxides, (Ohashi and Burnham, 1972), we can derive approximate values of D_A and D_B from the equations for equilibrium in the spinel structure:

$$\frac{dU'}{da} = 0 \text{ at } a = a_0 \tag{19}$$

$$\frac{dU'}{du} = 0 \text{ at } u = u_0 \tag{20}$$

where a_0 and u_0 are the lattice constant and oxygen parameter calculated for the equilibrium cation distribution, and $U' = U_E + U_R'$. If independent values for D and ρ could be found, as suggested above, then the interionic distances could be calculated from the lattice energy model, and would provide an interesting insight into our ionic radii and the assumptions we have made about their constancy from one spinel structure to another.

Such calculations as are possible with the present model suggest that the coefficients α_R' and β_R' are again approximately equal in magnitude, and opposite in sign to each other. Moreover, they are both opposite in sign to the analogous coefficients α_E and β_E derived from the electrostatic energy equation. Thus the dependence of U on x will result from a small difference between the relatively large quantities U_E and U_R'. Under such conditions other minor terms that appear to be of negligible significance in the lattice energy equation may exert an appreciable effect, such as next-nearest-neighbor repulsions, oxygen–oxygen interactions, and the "Van der Waals" terms. These also may be shown to take on a quadratic dependence in x as a first approximation. Thus, clearly the true *form* to be considered for the change in enthalpy on disordering (ΔU_D in Equation (8)) if one neglects the *PV* term) is also a quadratic one, which we will simply write as:

$$\Delta H_D \approx \Delta U_D = \alpha x + \beta x^2 \tag{21}$$

and in which α and β are generally expected to be of approximately equal magnitude and opposite sign. The effect of crystal field stabilization energies may be included in this model; since this term is assumed to depend linearly on x, it may be added onto the α term. Also, since both ΔU_E and $\Delta U_R'$ have been shown to depend mainly on the difference in radii of the two ions, so too will the coefficients α and β.

One may question the validity of applying a traditional lattice energy approach (Coulombic plus short range terms) to oxides in which much of the bonding can be described as being covalent in character. Indeed the lattice energy calculations considerably overestimate the magnitude of disordering energies, compare Tables 3 and 5. This may suggest that the actual charge on an ion in a crystal is some fraction (0.2 to 0.5) of its formal charge, as has been suggested for albite feldspar by Senderov (1980) on the basis of lattice energy calculations for the order-disorder reaction. The point of such electrostatic lattice energy calculations is not to calculate the actual energy of disordering but to predict the *relative* stability of various possible configurations. As long as the degree of covalency (however defined) and the nature of each metal-oxygen bond are not strongly affected by changing next-nearest neighbor configurations, this approach will correctly predict the most stable structure, though it will not give an accurate prediction of energetics. Molecular orbital calculations also predict configurations more readily than absolute energies, and their application to molecular clusters as big as the spinel unit cell is very difficult. Thus, at present, the enthalpy of transformation or of disordering remains an empirical parameter, though its form can receive theoretical justification from calculations such as those above.

Effect of short-range order

Before leaving the topic of lattice energies, we wish to point out one more effect that may be explained, at least qualitatively, by this model. Earlier, it was noted that the observed cation distribution for most 2–3 spinels is compatible, from the electrostatic point of view, with the measured u parameter, in that the Madelung constant for this u is larger for this distribution than for the alternative limiting distribution. The same does not always hold for the 4–2 spinels, however, in that the measured u values for many of the inverse spinels, while in agreement with those calculated from the ionic radii, are still less than the cross-over point for the Madelung constant at u = 0.2526 (see Fig. 2).

There are, however, two lines of evidence indicating that such inverse 4–2 spinels may possess a considerable amount of short-range order of the two ions in the octahedral site. It has been shown that, with decreasing temperature, a number of these compounds undergo a phase transition to a derivative structure (tetragonal, space group $P4_322$) in which the two octahedral cations are ordered into two non-equivalent sites. This phenomenon has been reviewed recently by Preudhomme and Tarte (1980) who suggest that the temperature of the transition decreases with decreasing difference in the radii of the two ions. The highest temperature found so far is ~770°C for Mn_2TiO_4 (Hardy *et al.*, 1964). In addition, Jacob and Alcock (1975) have argued, from thermodynamic evidence, that Zn_2TiO_4 shows a large degree of residual short-range ordering at higher temperatures (900–1100K), well above the transition point.

Hermans *et al.* (1974) have shown that the ordering of two ions with different charges into an ordering scheme like that in magnetite results in a large increase of about 4.0 units in the Madelung constant. This increase would enhance the stability of an inverse 4–2 spinel with $a_0 = 8.5$Å by about 650 kJ/mol. The type of ordering and distortion found in these titanate spinels is not identical to that in magnetite, and so the precise magnitude of the effect for titanates is not known. A similar increase of 4.0 units in the Madelung constant would, however, move the cross-over point down to $u = 0.257$ (see Fig. 3). This effect is therefore of great potential importance in stabilizing the inverse structure. Note too that any appreciable short-range order will cause a deviation from the ideal configurational entropy, and may therefore lead to apparent excess entropies of disordering (ΔS_D) if the simple approach of Equation (8) is used.

The effect of electronic entropy in transition-metal spinels

Another hitherto neglected factor that may influence the cation distribution and its change with temperature in certain spinels is that crystal field theory, in addition to predicting an excess octahedral crystal field stabilization *enthalpy* for many transition metal cations, also suggests that there will be a change in electronic *entropy* for these ions in going from octahedral to tetrahedral coordination. In crystal field theory, this entropy is given by, (Wood, 1981):

$$S_{el} = -R\Sigma P_1 \ln P_i \tag{22}$$

where P_i is the probability of the ith state occurring. In Table 4 we have listed S_{el} for perfectly regular tetrahedral and octahedral coordination for some cations of interest, and also ΔS_{el}, which would be the electronic contribution to any change in entropy with cation distribution. In fact, the octahedral site is generally slightly distorted, which leads to removal of the degeneracy of the relevant *d*-orbitals and a lowering of the octahedral site electronic entropy. However, at the high temperatures encountered in spinel studies this effect may not be significant.

Compared to the CFSE, the electronic entropy effect is small. But note for example, that ΔS_{el} for V^{3+} reinforces the relatively small (~50 kJ/mol according to Dunitz and Orgel (1957)) excess octahedral CFSE for this ion, thereby keeping all V^{3+} spinels exclusively normal despite this ion's large ionic radius. Conversely ΔS_{el} for Ni^{2+} favors the tetrahedral site, thus contributing towards the randomization of $NiAl_2O_4$.

Application of the model

Substituting Equation (21) into Equation (8), we obtain a form similar to that suggested empirically by Kriessman and Harrison (1956), namely:

$$\ln \frac{x^2}{(1-x)(2-x)} = \ln K = -\frac{(\alpha + 2\beta x)}{RT} - \frac{P - \partial \Delta V_D/\partial x}{RT} + \frac{T\partial \Delta S_D/\partial x}{R} \tag{23}$$

In Table 5 we present the results of least squares regression analyses for α and β obtained from the variation of x with temperature as reported in the literature. All these studies are at atmospheric pressure, and hence the ΔV_D term is negligible. The accuracy of the data does not warrant fitting more than two parameters, so we have elected to ignore any possible excess entropy (ΔS_D) term. Despite the variation found in the values for nominally the same spinel in different studies, α and β are approximately equal in magnitude and opposite in sign to each other for all these substances, which is in excellent agreement with the predictions of the lattice energy model. However, these data should be treated with due caution, as: (1) Many of these spinels are known to be slightly nonstoichiometric (*e.g.* $MgFe_2O_4$) or to contain ions in variable oxida-

Table 4. Change of electronic entropy with disorder for some transition metal ions

Cation	Electronic Configuration	S_{el}^{tet}	S_{el}^{oct}	$\Delta S_{el}(JK^{-1}mol^{-1})$
Ti^{4+}	d^0	0	0	0
V^{4+}	d^1	R ln 2	R ln 3	-3.37
V^{3+}	d^2	0	R ln 3	-9.13
Cr^{3+}	d^3	R ln 3	0	9.13
Mn^{3+}	d^4	R ln 3	R ln 2	3.37
Mn^{2+}	d^5	0	0	0
Fe^{2+}	d^6	R ln 2	R ln 3	-3.37
Co^{3+} H.S.	d^6	R ln 2	R ln 3	-3.37
L.S.		-	0	-
Co^{2+}	d^7	0	R ln 3	-9.13
Ni^{2+}	d^8	R ln 3	0	9.13
Cu^{2+}	d^9	R ln 3	R ln 2	3.37

H.S. = high spin, L.S. = low spin

Table 5. Values of α and β in Equation (22) found by regression analysis of experimental data on the change of x with temperature

Spinel	α ($kJmol^{-1}$)	β ($kJmol^{-1}$)	Method of Determination of x	Reference
$MgGa_2O_4$	19.2	-21.8	XRD	Schmalzried (1961)
$MgFe_2O_4$	15.9	-17.6	SM	Kriessmann and Harrison (1956)
	16.7	-18.0	SM	Epstein and Frankiewicz (1958)
	-5.9	0.0	SM	Tellier (1967)
	3.8	-8.8	SM	Pauthenet and Bochirol (1951)
$Mg_{1.06}Fe_{1.94}O_{3.97}$	15.5	-18.4	SM, XRD	Mozzi and Paladino (1963)
$NiAl_2O_4$	25.9	-23.0	XRD	Schmalzried (1961)
	32.2	-27.2	XRD	Cooley and Reed (1972)
$NiMn_2O_4$	25.1	-20.1	ND	Boucher et al. (1969)
$CuFe_2O_4$	4.6	-10.5	SM	Neél (1950)
	13.8	-16.7	SM	Pauthenet and Bochirol (1951)
	32.2	-25.1	XRD	Ohnishi and Teranishi (1961)

(SM = saturation magnetization, XRD = powder X-ray diffraction, ND = neutron diffraction).

tion states (*e.g.* $NiMn_2O_4$). (2) $CuFe_2O_4$ transforms to a tetragonal structure on quenching. (3) There is always the possibility that the kinetics of the change in cation distribution are so slow at low temperature as to prevent equilibrium or, conversely, are sufficiently fast at high temperature that the cation distribution cannot be quenched. None of these studies contain reversal experiments. Nevertheless, the data seem consistent and support the model.

A recent study by Wu and Mason (1981) using the variation of the Seebeck coefficient as a function of x in Fe_3O_4 deserves separate consideration. Here the range of temperatures investigated was large enough to be sure of a substantial variation in x, and the precision of the determinations was far better than in any of the above studies. Moreover, the rate of attainment of equilibrium was demonstrated to be rapid, and the measurements were carried out at the temperature of interest, thereby obviating quenching problems. An unusual feature of the data is that, unlike the other studied spinels, x in Fe_3O_4 appears to actually reach the random value of 2/3 at high temperatures, and perhaps go slightly beyond it. This suggests that an excess entropy term is necessary. Using a linear form for ΔS_D, we obtained from a nonlinear regression analysis: $\alpha = 24.284 \pm 19.15$ kJ/mol, $\beta = -22.995 \pm 19.15$ kJ/mol, $\Delta S_D = -3.27 \pm 4.47$ J/K mol, $r^2 = 0.986$. Wu and Mason themselves chose to analyze their data according to a simple linear enthalpy plus linear entropy model, which, using the same regression program, gave: $\alpha = -23.643 \pm 0.78$ kJ/mol, $\beta = 0$, $\Delta S_D = -13.83 \pm 0.61$ J/K mol, $r^2 = 0.982$. A nonlinear enthalpy-only model gave: $\alpha = 41.141 \pm 1.65$ kJ/mol, $\beta = 31.195 \pm 0.90$ kJ/mol, $\Delta S_D = 0$, $r^2 = 0.980$, which represents, however, a *metastable* solution at temperatures below about 1000K. The dramatically larger standard deviations of the parameters in the three-parameter fit reflect a high degree of apparent correlation. It therefore does not seem possible to distinguish between the relative merits of these models on statistical grounds alone by using the quality of fit to the data as a criterion. This is one of the reasons we feel it is so important to show that a non-linear enthalpy is to be expected from theoretical considerations.

It is not clear why Fe_3O_4 alone should require an excess entropy term. Moreover, the sign of this is opposite to what one would expect for the electronic entropy effect in Fe^{2+} (see Table 4). Nevertheless, an essentially random cation distribution in Fe_3O_4 at high temperature is consistent with analyses of defect concentrations and transport properties, although nonstoichiometry is again a complication (Dieckmann and Schmalzried, 1977). The question remains whether Fe^{2+} and Fe^{3+} are distinguishable ions on the octahedral sublattice and show a configurational entropy of mixing, or whether they are essentially indistinguishable and an entropy arises from partial electron delocalization, despite the fact that Fe_3O_4 does not exhibit metallic properties. In the latter case, the models developed above would clearly be inapplicable.

All the spinels listed in Table 4 are largely inverse ($x > 2/3$). Much less data exist on the change of cation distribution with temperature for the normal 2–3 spinels. $CoAl_2O_4$ has been examined a number of times (Schmalzried, 1961; Greenwald *et al.*, 1954; Furuhashi *et al.*, 1973), but the results are somewhat contradictory (apart from all authors agreeing that $CoAl_2O_4$ is a basically normal spinel) and no one study covers a sufficient temperature range to apply anything but a one-parameter model. Similar conclusions hold for other 2–3 normal spinels, with the possible exception of $MgAl_2O_4$. Schmocker *et al.* (1972) and Schmocker and Waldner (1976) have used the electron spin resonance of impurity Cr^{3+} ions to measure x from about 700°C to 1000°C with a reported high degree of precision. The two samples used were natural spinels, and therefore not chemically pure, and, rather disconcertingly, each one gave somewhat different results. Nevertheless, the form of the curves of x against T is very similar to that obtained by Navrotsky and Kleppa (1967) for the change in heat of solution for another natural sample of "$MgAl_2O_4$" annealed at various temperatures. This is illustrated in Figure 5.

None of the models used for Fe_3O_4 are able to reproduce the form of the curves shown for $MgAl_2O_4$. Indeed, the apparent sudden and rapid increase in x (and in the heat of solution) over a short temperature interval followed by no further change at higher temperatures suggests to us the possibility of a second-order phase transition in this spinel, which has been wisely postulated and hotly debated in the literature (see Smith (1978) for a recent review). Observation of a second-order transition has been claimed by Mishra and Thomas (1977) at ~450°C on a synthetic spinel grown by the Czochralski method, and anomalous thermal expansion has been measured on another synthetic specimen at 660°C by Suzuki and Kumazawa (1980). The wide range in temperatures reported for these phenomena may be related to the thermal history of the spinel, impurities, or kinetic factors. Indeed, the shapes of the curves describing the variation of cation distribution and enthalpy with temperature may be controlled by kinetic factors, since the changes have not been shown to be reversible. Nevertheless, it does appear that $MgAl_2O_4$, despite lending its name to the whole group of structures, is a rather unusual spinel.

Conclusions

The unit cell parameters, *a*, and oxygen parameters, u, of simple spinels can be predicted accurately using a set of ionic radii which are modified slightly from those of Shannon and Prewitt. Both a and u depend on the degree of inversion, x. Lattice energy calculations have been performed which take into account the depencence of u and a on x. They predict a general quadratic form for the enthalpy of disordering, $\Delta H_D = \alpha x + \beta x^2$.

Most of the data on the change in cation distribution of 2–3 spinels with temperature can be fitted satisfactorily to this simple quadratic "enthalpy only" model. We therefore believe that any vibrational entropy accompanying the disordering process is probably small, and that it is generally not

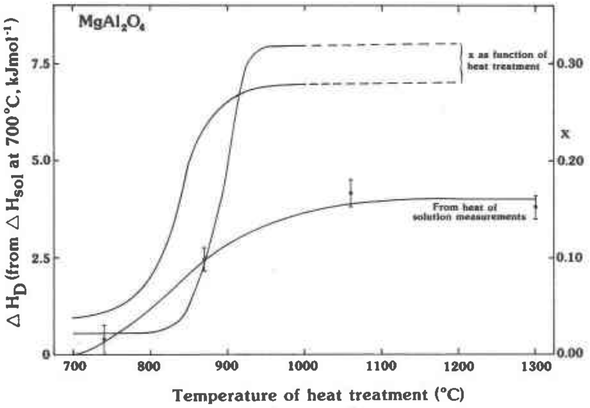

Fig. 5. Degree of disorder (x) versus temperature of heat treatment (°C) for two natural samples of $MgAl_2O_4$ from Schmocker and Waldner (1976), and the change in heat of solution with temperature of heat treatment for another natural sample of $MgAl_2O_4$ from Navrotsky and Kleppa (1967). Note the similarity in the forms of the curves.

necessary to assume a temperature dependence for the free energy of disordering which would be necessitated by such a nonconfigurational entropy term, except possibly for Fe_3O_4 where electronic effects may play a role.

For the 4–2 spinels the change in lattice energy with cation distribution is calculated to be much larger than for the 2–3 spinels. This is confirmed by the fact that the former do not generally show intermediate cation distributions, but show only the normal or the inverse extremes. Short-range order in the octahedral sites of these spinels is probably an important factor in stabilizing the inverse distribution. The volume change on disordering a normal 4–2 spinel is predicted to be slightly positive.

The non-linear nature of the enthalpy term means that the apparent "site preference energy" of an ion depends on the structure of the spinel into which it is substituting. This will have an important effect on cation arrangements in spinel solid solutions, and will be discussed in a subsequent paper.

Acknowledgments

We thank T. R. Mason for providing data prior to publication on the cation distribution in magnetite and J. Stuart for help with statistical analysis. This work was supported by the National Science Foundation, Grants DMR 78-10038 and 81-06027.

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Manuscript received, January 26, 1982;
accepted for publication, August 23, 1982.