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Thermodynamics of nonconvergent cation ordering in minerals: II. Spinels and the orthopyroxene solid solution

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ABSTRACT

A linear term in the order parameter, Q, has been added to a normal Landau free energy expansion to describe the thermodynamics of nonconvergent cation ordering in normal and inverse spinels and in the orthopyroxene solid solution. The excess free energy due to ordering, with respect to a fully disordered state, is given by

$$G = -hQ + \tfrac{1}{2}a(T - T_c)Q^2 + \tfrac{1}{6}cQ^6.$$

Using published experimental data for Q as a function of temperature, T, and for the excess enthalpy as a function of Q, values for the Landau coefficients have been determined. For $NiAl_2O_4$, these are $h = -69400$, $a = 444$, $T_c = 686$ K, and $c = 7\,680\,000$; for $MgAl_2O_4$, $h = 8580$, $a = 19.7$, $T_c = 395$ K, and $c = 16400$; and for $En_{50}Fs_{50}$, $h = 7750$, $a = 22.5$, $T_c = 195$ K, and $c = 12100$, with h and c expressed in units of J/mol, and a in J/mol·K.

The observed a coefficients differ from the values that would be expected if the entropy changes were exclusively configurational and due to long-range ordering. In the case of $NiAl_2O_4$, the large additional excess entropy is consistent with the suggestion that some other process accompanies Ni-Al ordering. For $MgAl_2O_4$, a reduced excess entropy would be consistent with some short-range ordering. For $En_{50}Fs_{50}$, an apparently additional entropy could be accounted for by nonconfigurational contributions, though the uncertainty propagated from calorimetric data is large. Nonlinear compositional dependence for the a and c coefficients allows the effects of Mg-Fe^{2+} ordering on the mixing properties of the enstatite-ferrosilite solid solution to be assessed quantitatively, though a fully analytical description has not been derived.

The Landau expansions are compared with more widely used models of nonconvergent ordering. The principal differences are in the simplification of the excess entropy description ($S \propto Q^2$) and in the extension of the description of excess enthalpy to three terms, one linear in Q, the second quadratic in Q, and one higher order term. In principle, both configurational and nonconfigurational entropy contributions can be accounted for.

INTRODUCTION

In a companion paper (Carpenter et al., 1994), the formal basis on which Landau theory may be adapted to describe the thermodynamics of nonconvergent processes was set out. Some theoretical justification and an analysis of the inherent assumptions involved were also presented. The main aims were to develop a unified treatment of order-disorder behavior and, more specifically, to generate thermodynamic expressions that can be used to account for nonconvergent ordering in individual minerals or mineral solid solutions with a wide variety of structures. A purely macroscopic approach has been adopted and, for the present, inquiries concerning microscopic driving forces and mechanisms are not carried far.

In this paper, Landau expansions are used to describe nonconvergent ordering in spinels and the orthopyroxene solid solution. In a third paper (Carpenter and Salje, 1994) a system with order parameter coupling, potassium feldspar, is treated. These systems have been selected for two reasons. In the first place, they illustrate different types of general nonconvergent behavior that are encountered in minerals. Secondly, sufficient experimental data are available for them to illustrate thoroughly how the approach may be applied to real systems, yielding quantitative descriptions of the thermodynamic changes accompanying cation ordering. The form of the Landau free energy expansion adopted is (from Carpenter et al., 1994)

$$G = -hQ + \tfrac{1}{2}a(T - T_c)Q^2 + \tfrac{1}{n}e_nQ^n \qquad (1)$$

where Q is the order parameter, h, a, and e_n are Landau coefficients, T_c is some particular temperature, and n is a constant expected to be 3, 4, or 6. Similarities and differences between this expansion and existing thermodynamic models for nonconvergent cation ordering are also discussed.

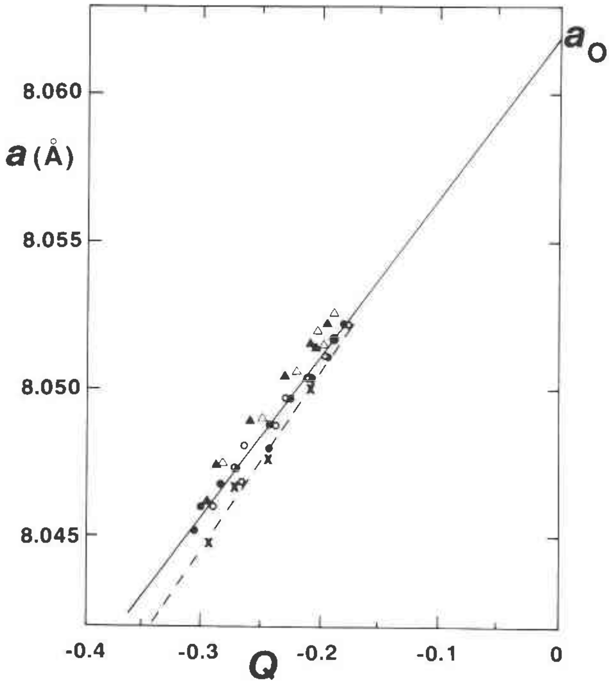

Fig. 1. Variation of the unit-cell dimension, *a*, with *Q* for $NiAl_2O_4$, showing a linear relationship. Solid and open circles, from O'Neill et al. (1991); solid and open triangles, from Roelofsen et al. (1992) for crystals annealed initially at 800 and 1300 °C, respectively; Xs are lattice parameter data from Mocala and Navrotsky (1989) plotted against *Q* from O'Neill et al. (1991) for samples with equivalent equilibration temperatures. The solid line is a least-squares fit to the O'Neill et al. (1991) data giving a_0 (at $Q = 0$) = 8.0620 Å. The broken line is a least-squares fit to the Mocala and Navrotsky data.

SPINELS: $NiAl_2O_4$ AND $MgAl_2O_4$

The degree of order in oxide spinels of the form AB_2O_4 is usually defined in terms of an inversion parameter, *x*. This parameter varies between $x = 0$, when all the A atoms are on the tetrahedral site and all B atoms on the octahedral sites (normal spinel), and $x = 1$, when all the A atoms are on octahedral sites and the B atoms occupy both tetrahedral and octahedral sites (inverse spinel). A random distribution of A and B atoms between the tetrahedral and octahedral sites has $x = 0.67$. In a Landau free energy expansion, the excess energy due to ordering is defined with respect to the fully disordered state, for which the order parameter, *Q*, is zero. It is necessary to convert the values of *x* usually quoted in papers on spinels to a Landau order parameter using

$$Q = -\tfrac{3}{2}x + 1. \tag{2}$$

This gives $1 > Q > 0$ for spinels with normal order and $0 > Q > -0.5$ for spinels with inverse order.

Representatives of the two types of ordering in spinel for which appropriate experimental data are available in the literature are $NiAl_2O_4$ and $MgAl_2O_4$.

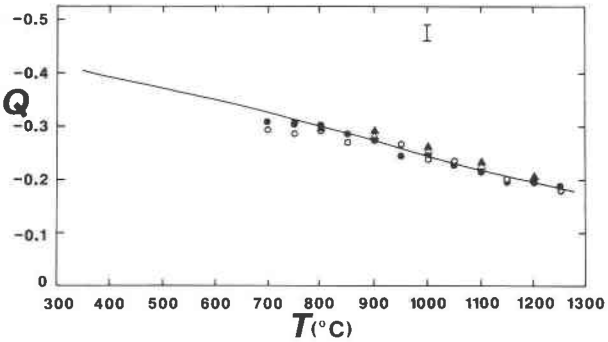

Fig. 2. Temperature dependence of *Q* for $NiAl_2O_4$; data and symbols as in Fig. 1. The curve is a solution to Equation 4, with $a/h = -0.0064$, c/h ($\equiv e_6/h$) = -110.6, $T_c = 686$ K. The scale bar indicates a typical magnitude of 2σ for the data of O'Neill et al. (1991).

$NiAl_2O_4$

$NiAl_2O_4$ is a largely inverse spinel that has been investigated extensively (O'Neill et al., 1991, and references therein). Use is made here of the crystallographic data of O'Neill et al. (1991) and the calorimetric data of Mocala and Navrotsky (1989). The more recent crystallographic data of Roelofsen et al. (1992) are almost indistinguishable from the results of O'Neill et al. (1991), as shown in Figures 1 and 2.

For any material undergoing nonconvergent ordering, the expected relationship between *Q* and any lattice strain accompanying the ordering is $e_{ik} \propto V_s \propto Q$ (Carpenter et al., 1994). V_s is the volume strain and e_{ik} ($i,k = 1$–6) represents the components of a spontaneous strain tensor. For a cubic material, the only nonzero strain components are given by

$$e_{11} = e_{22} = e_{33} = \frac{a - a_0}{a_0} \tag{3}$$

with *a*, here, as the lattice parameter of a crystal that has some nonzero value of *Q*, and a_0 as the lattice parameter of a crystal with $Q = 0$. Strain-order parameter relationships of this type appear to be valid even if the lattice parameters are measured at room temperature from quenched samples rather than, more rigorously, at the relevant equilibration temperature (e.g., Carpenter et al., 1990). The data of O'Neill et al. (1991) for *Q* (calculated from values of *x* given in their Table 5) as a function of *a* are shown in Figure 1. The linear least-squares fit to the data gives a value of $a_0 = 8.0620$ Å and a slope of 0.0547 Å per unit of *Q*. Thus Equation 3 gives $e_{11} = 0.0068Q$ and $V_s \approx 3e_{11} = 0.0204Q$ at room temperature. At $Q = -0.5$, i.e., for complete inverse order, the linear strain is ~3‰, and the volume strain is ~1%. Strains of this magnitude are almost certainly large enough to ensure that the interaction length of *Q* is effectively determined by strain fields in $NiAl_2O_4$ and also that the system will not behave as if at the pure order-disorder limit (Carpenter et al., 1994). In addition, the problem of higher order entropy terms, needed to correct the predictions of simple Landau expansions at large values of Q, does not arise because $|Q|$ is smaller than 0.5 for inverse ordering. It is therefore reasonable to proceed with Equation 1 as a basis for describing the thermodynamic changes.

The equilibrium condition from Equation 1 is

$$\frac{\partial G}{\partial Q} = 0 = -1 + \frac{a}{h}(T - T_c)Q + \frac{e_n}{h}Q^{n-1}. \tag{4}$$

Observed values of Q and T were substituted into this equation to yield a series of linear equations in a/h, T_c, and e_n/h. Values for these coefficients were then found using a linear least-squares program kindly provided by T.J.B. Holland. An initial choice of $n = 4$ did not give a particularly well-constrained fit, whereas $n = 6$ gave a much better fit (Fig. 2) with $a/h = -0.0064$, $T_c = 686$ K, and $c/h = -110.6$ (relabeling e_6 more conventionally as the Landau coefficient c). This gives an extrapolated temperature of −82 K for $Q = -0.50$, which is within realistic uncertainty limits of 0 K.

Mocala and Navrotsky (1989) measured the enthalpy changes that occurred when crystals with some degree of order, Q_T, reequilibrated at 780 °C in a drop calorimeter. The values of Q_T for their samples have been retrieved by comparing their lattice parameter data with those of O'Neill et al. (1991). A systematic difference of ~0.001 Å between the data in each set was attributed by O'Neill et al. to some slight nonstoichiometry in the Mocala and Navrotsky (MN) samples. A second calibration of the lattice parameter a as a function of Q is shown for the MN samples in Figure 1. It was assumed that the refined site occupancies of O'Neill et al. are more accurate than those of Mocala and Navrotsky and that the results from samples annealed at 800, 900, 1000, and 1100 °C represent equilibrium states. The values of a for the MN samples annealed at these temperatures have been plotted against the O'Neill et al. values of Q to give, by least-squares fitting, $a = 8.0626 + 0.0599Q$ Å. This relationship has then been used to calculate Q_T for all the values of a of the MN samples prepared for calorimetry.

The next assumptions are that the equilibrium value of Q at the calorimeter temperature, 780 °C, is −0.30 (see Fig. 2) and that the values of ΔH_{annl} discussed by Mocala and Navrotsky are the enthalpy differences between crystals with $Q = Q_T$ and crystals with $Q = -0.30$. From Equation 1 (and see Carpenter et al., 1994), the Landau excess enthalpy for ordering in $NiAl_2O_4$ is expected to be

$$H = -hQ - \tfrac{1}{2}aT_cQ^2 + \tfrac{1}{6}cQ^6. \tag{5}$$

The difference $H_{Q=-0.30} - H_{Q=Q_T}$ should be equal to ΔH_{annl}. Taking the ratios of a/h and c/h as determined above, together with $T_c = 686$ K and the retrieved values of Q_T, values of h were determined for the four samples of Mocala and Navrotsky: $h = -86580 \pm 15873$, -66667 ± 5797, -55801 ± 5525, and -68599 ± 8696 J/mol. Uncertainties were propagated from the calorimetric values to show the range of scatter in the data. An average value of $h = -69412$ J/mol was then used to calculate $a = 444$ J/mol·K and $c = 7\,676\,967$ J/mol. Finally, H as a function of Q was calculated with these values of the coefficients in Equation 5; a comparison with experimental data is shown in Figure 3. The experimental values of H shown in Figure 3 are given by $H_{Q=-0.30} - \Delta H_{\text{annl}}$, with $H_{Q=-0.30}$ calculated as −33.6 kJ/mol. Some idea of the magnitude of uncertainties in the thermodynamic parameters Q and H, and hence also in S and G, is provided by the scatter of data around the calculated degrees of order and excess enthalpies shown in Figures 2 and 3. Only enthalpy data for the MN samples annealed at $T > 1500$ °C show a substantial deviation from the calculated values. Taking the best available experimental data at face value in this way thus yields the excess free energy due to nonconvergent ordering in $NiAl_2O_4$ spinel as (in J/mol)

$$G = 69412Q - 222(T - 686)Q^2 + 1\,279\,500Q^6. \tag{6}$$

Five significant figures are given for the coefficients only for the benefit of internally consistent calculations and do not signify any confidence in such a degree of accuracy.

As stressed by Carpenter et al. (1994), the microscopic origin of individual terms in this series expansion is only understood at a qualitative level. The large linear term (the effective field) implies that most of the energy of ordering comes from some intrinsic structural advantages of placing Al on tetrahedral sites and Ni on octahedral sites rather than the other way around. Energy changes due to interactions of the nearest neighbor type (Al-Ni, Ni-Ni, and Al-Al) can be associated with the coefficient of the Q^2 term and are much smaller overall. The excess entropy is

$$S = -\tfrac{1}{2}aQ^2 \tag{7}$$

and the value of the a coefficient can be used to raise questions concerning different sources of entropy related to the ordering in the usual way. A purely configurational entropy change associated with ordering from $Q = 0$ to $Q = -0.50$ would be $3R(\tfrac{1}{3}\ln\tfrac{1}{3} + \tfrac{2}{3}\ln\tfrac{2}{3}) - 2R(\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}\ln\tfrac{1}{2}) = -4.35$ J/mol·K. The purely configurational contribution to the a coefficient would therefore be 34.8 J/mol·K. An electronic contribution of R ln 3 associated with transferring Ni^{2+} from octahedral coordination to tetrahedral coordination has been suggested (O'Neill and Navrotsky, 1983; Navrotsky, 1986; O'Neill et al., 1991). For the change $Q = 0$ to $Q = -0.50$, this would give an excess entropy of $\tfrac{1}{3}R\ln 3 = -3.04$ J/mol·K and, hence, a contribution of 24.3 J/mol·K to the a coefficient. These two effects are small in relation to the observed value of 444 J/mol·K (with an uncertainty of at least ±70 J/mol·K), however. If the calorimetric enthalpies are correct, either the remaining excess entropy is vibrational, which seems unlikely for such a large difference, or there are other configurational effects accompanying the ordering. Mocala and Navrotsky (1989) proposed Al ordering onto normally vacant octahedral sites as an additional possi-

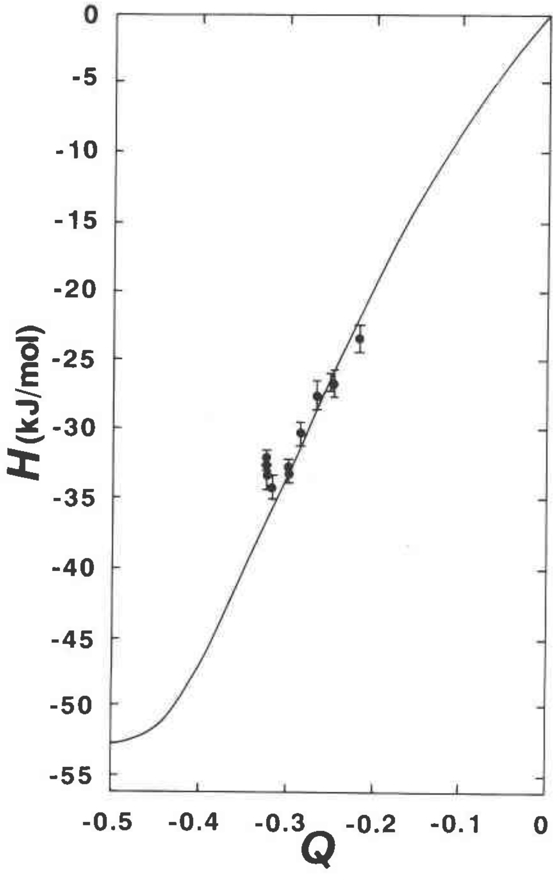

Fig. 3. Excess enthalpy, H, as a function of Q for $NiAl_2O_4$, calculated using Equation 5 with $h = -69.4$ kJ/mol, $a = 444$ J/mol·K, $T_c = 686$ K, $c = 7680$ kJ/mol. Data from Mocala and Navrotsky (1989).

bility, and a Landau treatment of such ordering might be based on order parameter coupling, with separate order parameters to describe the inverse and vacancy ordering.

$MgAl_2O_4$

Ordering in $MgAl_2O_4$ spinel is normal in character. Experimental data defining the extent of disorder as a function of temperature (Wood et al., 1986; Peterson et al., 1991; Millard et al., 1992) are just sufficient, when combined with limited calorimetric data (Navrotsky and Kleppa, 1967; Navrotsky, 1986), to place constraints on the values of the coefficients in a Landau free energy expansion. The only room-temperature lattice parameter measurements for crystals with different degrees of order appear to be those of Wood et al. (1986), who showed that there is a measurable change of cell edge, a, with Q. There is therefore a measurable lattice strain, with the implication (see Carpenter et al., 1994) that the interaction length of Q should be determined by strain fields rather than purely local atomic effects. Only three data points are given by Wood et al. (1986), however, with the result that the quantitative relationship between Q and lattice strains cannot yet be determined.

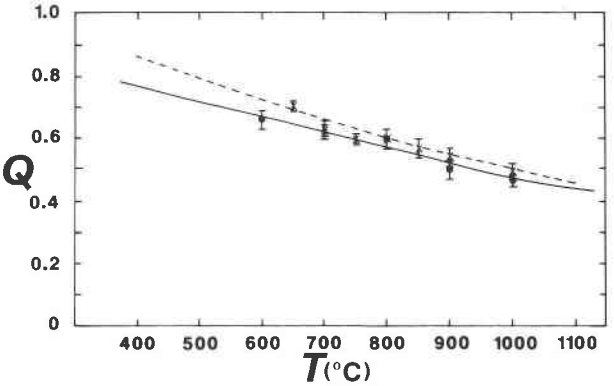

Fig. 4. Variation of Q as a function of T for $MgAl_2O_4$. Data from Peterson et al. (1991): Xs, sample from Union Carbide; solid circles, sample given to Peterson et al. by Wood. The solid line is a solution to Equation 4 with $a/h = 0.0023$, $T_c = 395$ K, c/h ($\equiv e_6/h$) = 1.91. The broken line is the fit obtained by Peterson et al. (1991) to the equation for equilibrium of O'Neill and Navrotsky (1983), with $\alpha = 31$, $\beta = -10$ kJ/mol.

There are discrepancies between the three most recent determinations of Q variations with T (Wood et al., 1986; Peterson et al., 1991; Millard et al., 1992). The results of Peterson et al. have been preferred here (Fig. 4) as they were obtained by refinement of neutron powder diffraction data collected in situ at high temperatures and are not subject to problems of reordering during quenching. Values of a/h, T_c, and e_n/h in Equation 4 were extracted by the same least-squares fitting procedure as before for a series of simultaneous equations involving the value of Q (or the average of two values from different samples where given by Peterson et al.) at each equilibration temperature. Data collected at 600 and 650 °C were excluded because of doubts over whether they represent equilibrium states (Peterson et al., 1991). The scatter and limited range of the data are such that large correlations occurred between the coefficients during the fitting procedure, and it was found to be necessary to include $Q = 1$ at 0 K if reasonably well-constrained values were to be extracted. The fit was found to be much improved, also, if $n = 6$ was used in place of $n = 4$ in Equation 4. The final preferred solution had $a/h = 0.0023$, $T_c = 395$ K, and c/h ($\equiv e_6/h$) = 1.908 and yields the variation of Q with T shown in Figure 4.

Two separate measurements of enthalpy changes accompanying changes in the degree of order are available with which to define absolute values for the coefficients from the ratios above. Navrotsky (1986) used synthetic samples and transposed drop calorimetry to measure enthalpy differences between crystals annealed at (and then quenched from) 1200 or 1400 °C and crystals equilibrated in the calorimeter at 700 °C. Reordering during quenching from temperatures above ~1000 °C seems to give a reproducible degree of order corresponding approximately to the equilibrium value of Q at 1000 °C (Wood et al., 1986; Millard et al., 1992). Taking the average value of enthalpy differences measured by Navrotsky (1986) as

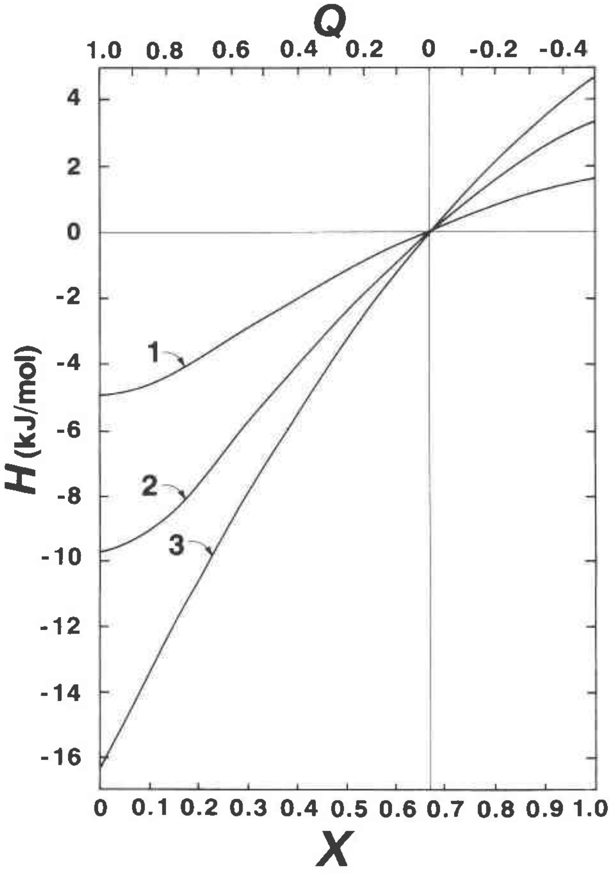

Fig. 5. Variation of excess enthalpy, H, as a function of Q for $MgAl_2O_4$. Curves 1 and 2 are from Equation 5 with $h = 4.29$ kJ/mol, $a = 9.87$ J/mol·K, and $c = 8.19$ kJ/mol, and $h = 8.58$ kJ/mol, $a = 19.7$ J/mol·K, and $c = 16.4$ kJ/mol, respectively. Curve 3 is for ΔH_D from Equation 9, with $\alpha = 31$, $\beta = -10$ kJ/mol.

-900 ± 530 J/mol and values of $Q = 0.625$ and $Q = 0.475$ for crystals equilibrated at 700 and 1000 °C, respectively, then yields $h = 4292 \pm 2527$ J/mol, $a = 9.87 \pm 5.81$ J/mol·K, and $c = 8189 \pm 4822$ J/mol, with $T_c = 395$ K. The uncertainties quoted here are only those derived from the uncertainty in the enthalpy measurement.

If it is alternatively assumed that synthetic $MgAl_2O_4$ crystals can only partially reequilibrate at 700 °C during a characteristic measuring time of 45–60 min, larger values of the coefficients are obtained. Repeating the calculations assuming $Q = 0.55$ instead of $Q = 0.475$, i.e., allowing for only half the total possible change in Mg-Al order, yields $h = 8575 \pm 5048$ J/mol, $a = 19.72 \pm 11.61$ J/mol·K, and $c = 16361 \pm 9632$ J/mol. The variation of H as a function of Q for both sets of coefficients is shown in Figure 5.

The high-temperature solution calorimetric results of Navrotsky and Kleppa (1967), as quoted by Navrotsky (1986), provide a second measurement of the enthalpy change accompanying disordering in $MgAl_2O_4$. The difference in heat of solution between a natural sample and the same sample quenched from annealing temperatures of 1000–1300 °C is given by Navrotsky (1986) as 4.0 ± 0.4 kJ/mol. Taking this result at face value would rule out the solution with $a = 9.9$ J/mol·K, since the predicted enthalpy difference between crystals with $Q = 0.475$ (the assumed structural state of the annealed samples) and crystals with $Q = 1$ would only be 2.4 kJ/mol (Fig. 5). On the other hand, an enthalpy difference of 4 kJ/mol would be consistent with $Q = 0.83$ and an apparent equilibration temperature of ~250 °C for the natural spinel, if the set of coefficients with $a = 19.7$ J/mol·K is used. An uncertainty of ±400 J/mol in the calorimetric result extends the apparent equilibration temperature up to a possible high-temperature limit of ~350 °C. Clearly, further enthalpy measurements are needed to constrain the absolute values of coefficients more accurately, but the latter solution may at least be consistent with what data there are.

The excess free energy due to ordering can be given as (for $a = 19.7$)

$$G = -8600Q + 9.85(T - 395)Q^2 + 2733Q^6. \quad (8)$$

As in the case of $NiAl_2O_4$, the largest proportion of the stabilization energy for ordering is due to the linear term and can thus be associated with an intrinsic structural advantage of placing Mg in tetrahedral sites and Al in octahedral sites of the spinel structure. The contribution of nearest neighbor interaction effects of the types Mg-Al, Mg-Mg, and Al-Al, although apparently energetically favorable overall, since T_c is positive, is evidently somewhat less. In contrast with the case of $NiAl_2O_4$, the a coefficient (~19.7 J/mol·K) is smaller than what would be expected if the excess entropy were purely configurational from long-range order. The ideal configurational entropy change due to a change in structural state from $Q = 0$ to $Q = 1$ would be $3R(\frac{1}{3}\ln\frac{1}{3} + \frac{2}{3}\ln\frac{2}{3}) = -15.88$ J/mol·K, with the result that the empirical a coefficient would be expected to have a value in the vicinity of 32 J/mol·K (from Eq. 7). The low excess entropy is consistent with the analysis of Wood et al. (1986), who suggested that phase-equilibrium data for the reaction 2enstatite + spinel = pyrope + forsterite require the spinel to have less configurational entropy than what would be calculated from average site occupancies. They proposed short-range ordering, perhaps due to local charge-balance requirements, as a possible explanation. The value of the a coefficient obtained here is not sufficiently well constrained by the calorimetric data to provide an independent confirmation of the phase equilibrium analysis, however.

Comparison with other models for nonconvergent ordering in spinels

O'Neill and Navrotsky (1983) gave the enthalpy change, ΔH_D, due to disordering of a fully ordered ($x = 0$) normal spinel as

$$\Delta H_D = \alpha x + \beta x^2 \quad (9)$$

where x is the inversion parameter (see also Navrotsky, 1986; O'Neill et al., 1991). In practice, the coefficients α and β are treated as empirical constants, though O'Neill and Navrotsky were able to justify their physical origin on a more microscopic basis. The Landau excess enthalpy, which is defined with respect to complete disorder ($x = 0.67$, $Q = 0$) is also nonlinear in the degree of order, and the form of Equation 5 is the same as that of Equation 9. The only substantial difference is that the Landau expansion has a higher order term. The fact that best fits to both the $NiAl_2O_4$ and $MgAl_2O_4$ data have Q^6 rather than Q^4 as the high-order term may simply indicate that the former provides a better approximation for several significant high-order terms. In studies of phase transitions, tricritical behavior has been found to be common, which implies that the fourth-order term is probably small for sound physical reasons.

We compared our predicted enthalpy changes for $MgAl_2O_4$ with those calculated from Equation 9, using values of $\alpha = 31$ and $\beta = -10$ kJ/mol, which were obtained by Peterson et al. (1991) as the best fit to their structure refinement data. Values calculated from Equation 9 were then redefined relative to $\Delta H_D = 0$ at $x = 0.67$ to give excess enthalpies that are directly comparable with the Landau excess enthalpies (Fig. 5). Although they give different enthalpies, the coefficients used to calculate the three curves shown in Figure 5 (Landau, $a = 9.9$ J/mol·K; Landau, $a = 19.7$ J/mol·K; and O'Neill and Navrotsky, $\alpha = 31$, $\beta = -10$ kJ/mol), all give equally good fits to the data for Q (or x) as a function of T. More experimentally determined enthalpies are needed to determine which model provides the best representation of the real thermodynamic properties of $MgAl_2O_4$.

O'Neill and Navrotsky (1983) separated the entropy due to disordering of a fully ordered normal spinel into two contributions: an ideal configurational entropy, ΔS_C, and a nonconfigurational entropy, ΔS_D. The form of ΔS_C is given in the normal way as some function of average site occupancies or as an explicit function of x. In general, ΔS_D might be expected to be small, but it need not be if there are entropy changes due, for example, to differences in the degeneracy of electron orbitals of transition metals in tetrahedral or octahedral coordination, or to significant vibrational effects accompanying changes in the degree of order, or to local ordering. Wood et al. (1986) and O'Neill et al. (1991) expressed ΔS_D as a linear function of x, such as $x\Delta S^0_D$, where ΔS^0_D is the difference in standard-state entropy between fully normal and fully inverse end-member structures. The Landau excess entropy includes both these contributions in the a coefficient of Equation 7 under the assumption that they are approximately proportional to Q^2 (Carpenter et al., 1994).

The full free energy due to disordering, ΔG_D, in the O'Neill and Navrotsky model is

$$\Delta G_D = \alpha x + \beta x^2 - T(x\Delta S^0_D + \Delta S_C) \qquad (10)$$

Since ΔS_C is a straightforward function of x, there are three constants, α, β, and ΔS^0_D, that must be extracted from experimental data. This contrasts with the four unknowns, h, a, e_n, and T_c, in a Landau expansion of the form of Equation 1. If the constraint that $Q = 1$ at 0 K is added to the Landau description, it follows that $h = e_n - aT_c$ and, therefore, that the number of independent variables is reduced to three. In both approaches the accuracy of predicted thermodynamic changes accompanying atomic ordering depends on the accuracy of the experimental data, for Q and H as a function of T, say; in the range where these data are collected each model should provide the same quality of fit. A Landau expansion perhaps provides the more valid description for systems in which nonconfigurational entropy contributions become significant because of the way in which such entropies are automatically accounted for.

Sack and Ghiorso (1991a) have approached the problem of nonconvergent ordering in spinels from a slightly different point of view (see also Sack and Ghiorso, 1991b; Ghiorso and Sack, 1991). Their order parameter, s, is also scaled to vary between zero and unity, but $s = 0$ for a fully inverse spinel, and $s = 1$ for a fully ordered normal structure. They used different coefficients, but their treatment of ordering in pure end-member crystals is ultimately identical to that of O'Neill and Navrotsky (1983), though they assumed $\Delta S^0_D = 0$. Their coefficients are related to α and β by

$$\alpha = W - \Delta H^* \qquad (11)$$

$$\beta = -W \qquad (12)$$

where ΔH^* is the enthalpy difference between states with $x = 0$ and $x = 1$, and W is a regular solution parameter describing the excess enthalpy of mixing between fully inverse and fully normal ordered states. Comparison with the thermodynamic model of Della Giusta and Ottonello (1993) is not as straightforward because their parameterization, involving interionic potentials, is quite different.

O'Neill and Navrotsky (1984), Nell and Wood (1989), and Sack and Ghiorso (1991a) have extended earlier models to treat spinel solid solutions (see also Anderson and Lindsley, 1988; Nell et al., 1989; Wood et al., 1991). Comparable extensions using Landau free energy expansions are beyond the scope of this present paper but could be achieved simply by allowing the coefficients to become composition dependent (Carpenter et al., 1994). Linear variations with composition might be adequate for solid solutions in which the degree of order is not particularly sensitive to the substitutions involved, but nonlinear variations may be required for solid solutions with significant singularities.

Order parameter coupling

Landau formalism opens the possibility of providing widely applicable thermodynamic descriptions of spinels that undergo more than one structural change. The basis for this has been well explored in the treatment of order parameter coupling during phase transitions (recent reviews by Salje, 1990, 1992; Carpenter, 1992). For ex-

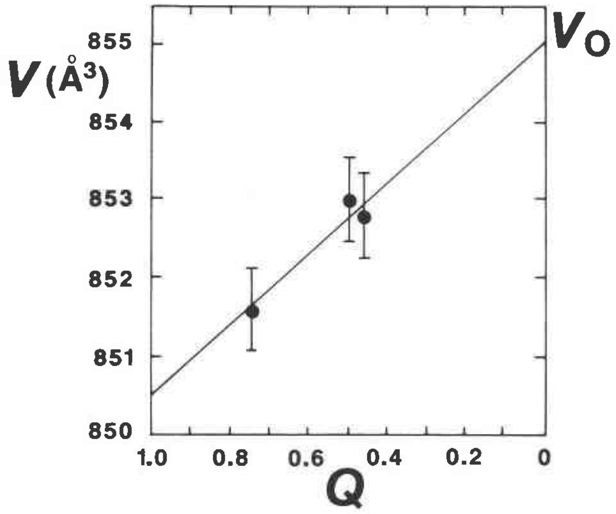

Fig. 6. Unit-cell volume, V, as a function of Q for orthopyroxene crystals with $X_{Fs} \approx 0.50$. Data from Domeneghetti et al. (1985). The straight line is a least-squares fit to the data, though it is clearly subject to a large uncertainty. The unit-cell volume, V_0, corresponding to $Q = 0$ is 855.1 Å³.

ample, cation ordering and magnetic ordering processes might interact, or there might be a discrete phase transition in the spinel that is influenced by the extent of nonconvergent order. The two most likely general solutions, using two order parameters, Q_1 and Q_2, to describe the two processes of interest, would be, for bilinear coupling

$$G = -h_1Q_1 + \tfrac{1}{2}a_1(T - T_{c1})Q_1^2 + \tfrac{1}{n_1}e_{n1}Q_1^{n_1} - h_2Q_2 + \tfrac{1}{2}a_2(T - T_{c2})Q_2^2 + \tfrac{1}{n_2}e_{n2}Q_2^{n_2} + \lambda Q_1Q_2 \qquad (13)$$

or, for linear-quadratic coupling:

$$G = -h_1Q_1 + \tfrac{1}{2}a_1(T - T_{c1})Q_1^2 + \tfrac{1}{n_1}e_{n1}Q_1^{n_1} + \tfrac{1}{2}a_2(T - T_{c2})Q_2^2 + \tfrac{1}{4}bQ_2^4 + \tfrac{1}{6}cQ_2^6 + \lambda Q_1Q_2^2. \qquad (14)$$

In Equation 13, both Q_1 and Q_2 represent nonconvergent processes, whereas in Equation 14 Q_1 represents a nonconvergent process and Q_2 a convergent process. In each case, λ represents a coupling coefficient describing the strength of interactions between the separate processes. An example of how the linear-quadratic coupling equation may be applied in practice is given elsewhere for Al-Si ordering in potassium feldspar (Carpenter and Salje, 1994).

ORTHOPYROXENE SOLID SOLUTION: $MgSiO_3$-$FeSiO_3$

Thermodynamic models of the $MgSiO_3$-$FeSiO_3$ (enstatite-ferrosilite) solid solution in effect distinguish conveniently between energies due to random mixing of Mg and Fe^{2+} on M1 and M2 sites in the series $Mg^{M1}Mg^{M2}Si_2O_6$-$Fe^{M1}Fe^{M2}Si_2O_6$ and energies from ordering in the series $Mg^{M1}Fe^{M2}Si_2O_6$-$Fe^{M1}Mg^{M2}Si_2O_6$ (Sack, 1980; Ganguly, 1982; Davidson and Lindsley, 1985, 1989; Sack and Ghiorso, 1989; Shi et al., 1992; and references therein). Comparable energy contributions are incorporated into a Landau free energy expansion but are treated differently. Carpenter et al. (1994) showed that the energy due to independent mixing on sites appears primarily in the Q^2 term, and the additional ordering energy is described by the full series expansion in Q. A full treatment of the solid solution may be accomplished by allowing the Landau coefficients to vary with composition. In this section, ordering at $En_{50}Fs_{50}$ is treated first, before proceeding to derive mixing properties that combine both ordering and solid-solution effects. With regard to the latter, it should be emphasized that the main objective here is to make use of the extensive data for orthopyroxenes to examine the manner in which Landau coefficients might vary with composition in nonconvergent systems.

Ordering in crystals with composition $En_{50}Fs_{50}$

The order parameter used here to describe the degree of Mg-Fe^{2+} order between M1 and M2 sites is taken as

$$Q = X^{M2}_{Fe^{2+}} - X^{M1}_{Fe^{2+}} \qquad (15)$$

where $X^{M2}_{Fe^{2+}}$ and $X^{M1}_{Fe^{2+}}$ represent the mole fraction of Fe^{2+} occupying the M2 and M1 sites, respectively. There are just sufficient data in the literature to suggest that variations in Q for crystals close to $En_{50}Fs_{50}$ are accompanied by significant lattice strains. From simple strain coupling considerations (Carpenter et al., 1994) a relationship of the form $Q \propto V_s$ is expected, where the volume strain, V_s, is given by

$$V_s = \frac{V - V_0}{V_0}. \qquad (16)$$

V is the unit-cell volume of a crystal with some nonzero value of Q, and V_0 is the unit-cell volume of a crystal at the same temperature, but with $Q = 0$. In practice, the unit-cell volume at room temperature is expected to be a linear function of Q. A linear fit to three data points from Domeneghetti et al. (1985), who determined site occupancies by structure refinement from single-crystal X-ray data, gives $V_0 = 855.1$ Å³ (ignoring the large uncertainties), and, hence, $V_s = -0.005$ for a crystal with $Q = 1$ held at room temperature (Fig. 6). The importance of such a strain would be, firstly, that it points to the probability of some nonconfigurational entropy being associated with the cation ordering. The thermodynamic behavior of the system is therefore not expected to be at the pure order-disorder limit. Secondly, local fluctuations in Q are unlikely to be significant. The lattice parameters given by Chatillon-Colinet et al. (1983) confirm the trend of decreasing unit-cell volume with increasing order, but the degree of order for each sample was not specified. A reliable strain analysis will require a more extensive data set.

Besancon (1981) used Mössbauer spectroscopy to determine the distribution of Fe^{2+} and Mg between the M1 and M2 crystallographic sites, as a function of temperature, in crystals with composition close to $En_{50}Fs_{50}$. Values of Q from his data have been used to determine values for T_c and the coefficient ratios a/h and e_n/h in Equation 4, following the same procedure as was applied to spinels. The results from annealing crystals at high temperatures did not allow tight constraints to be placed on the values of these parameters because they displayed high correlations in the linear least-squares fitting procedure. $Q = 1$ at 0 K was therefore included as an additional data point. Two results from synthetic samples with almost the same composition due to Grammenopoulu (1981) were also used to reduce the uncertainties at high temperatures. Values of $n = 4$ and $n = 6$ in Equation 4 yielded equally good fits, but, on the basis of the experience gained from analyzing spinels and the results for orthopyroxenes with other compositions (see below), $n = 6$ has been preferred. A best-fit solution with $a/h = 0.0029$, $T_c = 195$ K, and c/h ($\equiv e_6/h$) $= 1.565$ is shown in Figure 7. These values give an apparent equilibration temperature of 271 °C for the natural sample of Besancon (1981), for which $Q = 0.71$.

Chatillon-Colinet et al. (1983) measured an enthalpy difference of 3556 ± 1381 J/mol at 750 °C between a natural ordered crystal with composition close to $Mg_{0.5}Fe_{0.5}SiO_3$ and the same sample heat-treated at 1150 °C. Reordering in orthopyroxenes annealed at high temperatures occurs rapidly with the result that samples quenched from above ~1000 °C tend to show a degree of order corresponding to an apparent equilibration temperature of ~950–1000 °C (Besancon, 1981; Chatillon-Colinet et al., 1983). With the results of Besancon (1981) and the fit parameters given above, it is assumed that the natural sample of Chatillon-Colinet et al. had $Q = 0.71$ and the heat-treated sample had $Q = 0.32$ (corresponding to 950 °C). The measured enthalpy difference corresponding to this difference in states of order and the expression for excess enthalpies (Eq. 5) then yield absolute values of the Landau coefficients: $h = 7750 \pm 3010$ J/mol, $a = 22.5 \pm 8.7$ J/mol·K, and $c = 12130 \pm 4710$ J/mol for $T_c = 195$ K. The uncertainties are derived from the uncertainty in the calorimetric data.

The purely configurational excess entropy, S_{config}, associated with complete ordering in crystals with composition $Mg_{0.5}Fe_{0.5}SiO_3$ would be −5.76 J/mol·K. This would give a value for the Landau a coefficient of 11.52 J/mol·K (from Eq. 7). The observed a coefficient of 22.5 ± 8.7 J/mol·K is significantly larger at a $\pm 1\sigma$ level, implying that there could be some nonconfigurational entropy accompanying the ordering. Essentially the same result is obtained from the fit to Equation 4 with $n = 4$, though the extracted value of h is smaller and the value of T_c larger than for the case of $n = 6$.

The excess free energy of ordering in crystals of $Mg_{0.5}Fe_{0.5}SiO_3$ may thus be written as

$$G = -7747Q + 11.25(T - 195)Q^2 + 2020Q^6. \quad (17)$$

The excess enthalpy is given by

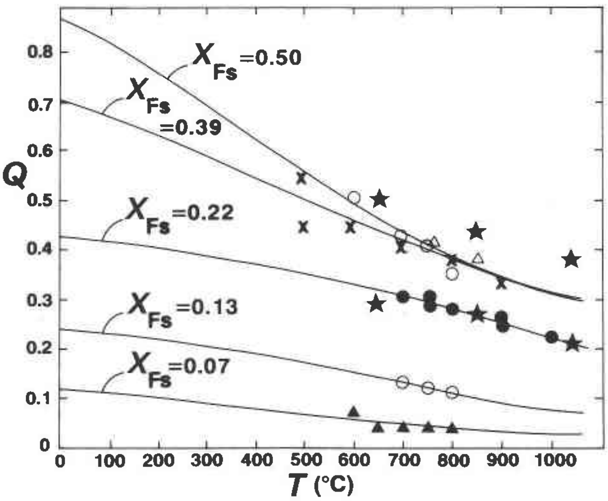

Fig. 7. Variation of Q as a function of T for orthopyroxene crystals with different compositions. Solid triangles, $X_{Fs} \approx 0.07$, Mössbauer data from Skogby (1992); open circles, $X_{Fs} \approx 0.13$ and $X_{Fs} \approx 0.50$, from Besancon (1981); solid circles, $X_{Fs} \approx 0.22$, from Molin et al. (1991); Xs, $X_{Fs} \approx 0.39$, from Anovitz et al. (1988); open triangles, $X_{Fs} \approx 0.50$, from Grammenopoulu (1981); stars, $X_{Fs} \approx 0.21$ and $X_{Fs} \approx 0.50$, from Domeneghetti and Steffen (1992). The curves are solutions to Equation 4 for each composition using the coefficients for three variable solutions given in Table 2. Note that the data of Domeneghetti and Steffen (1992) were not used to fit the curve for $X_{Fs} \approx 0.50$; they serve to indicate a level of uncertainty in the equilibrium variation of Q for this composition.

$$H = -7747Q - 2194Q^2 + 2020Q^6 \quad (18)$$

and is illustrated in Figure 8. Values of h and c derived from setting $a = 11.52$ J/mol·K are 3970 J/mol and 6220 J/mol, respectively. The variation of H as a function of Q using this set of coefficients is also shown in Figure 8 for comparison. According to these expressions, much of the driving force for ordering is due to the linear term and is thus associated with an intrinsic structural advantage of placing Fe^{2+} on M2 and Mg^{2+} on M1 rather than with nearest neighbor interactions of the Mg-Mg, Fe-Fe, and Mg-Fe type.

Ordering in the $MgSiO_3$-$FeSiO_3$ solid solution

Variations in Q as a function of composition taken from the literature are shown in Figure 9. The definition of Q given in Equation 15 has been used to define the degree of order. A compositional parameter X_{Fs}, the mole fraction of $FeSiO_3$ component, has been taken as

$$X_{Fs} = \frac{X^{M2}_{Fe^{2+}} + X^{M1}_{Fe^{2+}}}{2}. \quad (19)$$

Ideally, only crystals with compositions close to the En-Fs binary join, i.e., with low Ca, Al, Fe^{3+}, and Mn contents, should be considered on the basis of these definitions. The straight lines on Figure 9 show the limits of

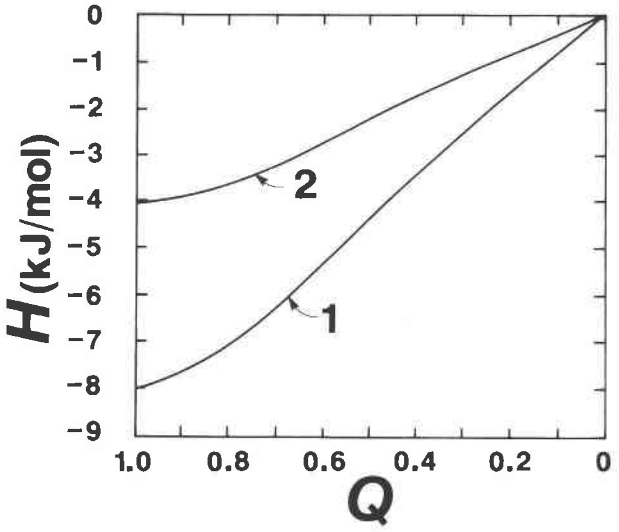

Fig. 8. Excess enthalpy as a function of Q for $En_{50}Fs_{50}$, calculated using Equation 5: curve 1 for $h = 7.75$ kJ/mol, $a = 22.5$ J/mol·K, $T_c = 195$ K, $c = 12.1$ kJ/mol; curve 2 for $h = 3.97$ kJ/mol, $a = 11.52$ J/mol·K, $T_c = 195$ K, $c = 6.22$ kJ/mol. The latter is a better representation of ordering behavior with small or negligible contributions from nonconfigurational entropy effects.

Table 1. Q as a function of temperature and composition for orthopyroxene crystals, as used in this paper

Composition (X_{Fs})	Annealing T (°C)	Q	Reference*
0.50	natural	0.71	1
	600	0.50	1
	700	0.43	1
	750	0.41	1
	800	0.36	1
	750	0.41	2
	850	0.38	2
0.39	natural	0.67	3
	500	0.45–0.55	3
	600	0.45	3
	700	0.41	3
	800	0.37	3
	900	≤0.34	3
0.22	natural	0.41	4
	700	0.31	4
	750	0.29–0.30	4
	800	0.28	4
	900	0.25–0.26	4
	1000	0.23	4
0.13	natural	0.20	1
	700	0.13	1
	750	0.12	1
	800	0.11	1
0.07	natural	0.083	5
	600	0.069	5
	650	0.048	5
	700	0.045	5
	750	0.041	5
	800	0.039	5

* 1, Besancon (1981); 2, Grammenopoulu (1981); 3, Anovitz et al. (1988), sample no. M32b; 4, Molin et al. (1991); 5, Skogby (1992), sample no. AV77 (Mössbauer data).

complete order, with either all Fe^{2+} on M2 (for $0 < X_{Fs} < 0.5$) or the M2 site fully occupied by Fe^{2+} (for $0.5 < X_{Fs} < 1$). The data are sufficiently scattered that any asymmetry in the solid solution would be difficult to prove. For present purposes the properties of the solid solution will be treated as being symmetric about $X_{Fs} = 0.5$.

Data from Anovitz et al. (1988), Molin et al. (1991), Besancon (1981), and Skogby (1992) have been used to extract values for Q as a function of temperature in crystals with compositions $X_{Fs} = 0.39$, 0.22, 0.13, and 0.07, respectively. Skogby et al. (1992) suggested that site occupancies determined by Mössbauer spectroscopy can give apparently lower degrees of order than those determined by structure refinements using X-ray diffraction data. On the other hand, Domeneghetti and Steffen (1992) found good agreement between the two techniques. An uncritical view has been adopted here, and the published data have been taken at face value; the resulting values of Q are all given in Table 1. The real uncertainties associated with these values are not well known, since there may be interlaboratory variations in the structural state determinations.

Values of a/h, T_c, and c/h were determined at each of the four compositions in the same way as for the crystals with $X_{Fs} = 0.50$. It was found that $n = 6$ tended to give tighter constraints on these values than $n = 4$. As before, the point $Q = Q_{max}$ at 0 K was also included in the fitting procedure, where Q_{max} is the maximum possible degree of order at each composition, and is given by $Q_{max} = 2X_{Fs}$. The solutions are given in Table 2 and shown graphically in Figure 7. They give apparent equilibration temperatures for the natural samples of ~90–350 °C (Table 2).

There are no additional calorimetric data to allow absolute values of the coefficients to be extracted at each composition, and a further assumption is therefore necessary. Of all the Landau parameters, h is the least likely to show a strong compositional dependence, since it is a reflection of the intrinsic structural differences between M1 and M2 sites in orthopyroxenes. The value of $h = 7750 \pm 3010$ J/mol, derived earlier from the solution calorimetric results of Chatillon-Colinet et al. (1983), has therefore been assumed to apply to the complete solid solution. The resulting values of the a coefficient are given in Table 2 and Figure 10a, again with uncertainties propagated only from the calorimetric measurement. A solid line in Figure 10a shows the expected variation of ln a with X_{Fs}, with the assumption that the excess entropy due to ordering is exclusively configurational in origin, i.e., that:

$$a_{config} = -\frac{2S_{config}}{Q^2_{max}}. \qquad (20)$$

It is evident that the observed values of a are, within the $\pm 1\sigma$ uncertainty limits, indistinguishable from purely configurational values for all compositions except as X_{Fs}

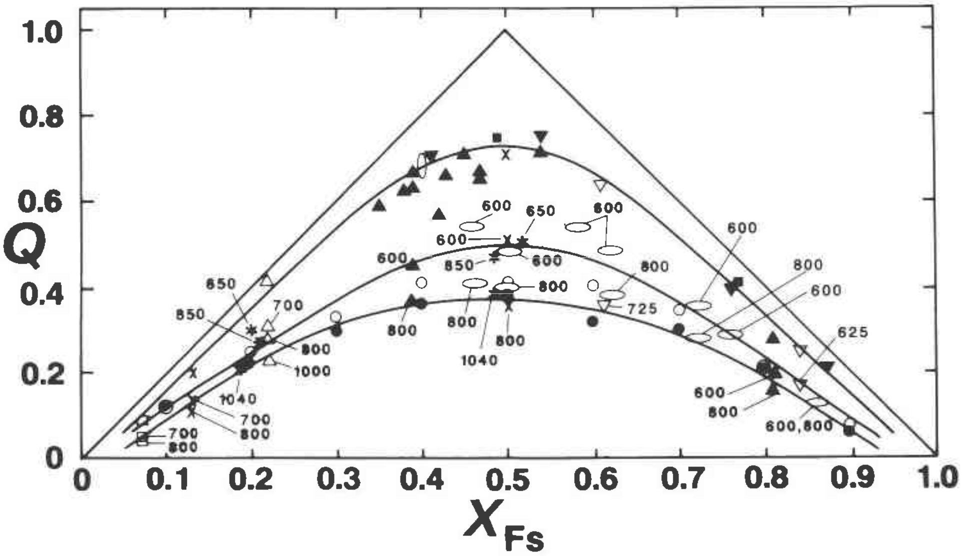

Fig. 9. Data for Q as a function of T and mole fraction of $FeSiO_3$ component, X_{Fs}, for the En-Fs solid solution. Horizontal ovals, from Saxena and Ghose (1971); solid inverted triangles, metamorphic samples from Ghose and Hafner (1967); open triangles, from Molin et al. (1991); open squares, Mössbauer data from Skogby et al. (1992); open inverted triangles, from Sykes-Nord and Molin (1993); solid squares, from Domeneghetti et al. (1985); vertical ovals, from Tribaudino and Talarico (1992); solid (850 °C) and open (750 °C) circles, from Grammenopoulu (1981); Xs, from Besancon (1981); stars, from Domeneghetti and Steffen (1992); solid triangles, from Anovitz et al. (1988). The straight lines indicate the maximum possible degree of order attainable. The highest values of Q refer to natural specimens; annealing temperatures (in °C) are given for the experimental samples. Curves are drawn in as a guide to the eye for natural specimens and for annealed samples with equilibration temperatures of 600 and 800 °C.

$\rightarrow 0.5$. In the range $\sim 0.3 < X_{Fs} < 0.5$, the a coefficient is apparently approximately constant. The variation of the c coefficient is shown in Figure 10b, and the variation of T_c in Figure 10c.

These individual solutions may now be used to produce smoothed variations of the Landau coefficients as a function of composition in order to produce a complete thermodynamic model for the solid solution. Both a and c clearly diverge as $X_{Fs} \rightarrow 0$ (Fig. 10a, 10b), and a linear composition dependence would be incorrect. In contrast, T_c varies to a lesser extent (Fig. 10c) and can be represented adequately by the linear relation

$$T_c = 629 - 868X_{Fs}. \tag{21}$$

Using fixed values of T_c (K) from this fit, new values of a/h and c/h were extracted by repeating the fitting procedure, now with only two variables for each of the experimental data sets. The new values are given in Table

Table 2. Values for the Landau coefficients obtained by fitting values of Q at different T (as given in Table 1) in Equation 4

X_{Fs}	a/h	aT_c/h	c/h	T_c (K)	$T_{nat,equil}$ (°C)	a (J/mol·K)*
			three-variable solutions			
0.50	0.0029(3)	0.565(315)	1.565(315)	195	271	22.5(8.7)
0.39	0.0029(1)	0.565(151)	4.985(409)	195	91	22.5(8.7)
0.22	0.0073(11)	5.32(1.34)	167.3(30.1)	729	143	56.6(22.0)
0.13	0.0187(7)	11.43(71)	3337(155)	611	320	144.9(56.3)
0.07	0.0342(26)	10.99(2.63)	47186(6853)	321	335	264.9(102.9)
			two-variable solutions using $T_c = 631 - 872X_{Fs}$ (K)			
0.50	0.0029(3)		1.565(316)	195	271	22.5(8.7)
0.39	0.0033(0)		6.053(54)	290	100	25.6(9.9)
0.22	0.0047(1)		94.32(1.95)	438	117	36.4(14.1)
0.13	0.0154(1)		2579(17)	516	300	119.3(46.3)
0.07	0.0534(14)		97468(2263)	568	434	413(161)

Note: $T_{nat,equil}$ is the calculated equilibration temperature for the natural sample at each composition using the given coefficient ratios. Numbers in parentheses represent the uncertainties (1σ) derived from the least-squares fits; they are shown only to indicate how tightly constrained the coefficients are by the experimental data. For the three variable solutions, values of a/h, aT_c/h, and c/h were obtained; the value quoted for T_c is taken from these, and its uncertainty can be propagated from the uncertainty in a/h and aT_c/h.

* For $h = 7750 \pm 3010$ J/mol.

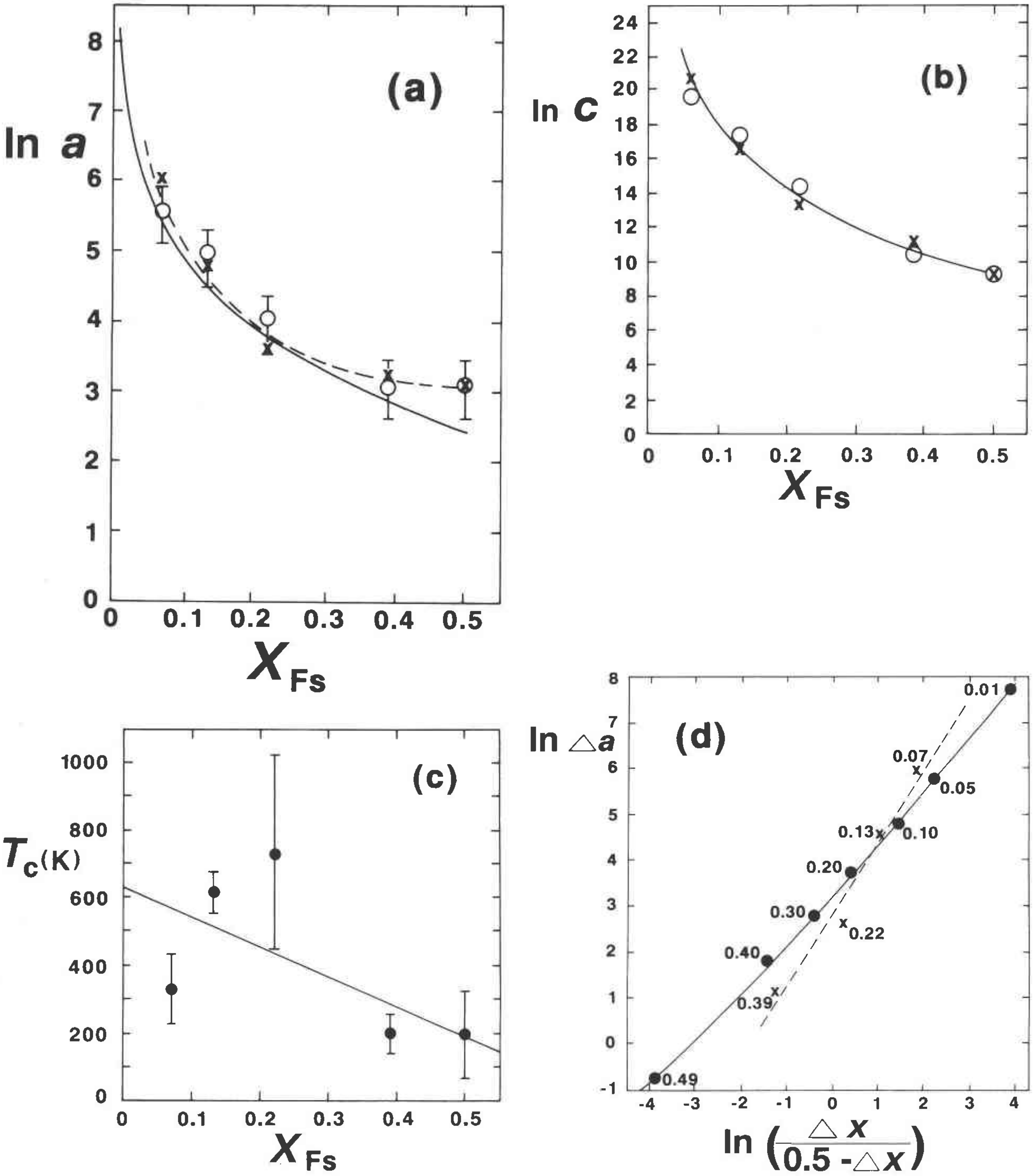

Fig. 10. Variations of Landau coefficients with composition for $0 > X_{Fs} > 0.5$. (**a**) A plot of ln a: open circles (with experimental uncertainties) derived from three-variable solutions to Equation 4 (a/h, T_c, and c/h); Xs derived from two-variable solution (a/h and c/h), with smoothed values of T_c. The solid line gives the expected variation if the excess entropy is purely configurational, and the broken line is the smoothed fit to the data calculated using Equation 23. (**b**) A plot of ln c: symbols as in **a**. The solid line is the calculated variation with $h = 7.75$ kJ/mol, the smoothed values of a and T_c, and $Q = Q_{max}$ at 0 K. (**c**) T_c: uncertainties are derived from the least-squares fitting procedure for a/h, T_c, c/h in Equation 4. The solid line is a least-squares fit to the data, constrained to pass through 195 K at $X_{Fs} = 0.5$. (**d**) A plot of ln Δa as a function of $\ln[\Delta X/(0.5 - \Delta X)]$. Xs indicate observations, with the broken line as a least-squares fit yielding Equation 23. The solid line is the expected variation if the excess entropy is entirely configurational in character. Numbers by each point give composition as the mole fraction of the Fs component.

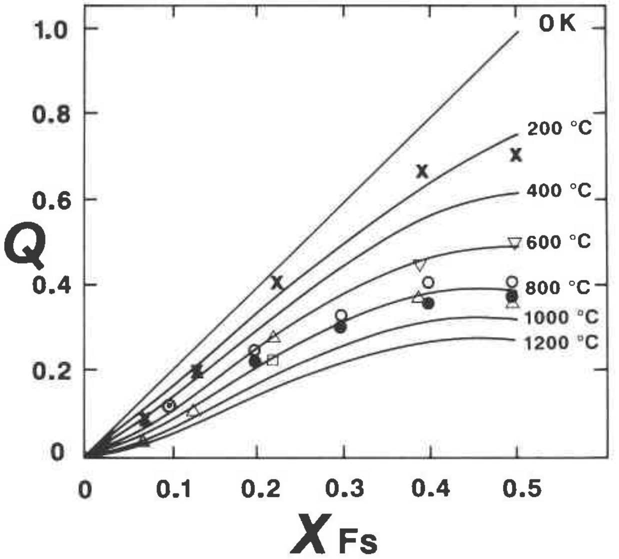

Fig. 11. Calculated variation of Q as a function of T and X_{Fs} (smooth curves). Xs, natural samples; open inverted triangles, 600 °C equilibration; open circles, 750 °C equilibration; open triangles, 800 °C equilibration; solid circles, 850 °C equilibration; open squares, 1000 °C equilibration.

2, with the derived values of a and c also displayed in Figure 10. On a purely empirical basis, and following from the discussion in Carpenter et al. (1994), it was found that the variation of a is consistent with a compositional dependence of the form

$$\Delta a \propto \left(\frac{\Delta X}{0.5 - \Delta X}\right)^{r} \qquad (22)$$

where Δa is the deviation of the a coefficient from its value at $X_{Fs} = 0.50$, ΔX is the deviation from $X_{Fs} = 0.50$, and r is a constant. This expression gives the right type of divergence as $\Delta X \rightarrow 0.5$, and calculated values of a_{config} from Equation 20 conform quite closely to it (Fig. 10d). The smoothed variation of a has therefore been taken (in J/mol·K) as:

$$a = 22.5 + 17.3\left(\frac{\Delta X}{0.5 - \Delta X}\right)^{1.58}. \qquad (23)$$

The fit of this equation to the observed data points is also shown in Figure 10a and 10d.

As also discussed by Carpenter et al. (1994), the c coefficient is not an independent parameter if the degree of order at a given temperature is specified. In this case, values of c were calculated by choosing $h = 7750$ J/mol, T_c as specified by Equation 21, and a as specified by Equation 22 and then by setting $Q = Q_{max}$ at 0 K. The results are in close agreement with the observed values (Fig. 10b). Finally, Q was calculated for different temperatures and compositions by substituting smoothed values of the coefficients into Equation 4 (with $n = 6$). These are compared with experimental values in Figure 11.

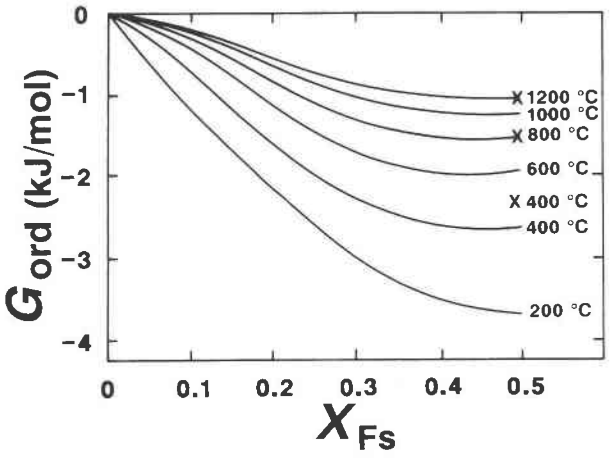

Fig. 12. Free energy of ordering, G_{ord}, as a function of T and X_{Fs} calculated using Equation 1, with h constant and a, T_c, and c ($\equiv e_6$) varying with composition (with $a = 22.5$ J/mol·K at $X_{Fs} = 0.5$, etc.). The Xs are G_{ord} calculated for 1200, 800, and 400 °C at $X_{Fs} = 0.5$, using $a = 11.52$ J/mol·K and the associated set of coefficients.

Mixing properties

The excess free energy due to ordering, G_{ord}, from smoothed values of the coefficients in Equation 1, is shown for different temperatures and compositions in Figure 12. Only the range $0 < X_{Fs} < 0.5$ is shown because the solid solution is assumed to behave symmetrically. Since the Landau excess free energy is defined with respect to completely disordered ($Q = 0$) states, the total free energy of mixing for ordered crystals, $\Delta G_{mix,o}$, is given by G_{ord} plus the free energy of mixing of the disordered solid solution, $\Delta G_{mix,d}$. The entropy of mixing of the disordered solid solution, $\Delta S_{mix,d}$, can be calculated in the normal way, assuming only configurational contributions. The enthalpy of mixing, $\Delta H_{mix,d}$, is obtained by combining the observed calorimetric enthalpy of mixing for crystals with some state of order, $\Delta H_{mix,o}$, with the Landau excess enthalpy of ordering, H_{ord}. Specifically,

$$\Delta H_{mix,d} = \Delta H_{mix,o} - H_{ord} \qquad (24)$$

as illustrated in Figure 13. Chatillon-Colinet et al. (1983) did not determine the structural state of the synthetic orthopyroxenes that provided evidence for a small positive excess enthalpy of mixing. Assuming that ordering of synthetic samples during cooling from high temperatures may be more rapid than ordering of natural samples, because of a higher concentration of defects in the former, the effective equilibration temperature of the synthetic samples has been taken as 900 °C. Equation 5 gives the excess enthalpy due to ordering in these samples if the equilibrium values of Q for 900 °C are used along with the smoothed coefficients. These values, combined with the regular solution fit $\Delta H_{mix,o} = 3975X_{En}X_{Fs}$ from Chatillon-Colinet et al. (1983), have been used to generate the curve for $\Delta H_{mix,d}$ shown in Figure 13. The disordered solid solution shows a significant deviation from

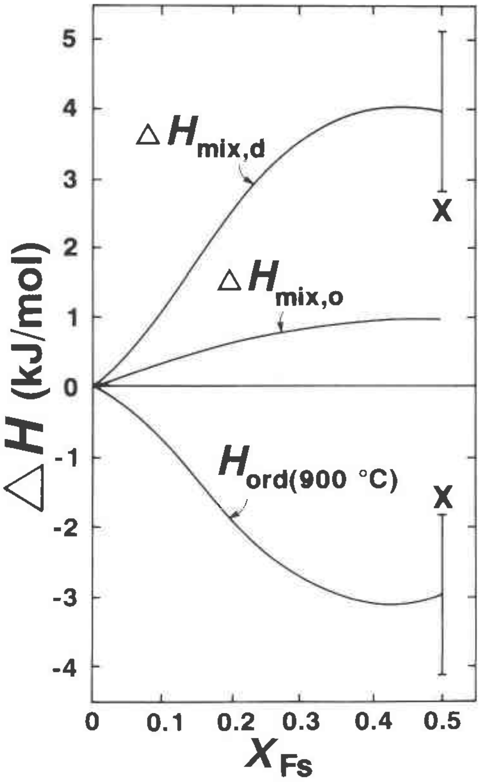

Fig. 13. Calculated enthalpy of ordering at 900 °C, H_{ord}, from the Landau solution, enthalpy of mixing of the partially ordered solid solution, $\Delta H_{mix,o}$, from Chatillon-Colinet et al. (1983) and the net enthalpy of mixing of the disordered solid solution, $\Delta H_{mix,d}$. The three enthalpies are related as in Equation 24, with $a = 22.5$ J/mol·K, etc. The error bars at $X_{Fs} = 0.5$ are given to indicate the range of possible values for H_{ord} and $\Delta H_{mix,d}$ as propagated from the calorimetric uncertainty ($\pm 1\sigma$) of the original measurement of the enthalpy due to disordering a natural sample, from Chatillon-Colinet et al. (1983). Xs indicate values of H_{ord} at 900 °C and $\Delta H_{mix,d}$, for the set of coefficients with $a = 11.52$ J/mol·K.

ideality, as in most other models of the mixing properties. Finally, assuming $\Delta H_{mix,d}$ to be independent of temperature, $\Delta G_{mix,o}$ was calculated at 1200, 800, and 400 °C from

$$\Delta G_{mix,o} = G_{ord} + \Delta H_{mix,d} - T\Delta S_{mix,d}. \quad (25)$$

The calculated values are shown in Figure 14.

It should be noted that a consequence of choosing the variation of Q_0 for 0 K shown in Figure 11 and a compositional dependence for a of the form given by Equation 22 is that the mixing curves have a discontinuous change in slope at $X_{Fs} = 0.50$ (e.g., in Fig. 14). No pretense is made that a properly analytic description of the mixing behavior has been obtained, but, for comparison with other models of the orthopyroxene solid solution, the activity of the Fs component, a_{Fs}, was estimated by a simple graphical treatment of the curves for $\Delta G_{mix,o}$. The results are shown in Figure 15a and show positive deviations from ideality with a dip, implying increased stability due to ordering, around the midcomposition range. In addition, the activities do not vary substantially in the temperature interval 400–1200 °C because of the balancing effect of contributions from G_{ord} and $\Delta H_{mix,d}$. At lower temperatures the free energy of ordering dominates, at least in the vicinity of $X_{Fs} = 0.50$, as shown by the calculated variation of γ_{Fs} ($=a_{Fs}/X_{Fs}$) for this composition (Fig. 15b). Uncertainty limits are shown at $X_{Fs} = 0.5$ in Figures 13, 14, and 15 to illustrate the propagated uncertainty derived from the calorimetric data used to calculate absolute values for the coefficients h, a, and c. The lower values of a_{Fs} may be preferred in that they are derived from an a coefficient that is closer to a value that would imply only a small nonconfigurational contribution to the excess entropy. If the calorimetric data for ordering are disregarded entirely and the a coefficient is set at 11.52 J/mol·K for $X_{Fs} = 0.5$, using the configurational entropy arguments set out earlier, the predicted enthalpy and free energy due to ordering are less negative (Figs. 8 and 12). Then $\Delta H_{mix,d}$ is less positive (Fig. 13), $\Delta G_{mix,o}$ is more negative (Fig. 14), and the activity of the Fs component is reduced (Fig. 15).

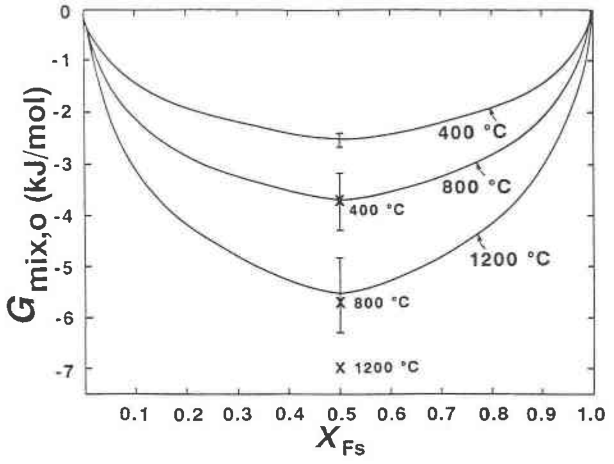

Fig. 14. Calculated free energies of mixing of partially ordered orthopyroxene solid solutions as a function of T. The error bars are the uncertainty limits propagated from the calorimetric measurement of disordering a natural sample, as in Fig. 13. As in Figs. 12 and 13, Xs indicate values calculated using the set of coefficients with $a = 11.52$ J/mol·K.

Comparison with other models

Positive deviations from ideal mixing have been predicted for the orthopyroxene solid solution, and these are qualitatively consistent with the more direct activity measurements of Kitayama and Katsura (1968) at 1204 °C and of Sharma et al. (1987) at 727 °C. Given that this is the first calculation of mixing properties in a nonconvergent system from a Landau perspective, the agreement is adequate. The principal source of experimental uncertainty in the present analysis derives from the calorimetric data for ordering, since these have been used to scale values for the *a* coefficients. A smaller value of *a* for $En_{50}Fs_{50}$ propagates through to smaller activities of the end-member components (Fig. 15), and these are more consistent with the activities derived by Shi et al. (1992) and Sack and Ghiorso (1989). The latter used Fe-Mg partitioning between olivine and orthopyroxene to constrain the orthopyroxene mixing behavior, as have also Koch-Müller et al. (1992) and von Seckendorff and O'Neill (1993). There must also be some concern with regard to the available data for Q as a function of T. Recent results of Domeneghetti and Steffen (1992) for crystals with compositions $X_{Fs} \approx 0.5$ and ≈ 0.21 are shown in Figure 7. A large discrepancy with the older data for $X_{Fs} \approx 0.5$ is evident. Improved structural and calorimetric data should allow values of the Landau coefficients to be extracted with more confidence.

As discussed by Carpenter et al. (1994), the Landau free energy expansion for nonconvergent ordering has a form similar to the expression proposed for the orthopyroxene solid solution by Sack (1980) and Sack and Ghiorso (1989). The latter gave, for the excess enthalpy relative to ideal mixing

$$\begin{aligned} H_{\text{excess}} = {} & \tfrac{1}{2}\Delta H^0_{\text{exch}}s + (\Delta H^0_{\text{rec}} + W_{\text{M1}} + W_{\text{M2}})X_{\text{En}}X_{\text{Fs}} \\ & - (\tfrac{1}{2} - X_{\text{Fs}})(W_{\text{M1}} - W_{\text{M2}})s \\ & - \tfrac{1}{4}(W_{\text{M1}} + W_{\text{M2}} - \Delta H^0_{\text{rec}})s^2 \end{aligned} \tag{26}$$

where W_{M1} and W_{M2} are regular solution parameters for Mg-Fe mixing on M1 and M2 sites, respectively, and ΔH^0_{exch} is the standard enthalpy for the exchange reaction $Fe^{M1}Mg^{M2} \rightleftharpoons Mg^{M1}Fe^{M2}$. From the reciprocal reaction, ΔH^0_{rec} is given by:

$$\Delta H^0_{\text{rec}} = H^0_{\text{Fe}^{\text{M2}}\text{Mg}^{\text{M1}}} + H^0_{\text{Mg}^{\text{M2}}\text{Fe}^{\text{M1}}} - H^0_{\text{Fe}^{\text{M2}}\text{Fe}^{\text{M1}}} - H^0_{\text{Mg}^{\text{M2}}\text{Mg}^{\text{M1}}}. \tag{27}$$

Because the order parameter, *s*, of Sack and Ghiorso (1989) is defined in the same way as Q, the values of their coefficients can be compared directly with the values of the Landau coefficients for $X_{Fs} = 0.5$. Sack and Ghiorso gave $\tfrac{1}{2}\Delta H^0_{\text{exch}} = -1956$ J/mol [all molar quantities given for (Mg,Fe)SiO_3], which compares with $-h = -7750$ or -3970 J/mol for the Landau coefficients corresponding to small and negligible nonconfigurational entropy, respectively. For $\tfrac{1}{4}(W_{M1} + W_{M2} - \Delta H^0_{\text{rec}})$ they gave 2312 J/mol, which compares with $\tfrac{1}{2}aT_c = 2194$ or 1123 J/mol. For the mixing behavior of the disordered solid solution, a regular solution mixing parameter describing the data shown in Figure 13 would be ~16 kJ/mol, or ~10 kJ/mol for the smaller *a* coefficient, which compares with $(W_{M1} + W_{M2} + \Delta H^0_{\text{rec}}) \approx 7.4$ kJ/mol given by Sack and Ghiorso. The contribution from the high-order Landau term is small; it is absent in the Sack and Ghiorso equation.

This comparison serves to show that the values derived for the parameters are at least of the same order of magnitude and emphasizes the similarity of the two formulations. However, Sack and Ghiorso (1989) assumed that all nonconfigurational entropy contributions are effec-

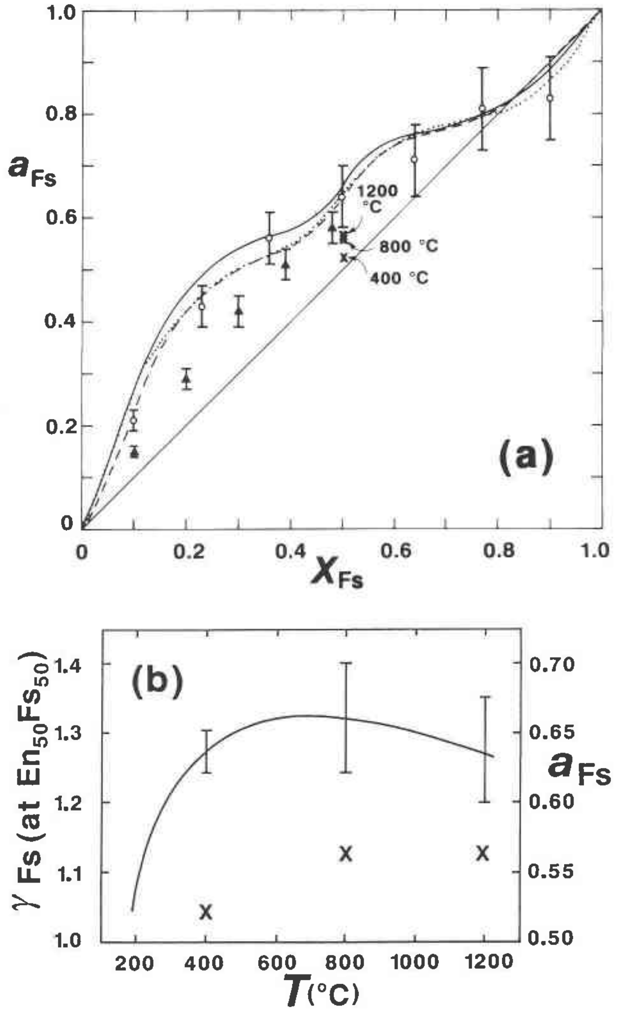

Fig. 15. (**a**) Calculated activities of Fs component, a_{Fs}, in the En-Fs solid solution for different temperatures. Dotted line, 400 °C; solid line, 800 °C; broken line, 1200 °C. Data are from Sharma et al. (1987, measurements made at 727 °C), circles; and from Kitayama and Katsura (1968, measurements made at 1204 °C), triangles. Note that no attempt has been made to constrain the calculated activities to fit the experimentally derived activities. Smaller calculated activities would be obtained if a smaller value of the enthalpy of ordering were used to derive the absolute values of the Landau coefficients *h*, *a*, and *c*; Xs indicate the results with the set of coefficients where $a = 11.52$ J/mol·K at 1200, 800, and 400 °C for crystals with $X_{Fs} = 0.5$. The uncertainty at $X_{Fs} = 0.5$, 1200 °C propagated from $\pm 1\sigma$ for the calorimetric measurement of the enthalpy of disordering a natural sample by Chatillon-Colinet et al. (1983) is slightly smaller than the uncertainty shown for the data point of Sharma et al. at this composition. (**b**) Calculated variation of the activity coefficient, γ_{Fs}, for $En_{50}Fs_{50}$ ($a_{Fs} = \gamma_{Fs}X_{Fs}$). Note that in the range ~400–1200 °C, a positive excess energy of mixing and a negative energy of ordering combine to give an approximately constant value of γ_{Fs}. At low temperatures, the energy of ordering dominates and γ_{Fs} decreases. The error bars indicate a propagated uncertainty, as in Figs. 13, 14, and 15a. Xs as in **a**.

tively zero. The Landau solution makes no such assumption but depends rather sensitively on the quality of the experimental data for Q as a function of T and for H as a function of Q in obtaining the correct value of the a coefficient. Davidson and Lindsley (1985, 1989) and Shi et al. (1992) assigned any nonconfigurational entropy effects to the temperature dependence of some or all of the coefficients, thereby increasing the number of adjustable parameters. If $W_{M1} \neq W_{M2}$ in Equation 26, it follows that a composition dependence for the linear term in s (or Q) might be expected.

Finally, in the present analysis it has also not been necessary to make assumptions concerning the mixing behavior of other solid solutions. As found by von Seckendorff and O'Neill (1993), for example, attempts to constrain the mixing properties of the En-Fs solid solution from Mg-Fe partitioning data between olivine and orthopyroxene highlight the strong correlations that can arise between fit parameters refined for each solid solution.

DISCUSSION

The primary objective of this paper has been to demonstrate that a modified Landau free energy expansion provides a practical and quantitative description of nonconvergent cation ordering in different types of minerals. In comparison with other models, possible advantages of the Landau approach relate to the simplification of the treatment of entropy and the more sophisticated treatment of enthalpy. Because nonconfigurational contributions to the excess entropy vary with Q^2 to a good approximation, any deviations of a system from the strict order-disorder limit will tend to give a progressively more Landau-like total excess entropy. In the two spinel systems and $En_{50}Fs_{50}$ orthopyroxene the observed excess entropies gave some evidence of contributions from effects other than ideal long-range ordering. On the other hand, contributions to the excess enthalpy affect different terms in the expansion. The linear term reflects energy changes due to structural differences between sites in a crystal, and the quadratic term reflects variations in interaction energies of the nearest neighbor type. Higher order terms, approximated by a single term in Q^4 or, with apparently more precision, in Q^6, can account for further neighbor interactions and interactions that are other than pairwise. In all three examples, the available experimental data are reconciled by a single form of equation.

Extension of the approach to solid solutions at this stage has been limited to an exploration of the compositional dependence of Landau coefficients in a system for which there are many experimental data available. Investigations of other solid solutions will indicate the extent to which linear and nonlinear variations of the Landau coefficients with composition might reproduce more general behavior. In the case of orthopyroxenes, with it established that the energetics of mixing and ordering can be reproduced by using selected data at different discrete compositions, it should be a straightforward matter to use all the available data for Q as a function of T and X to refine values of the coefficients. More reliable enthalpy measurements would still be needed, but any scatter in the structural data from different samples and different laboratories would be smoothed. Individual data points that might be incorrect would have less influence on the total thermodynamic description. The variations with composition of experimentally derived Landau coefficients from other solid solutions may also provide different patterns of behavior that shed light on the physical origin of the coefficients and also stimulate discussion of theoretical dependencies that eventually yield fully analytical expressions.

In the first paper of this series (Carpenter et al., 1994), an analogy was drawn between nonconvergent cation ordering and the known influence of externally applied fields on materials undergoing phase transitions. The relative strengths of the field energy and the normal driving energy, as expressed by the ratio $h{:}aT_c$, turn out to be quite comparable. Salje (1990) drew attention to the effects of fields with $h/aT_c \approx 0.20$. For nonconvergent ordering in minerals the Landau description appears to be adequate, at least for geological applications, up to values of 0.23 for $NiAl_2O_4$, 1.10 for $MgAl_2O_4$, and 1.77 for $En_{50}Fs_{50}$.

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