# Thermodynamics of the $R\overline{3}$ to $R\overline{3}c$ phase transition in the ilmenite-hematite solid solution

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### ABSTRACT

The thermodynamics of cation ordering in the ilmenite-hematite solid solution  $(FeTiO_3)_x(Fe_2O_3)_{1-x}$ were re-examined in view of a recent in-situ neutron diffraction study of the  $R\overline{3}$  to  $R\overline{3}c$  phase transition. A macroscopic thermodynamic model is developed, in which the excess enthalpy of ordering is described by a fourth-order polynomial function of the long-range order parameter, Q, and the excess entropy is described by the configurational point entropy. The enthalpy coefficients are determined as a function of composition by fitting to the neutron diffraction data. The fourth-order energy coefficient increases smoothly with increasing Ti-content, indicating a change in the character of the transition from second-order (x < 0.87) to first-order (x > 0.87). Monte Carlo simulations confirm that the excess enthalpy is well described by a fourth-order polynomial, and demonstrate that the reduction in configurational entropy due to short-range ordering can be described by simply scaling the point entropy. This allows the enthalpy coefficients in the macroscopic model to be corrected for the effects of short-range ordering, yielding a revised estimate of x = 0.92 for the position of the tricritical point.

Monte Carlo simulations are used to study both ordering and exsolution in the solid solution, allowing the paramagnetic portion of the equilibrium phase diagram to be derived. The changing character of the phase transition is reproduced successfully by treating Fe<sup>2+</sup>-Ti and Fe<sup>3+</sup>-Ti interactions separately in the simulations. Intralayer Fe<sup>2+</sup>-Ti interactions are negative (i.e., ordering of Fe<sup>2+</sup> and Ti within the 001 layers is favored) whereas Fe<sup>3+</sup>-Ti intralayer interactions are positive (i.e., separation of Fe<sup>3+</sup> and Ti is favored). The  $\lambda$ -line for the  $R\overline{3}$  to  $R\overline{3}c$  phase transition intersects the low-temperature miscibility gap at a tricritical point near x = 0.6 and T = 800 °C, in reasonable agreement with previous thermodynamic models of the solid solution.

#### INTRODUCTION

The rhombohedral oxide solid solution between ilmenite (FeTiO<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) is an important system in both petrology and paleomagnetism. Intermediate members of the solid solution are strongly magnetic, and contribute significantly to the paleomagnetic record. The magnetic properties of this material are of particular interest due to its ability to acquire self-reversed thermoremanent magnetization (Hoffman 1992; Nord and Lawson 1989, 1992). Together with the spinel oxides magnetite (Fe<sub>3</sub>O<sub>4</sub>) and ulvöspinel (Fe<sub>2</sub>TiO<sub>4</sub>), the FeTiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> solid solution forms the Fe-Ti oxide geothermometer, whereby the composition of coexisting rhombohedral and spinel oxides can be used to determine the temperature and oxygen fugacity at which a rock was equilibrated (Anderson and Lindsley 1988).

The thermodynamic and magnetic properties of this solid solution are dominated by a high-temperature phase transition at the FeTiO<sub>3</sub>-rich end, which involves the partitioning of Fe and Ti between alternating (001) layers of the structure. At high temperatures the symmetry is  $R\overline{3}c$ , and Fe and Ti are distributed randomly over all layers. Below the critical ordering tem-

perature,  $T_{\rm c}$ , Fe and Ti order onto alternating Fe-rich and Tirich layers, reducing the symmetry to  $R\overline{3}$ . The existence of this transition was first demonstrated using measurements of saturation magnetization on quenched material (Ishikawa 1958, 1962; Ishikawa and Akimoto 1957; Ishikawa and Syono 1963). It is not possible to quench-in completely the high-temperature disordered state in material containing more than 60% FeTiO<sub>3</sub>, preventing this technique being used in the region of temperature-composition space where cation ordering is of greatest significance (Brown et al. 1993). The problems associated with quenching can be overcome by determining the cation distribution directly using in-situ diffraction methods. An in-situ study of the  $R\overline{3}$  to  $R\overline{3}c$  phase transition using timeof-flight neutron powder diffraction (Harrison et al. 2000) constrains the equilibrium behavior over the range 400-1350 °C and 70-100% FeTiO<sub>3</sub>. These data allow a thorough re-examination of the thermodynamic properties of this system.

The aims of the thermodynamic analysis are (1) to predict the equilibrium cation distribution for a given temperature and composition (required for the interpretation of magnetic properties); (2) to calculate the equilibrium phase diagram (essential for understanding the magnetic and microstructural development of metamorphic ilmenite-hematites); (3) to determine accurate values for the enthalpy and entropy of the

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solid solution (an essential component of the Fe-Ti oxide geothermometer); (4) to determine the extent of short-range cation ordering (which has implications for both the magnetic and thermodynamic properties); and (5) to determine the structure of material which has undergone simultaneous cation ordering and compositional unmixing (which has possible implications for the occurrence of self-reversed thermoremanent magnetization in volcanic ilmenite-hematites).

These aims cannot all be achieved using a single approach. Applications in petrology require a closed-form thermodynamic model, which can reproduce the enthalpy and entropy of the solid solution as accurately as possible for a given set of conditions. A macroscopic model based on the Bragg-Williams approximation is commonly used (Ghiorso 1990, 1997; Ghiorso and Sack 1991; Holland and Powell 1996a, 1996b). The advantage of this approach is its speed and simplicity of application. Disadvantages are that it offers no insight into the origins of the phase transition, it does not account for spatial or temporal fluctuations in the degree of order or composition, and it incorrectly calculates the configurational entropy of the system when there is strong correlation between nearest-neighbor cation occupancies (short-range order). Accounting for these effects requires an atomistic approach, such as the cluster variation method (CVM, Burton 1984, 1985, 1991; Vinograd and Putnis 1999) or the Monte Carlo method (e.g., Myers et al. 1998). These approaches provide a more realistic thermodynamic description of the solid solution and can yield significant insight into the transition behavior at an atomistic level.

Here we take a combined approach to the problem. First, a simple macroscopic model for the equilibrium cation distribution is used to assess how the thermodynamic character of the phase transition changes as a function of composition, and to predict the equilibrium cation distribution as a function of temperature for those compositions that have not been studied using neutron diffraction. Second, the Monte Carlo method is used to simulate ordering and exsolution in the solid solution. Candidate interaction parameters for nearest-neighbor and nextnearest-neighbor cation-cation exchange are derived by fitting to the experimental data, the equilibrium phase diagram is derived, and the configurational entropy is determined as a function of composition and degree of order via thermodynamic integration. Based on these results, the macroscopic model is modified to account for the reduction in configurational entropy due to short-range ordering.

## **CRYSTAL STRUCTURE**

End-member FeTiO<sub>3</sub> adopts an ordered structure with space group  $R\overline{3}$ . The structure can be described in terms of a distorted hexagonal-close-packed arrangement of oxygen anions, with cations occupying 2/3 of the octahedral interstices to form alternating (001) layers of Fe<sup>2+</sup> and Ti cations. The alternating layers are labelled A and B. Convention dictates that Fe orders onto the A-layers and Ti onto the B-layers. End-member Fe<sub>2</sub>O<sub>3</sub> adopts a similar structure with space group  $R\overline{3}c$ . In this case, the A- and B-layers are both occupied by Fe<sup>3+</sup> and are symmetrically equivalent (related by the *c*-glide plane).

The cation arrangement within one layer of the ordered  $FeTiO_3$  structure (Fig. 1a) was drawn without the oxygen

sublattice, and bonds were drawn to represent the nearest-neighbor cation-cation distances. The cations form hexagonal rings parallel to (001). The hexagonal rings are puckered so that adjacent cations are displaced slightly up and down the [001] axis (Fig. 1b). In a perspective view of the nearest-neighbor cationcation relationships (Fig. 1c), the oxygen coordination octahedra share faces across the nearest-neighbor interlayer join (A-B) and share edges across the nearest-neighbor intralayer joins (A-A and B-B).

The solid solution between FeTiO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is formed by substituting 2 Fe<sup>3+</sup> cations for one Fe<sup>2+</sup> and one Ti<sup>4+</sup> cation. It is normally assumed that Fe<sup>3+</sup> enters the A- and B-layers in equal amounts (Brown et al. 1993). In the fully ordered case, this produces an A-layer which is occupied by a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup>, and a B-layer which is occupied by a mixture of Ti and Fe<sup>3+</sup>. Because the occupancies of the A- and B-layers are different, the symmetry of the ordered solid solution is  $R\overline{3}$ , as in end-member FeTiO<sub>3</sub>. With increasing temperature for a given Ti-content (or with decreasing Ti-content for a given temperature), the degree of long-range cation order decreases. At the critical temperature,  $T_c$ , the cation occupancy on each layer becomes equal, and there is a transition to the disordered phase with space group  $R\overline{3}c$ .

Below 650 °C, the thermodynamic properties of the solid solution are complicated by magnetic ordering at the Fe<sub>2</sub>O<sub>3</sub>rich end (Ishikawa and Akimoto 1957). The free energy changes associated with magnetic ordering have a large effect on the phase diagram at temperatures below 500 °C (Burton 1985; Ghiorso 1997). This study neglects the effects of magnetic ordering, and therefore restricts the thermodynamic analysis to temperatures above 500 °C, where the effect of magnetic ordering on the phase diagram is known to be small. The main aim of this study is to derive a thermodynamic description of cation ordering in FeTiO<sub>3</sub>-rich material (containing between 60% and 100% FeTiO<sub>3</sub>). Over this range in composition, magnetic ordering occurs close to or below room temperature, and therefore has a negligible effect on the  $R\overline{3}$  to  $R\overline{3}c$  transition. An extension of the analysis to include the effects of magnetic ordering will be examined. We also restrict the calculations to zero pressure so that we can compare the thermodynamic models directly with the results of neutron diffraction experiments (which were performed under vacuum). Because it is observed that the spontaneous volume strain due to the phase transition is negligible, the effect of pressure on the cation ordering phase transition will be small (Hazen and Navrotsky 1996). It is expected, therefore, that the thermodynamic model will also be valid at finite pressure.

## Macroscopic model for the $R\overline{3}$ to $R\overline{3}c$ transition

The excess free energy of ordering is described in terms of a long-range order parameter:

$$Q = \frac{\left(X_{\text{Ti}}^{\text{B}} - X_{\text{Ti}}^{\text{A}}\right)}{\left(X_{\text{Ti}}^{\text{B}} + X_{\text{Ti}}^{\text{A}}\right)} \tag{1}$$

where  $X_i^i$  is the fraction of *j*-sites occupied by *i*-cations. In the fully disordered state (with Fe and Ti statistically distributed



**FIGURE 1.** Topology of the ordered ilmenite structure, showing Fe (dark) and Ti (light) cation positions only. (a) View of a single A-cation layer down the [001] axis. (b) View of the ordered A- and B-cation layers down the [100] axis. (c) Definition of nearestneighbor A-A, B-B, and A-B cation-cation distances. Distances are quoted for ordered ilmenite at room temperature (Harrison et al. 2000).

between the A- and B-layers), Q = 0 and Q = 1 in the fully ordered state (with the A-layer fully occupied by Fe and all available Ti on the B-layer). Negative values of Q describe the twin-related ordered state with Fe on the B-layer and Ti on the A-layer (Nord and Lawson 1989, 1992).

In end-member FeTiO<sub>3</sub>, the cation distribution is fully defined by Q. In the solid solution, however, there is an additional degree of freedom because Fe is present as both Fe<sup>3+</sup> and Fe<sup>2+</sup>. Because the equilibrium distribution of Fe<sup>3+</sup> and Fe<sup>2+</sup> is difficult to determine experimentally, it is necessary to make some assumption about the site preference of these cations. It is commonly assumed that Fe<sup>3+</sup> is distributed equally over the A- and B-layers, because this scheme leads to the minimization of energetically unfavorable interlayer Ti-Ti pairs (Ghiorso 1990, 1997; Brown et al. 1993). With this assumption, the cation distribution is fully defined in terms of Q and x, where x is the mole fraction of FeTiO<sub>3</sub> ( $0 \le x \le 1$ ). The equations relating  $X_i^t$  to Q and x are in Table 1.

The configurational entropy of the solid solution is calculated assuming that random mixing of cations occurs on the Aand B-layers, and no correlation exists between nearest-neighbor interlayer pairs. This is referred to as the "point entropy," because the A- and B-layers are treated as isolated clusters of single cation sites:

$$S_{\text{point}} = -\mathbf{R} \sum_{i,j} X_i^j \ln X_i^j \tag{2}$$

The excess entropy change due to long-range cation ordering is defined relative to the fully disordered state (Q = 0):

$$\Delta S_{\text{point}} = S_{\text{point}}(Q) - S_{\text{point}}(0) \tag{3}$$

The corresponding enthalpy change is formulated as a polynomial-expansion in Q:

$$\Delta H = \frac{1}{2}aQ^2 + \frac{1}{n}bQ^n \tag{4}$$

where a and b are constants for a given composition, and n is required by symmetry to be an even integer. Combining Equations 3 and 4 gives the excess free energy of the transition:

$$\Delta G = \Delta H - T \Delta S_{\text{point}} \tag{5}$$

where T is temperature. If the enthalpy polynomial is truncated after the first term (i.e., b = 0 in Eq. 4), then the free energy

model reduces to the Bragg-Williams approximation. The equilibrium degree of long-range order is found by minimizing the free energy with respect to Q. Differentiating Equation 5 with respect to Q and setting  $\Delta G/dQ = 0$ , relates T and Q at equilibrium:

$$T = -\frac{aQ + bQ^{n-1}}{Rx(\ln[x + xQ] - \ln[x - xQ])}$$
(6)

For a continuous phase transition, the critical temperature,  $T_c$ , is given by the limit of Equation 6 as  $Q \rightarrow 0$ :

$$T_{\rm c} = -\frac{a}{2Rx} \tag{7}$$

Values for *a*, *b*, and *n* are derived by fitting to equilibrium cation distribution data, see Figure 2a. In ilm80, i.e., x = 0.8, ilm90 and ilm100, data points determined above 400 °C correspond to equilibrium states of the homogeneous material. The unusual behavior in ilm70 below 700 °C is caused by the development of chemical heterogeneities as this sample is quenched through, and subsequently annealed below the solvus (Harrison et al. 2000). The top of the solvus occurs between 600 and 700 °C, and hence for ilm70, only data points measured above 700 °C correspond to equilibrium states of the homogeneous material. An estimated error of 0.015 in *Q* was assumed for the neutron scattering results, based on the Rietveld refinements of Harrison et al. (2000) and an estimated 1% error in the bulk composition of the synthetic samples.

Equation 6 was fitted to the equilibrium ordering data (Q > 0) using a least-squares procedure. Initially, fitting was performed with a, b and n as non-integer variables. In all cases, the best fit was obtained with a value of n close to 4. Subse-

TABLE 1. Definition of cation distribution variables

X <sub>i</sub> <sup>j</sup>	Assuming Fe³+ equally distributed over A- and B-layers	Assuming Fe <sup>3+</sup> and Fe <sup>2+</sup> randomly distributed over A- and B-layers
$X_{\mathrm{Ti}}^{\mathrm{A}}$	$\frac{1}{2}x(1-Q)$	$\frac{1}{2}x(1-Q)$
$X_{\mathrm{Fe}^{^{2+}}}^{\mathrm{A}}$	$x - \frac{1}{2}x(1 - Q)$	$\frac{x(x-2-xQ)}{2(x-2)}$
$X_{\mathrm{Fe}^{3+}}^{\mathrm{A}}$	1 <i>-x</i>	$\frac{(x-1)(2+xQ-x)}{2}$
$X_{\mathrm{Ti}}^{\mathrm{B}}$	$\frac{1}{2}x(1+Q)$	$\frac{x-2}{\frac{1}{2}x(1+Q)}$
$X_{\mathrm{Fe}^{^{2+}}}^{\mathrm{B}}$	$x - \frac{1}{2}x(1+Q)$	$\frac{x(x-2+xQ)}{2(x-2)}$
$X_{\mathrm{Fe}^{3+}}^{\mathrm{B}}$	1 – <i>x</i>	$\frac{(x-1)(2-xQ-x)}{x-2}$



**FIGURE 2.** (a) Long-range order parameter, Q, as a function of temperature (K). Solid symbols show values of Q determined using in-situ neutron diffraction (Harrison et al. 2000). Open symbols show the quench-magnetization results of Brown et al. (1993). Solid lines are least-squares fits to the data using the macroscopic thermodynamic model (Eq. 6). The dashed line indicates the discontinuity in Q for the first-order transition in ilm100 (corresponding to the upper limit of metastability). (b) Variation in the enthalpy coefficients a and b as a function of composition (see Eq. 4). Solid symbols are values determined assuming full configurational entropy (Eq. 5), open symbols are values determined after correcting the entropy for the effects of short-range order (Eq. 12). The dashed line at x = 0.92 marks the point where b/a = 1/3. Compositions to the left of this line undergo a second-order phase transition, compositions to the right undergo a first-order transition.

quent fits constrained *n* as 4 (solid lines in Fig. 2a). The corresponding values of *a* and *b* and their estimated errors are in Table 2 and plotted in Figure 2b. The uncertainty in the *a* coefficient translates via Equation 7 to an uncertainty in the transition temperature. In ilm70, ilm80, and ilm90, this uncertainty is small because the transition was observed directly using insitu measurements (the error in *a* corresponds to an error of around 20 °C in  $T_c$ , i.e., approximately equal to the temperature resolution of the measurements). For ilm100 the error in *a* is greater because the transition temperature was not reached in the neutron diffraction experiments.

The character of the transition is determined by the ratio b/a. For b/a < 1/3, the transition is second-order, for b/a = 1/3 the transition is tricritical, and for b/a > 1/3 the transition is first-order. In ilm60, the *b*-coefficient is zero (within error), and the transition is second-order (ideal Bragg-Williams behavior). With increasing Ti-content, the *b*-coefficient increases smoothly relative to the *a*-coefficient, indicating a gradual change in the character of the transition. A tricritical point with b/a = 1/3 is reached at x = 0.87, beyond which the transition is predicted to

TABLE 2. Coefficients of the macroscopic model

Sample	Uncorrected*		Corrected <sup>†</sup>		
	a (kJ/mol)	b (kJ/mol)	a (kJ/mol	) <i>b</i> (kJ/mol)	f
ilm60	-11.2(2)	-0.3(5)	-6.6(2)	0(0)	0.832
ilm70	-14.8(2)	-2.7(3)	-9.7(2)	-0.4(3)	0.847
ilm80	-19.2(2)	-4.9(4)	-13.9(2)	-1.6(4)	0.862
ilm90	-23.9(3)	-8.6(5)	-19.0(3)	-4.9(5)	0.877
ilm100	-22.4(6)	-21.2(6)	-18.9(6)	-15.5(6)	0.8

\* Coefficients determined using uncorrected configurational entropy. † Coefficients determined using corrected configurational entropy. be first-order. The transition in end-member  $FeTiO_3$  is apparently strongly first-order. Figure 2a shows the upper limit of metastability for the first-order transition in ilm100.

The values of a and b in end-member FeTiO<sub>3</sub> lie significantly off the trend defined by the other four compositions. This may be an artefact due to the more limited range in Q used to fit the coefficients, or may indicate that the approximation used to calculate the configurational entropy (Eq. 2) becomes invalid close to the end-member. Structural evidence suggests that short-range ordering of Fe and Ti within the  $R\overline{3}c$ phase becomes increasingly important at compositions close to FeTiO<sub>3</sub>, where the Fe:Ti ratio on the A- and B-layers approaches 1:1 (Harrison et al. 2000). Short-range ordering leads to a reduction of the configurational entropy relative to the point entropy. With the corrected coefficients (see later section), the tricritical point is predicted to occur at x = 0.92, as shown by the dashed boundary in Figure 2b. The discrepancy between coefficients in the solid solution and the end-member is less pronounced after correction.

The second-order transition observed in compositions close to x = 0.6 is consistent with previous experimental studies (Ishikawa 1958). It is also consistent with the limited experimental observations of exsolution in this system, which suggest that the  $\lambda$ -line for the  $R\overline{3}$  to  $R\overline{3}c$  transition intersects the low-temperature miscibility gap at a tricritical point around x= 0.5–0.6 and T = 700-800 °C. Burton (1985) calculated a second tricritical point at the intersection of the paramagnetic to ferrimagnetic transition and the low-temperature miscibility gap around x = 0.25 and T = 525 °C. The predicted third tricritical point lies close to x = 0.92 and T = 1340 °C (Fig. 2b). The phase rule requires, therefore, that a miscibility gap develops at x > 0.92. Given the proximity to the melting point of endmember FeTiO<sub>3</sub> (1367 °C), the extent of this miscibility gap is expected to be limited.

The transition behavior in FeTiO<sub>3</sub> is comparable to that observed in the analogous oxide NiTiO<sub>3</sub> (Boysen et al. 1995). This material undergoes an abrupt (but apparently continuous) phase transition at  $T_c = 1560$  K. This temperature coincides precisely with the equilibrium transition temperature predicted by the macroscopic model for the first-order transition in FeTiO<sub>3</sub>.

## Monte Carlo simulation of the $R\overline{3}$ to $R\overline{3}c$ transition

The above macroscopic model illustrates the changing thermodynamic character of the  $R\overline{3}$  to  $R\overline{3}c$  transition, and provides a simple means of interpolating cation distribution data to temperatures and compositions which have not yet been investigated using in-situ neutron diffraction. However, the model is not rigorous because the configurational entropy is inadequately described (Eq. 2). Monte Carlo simulation provides a flexible and intuitive means of modelling the thermodynamics of complex systems, taking proper account of both long- and shortrange ordering effects (Ross 1991).

#### **Computational methods**

The first step in the Monte Carlo simulation is to generate a supercell of cation sites with the topology of the FeTiO<sub>3</sub> structure (see Fig. 1). The occupancy of each cation site can be defined as either Ti, Fe<sup>2+</sup>, or Fe<sup>3+</sup>, with the relative numbers of each cation type determined by the bulk composition. The internal energy of the supercell for a given cation configuration is calculated in terms of pairwise interaction energies,  $J_p^q$ , where *p* refers to the type of cation-cation pair ( $1 = Fe^{2+}$ -Ti;  $2 = Fe^{3+}$ -Ti;  $3 = Fe^{2+}$ -Fe<sup>3+</sup>) and *q* refers to the type of interaction (1 = nearest-neighbor interlayer interaction, 2 = nearest-neighbor intralayer interaction, etc.):

$$J_{p}^{q} = W_{X-Y}^{q} - \frac{1}{2} \Big( W_{X-X}^{q} + W_{Y-Y}^{q} \Big)$$
(8)

 $W_{X-Y}^q$ ,  $W_{X-X}^q$ , and  $W_{Y-Y}^q$  are the energies of formation of X-Y, X-X, and Y-Y cation pairs. A negative value of  $J_p^q$  favors the formation of X-Y pairs over X-X and Y-Y pairs. A positive value of  $J_p^q$ favors the formation of X-X and Y-Y pairs over X-Y pairs. The excess energy of a configuration, relative to the end-members Fe<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub>, is given by:

$$E = \frac{1}{2} \sum_{p,q} N_p^q J_p^q \tag{9}$$

where  $N_p^q$  is the number of interactions per supercell for a given cation pair *p* and interaction type *q* (counted using periodic boundary conditions).

At equilibrium, each configuration of the supercell occurs with a probability determined by the Boltzmann distribution  $\exp(-E/k_BT)$  where  $k_B$  is Boltzmann's constant. In a Monte Carlo simulation, the equilibrium thermodynamic properties are determined by averaging over a number of configurations generated with their correct thermodynamic probability. The supercell is generated with an arbitrary starting configuration. Pairs of atoms are chosen at random and their positions are swapped. If the energy after the swap is lower than before, then the swap is accepted with a probability of 1. If the energy is greater, then the swap is accepted with a probability of  $\exp(-\Delta E/k_BT)$ . After a sufficient number of swaps the system reaches equilibrium, with configurations generated independently of the starting configuration. The equilibrium properties (energy, degree of long- and short-range order, etc.) can then be determined by averaging over a number of steps until the desired statistical significance is reached.

We chose a supercell containing a total of 1536 cation sites. This was sufficiently large to minimize finite-size effects, and was the maximum size permitted by the computing resources available (single processor DEC Alpha workstation with 500 MHz). Two different geometries of supercell were chosen to investigate different types of distribution inhomogeneities introduced by the shape and size of the supercell. The first was a  $4 \times 4 \times 8$  supercell (approximately  $20 \times 20 \times 120$  Å<sup>3</sup> dimensions) and the second was an  $8 \times 8 \times 2$  supercell (approximately  $40 \times 40 \times 30$  Å<sup>3</sup> dimensions). The two supercells produced identical results for temperatures and compositions within the single-phase  $R\overline{3}$  field. Within the low-temperature two-phase field, the  $4 \times 4 \times 8$  supercell showed a strong tendency to exsolve into Fe<sub>2</sub>O<sub>3</sub>-rich and FeTiO<sub>3</sub>-rich lamellae, with the boundary between phases parallel to (001). In contrast, the  $8 \times 8 \times 2$  supercell showed a reduced tendency to produce largescale exsolution features. Exsolution is suppressed in this supercell because its shortest dimension is perpendicular to the preferred orientation of the boundary plane between exsolved phases. In effect, the  $4 \times 4 \times 8$  supercell allows one to simulate systems where exsolution is both thermodynamically and kinetically feasible, whereas the  $8 \times 8 \times 2$  supercell partly models systems where exsolution is kinetically hindered.

The free energy for a given temperature, F(T), can be calculated using the Bogoliubov integration scheme (Myers 1998; Myers et al. 1998; Yeomans 1992). Specifically:

$$F(T) = -TS_{\text{point}} + \int_{\lambda=0}^{1} E(T / \lambda) d\lambda$$
 (10)

where  $S_{\text{point}}$  is given by Equation 2 with Q = 0 and  $E(T/\lambda)$  refers to the equilibrium energy calculated at a temperature of  $T/\lambda$ . The integral in Equation 10 was approximated by varying  $\lambda$ from 0 to 1 in steps of 0.05, and performing Monte Carlo simulations at each temperature  $T/\lambda$ . The energy for  $\lambda = 0$  can be calculated directly from Equation 9 assuming a purely statistical distribution of cations at infinite temperature. From F(T)and E(T) one can calculate the configurational entropy S(T) = [E(T)-F(T)]/T.

#### **Choice of interaction parameters**

The number, magnitude, and sign of the interaction parameters,  $J_{p}^{q}$ , determine the overall thermodynamic behavior of the solid solution. In some cases, e.g., aluminosilicates, values of  $J_{p}^{q}$  can been determined by combining NMR and calorimetric data (e.g., Phillips et al. 1992). Alternatively, values of  $J_{p}^{q}$  can be determined from first-principles using empirical-potential or quantum-mechanical ab-initio calculations (e.g., Thayaparam et al. 1996; Dove et al. 1996; Becker et al. 1999; Warren et al. 1999). It is difficult to derive a set of empirical potentials for the FeTiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> solid solution due to problems associated with modelling a system containing mixtures of Fe<sup>2+</sup> and Fe<sup>3+</sup>. Attempts to determine interaction energies using ab-initio calculations were hampered by the difficulties in separating chemical and magnetic contributions to the total energy. Given these difficulties, we chose to derive a set of interaction parameters based on empirical observations. The signs of the parameters were determined using the general guidelines described by Burton and Kikuchi (1984). The magnitudes of the parameters were then refined by fitting to neutron diffraction data of Harrison et al. (2000).

The minimum set of interaction parameters required to reproduce the phase diagram topology discussed above is shown in Figure 3a. The strongest interactions are  $J_p^1$  (cation-cation separation approximately 2.94 Å) and  $J_p^2$  (cation-cation separation approximately 3.0 Å), which describe the nearest-neighbor inter- and intralayer interactions, respectively. The next-nearest-neighbor interactions are  $J_p^3$ ,  $J_p^4$ , and  $J_p^5$ , which describe interlayer interactions with cation-cation separations between 3.42 and 3.78 Å. For simplicity we assume that  $J_p^3$ , in the following.

The general guidelines (Burton and Kikuchi 1984) state that when the sum of interlayer interactions and the sum of intralayer interactions are both negative, the resulting phase transition is first-order in character. When the sum of interlayer interactions is negative and the sum of intralayer interactions is positive, the resulting phase transition is second-order. The sign of  $J_p^q$  is defined by Equation 8 and determined by crystal chemical factors such as the charge and size difference between cation pairs. In the FeTiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> solid solution,  $J_p^1$  is negative, because strong electrostatic repulsion across the poorly screened shared face of the oxygen coordination octahedra favors the formation of X-Y pairs over X-X and Y-Y pairs. The  $J_p^2$ , interaction can be either negative or positive, depending on the subtle balance of charge and size effects. To reproduce the first-order transition in end-member FeTiO<sub>3</sub>,  $J_1^2$  must be negative (i.e., intralayer Fe2+-Ti pairs are favored). This result is expected



**FIGURE 3.** (a) Definition of the interaction parameters  $J_p^a$  used in the Monte Carlo simulations. (b) Hypothetical ordered structure in end-member FeTiO<sub>3</sub>. The Fe<sup>2+</sup> and Ti cations order onto alternate sites within the layers, reducing the symmetry to *R*3. This arrangement may become stable above  $T_c$  for the  $R\overline{3}$  to  $R\overline{3}c$  transition due to the negative values of  $J_1^1$  and  $J_1^2$ , which favor nearest-neighbor Ti-Ti avoidance both between and within the A- and B-layers.

because the large difference in charge between Fe<sup>2+</sup> and Ti means that electrostatic repulsion dominates over other effects. The transition in the solid solution is predominantly secondorder, requiring that  $J_2^2$  is positive (i.e., intralayer Fe<sup>3+</sup>-Ti pairs are not favored). The sign of  $J_3^2$  (intralayer Fe<sup>2+</sup>-Fe<sup>3+</sup> pairs) is more difficult to define, because the character of the transition is largely independent of this parameter. Empirical potential calculations failed to produce accurate quantitative values for  $J_p^q$ . However, the qualitative results strongly suggested that  $J_3^2$ was negative, and furthermore, that the absolute values of  $J_3^q$ could be approximated by the relationship  $J_3^q = k J_1^q$ , where k is a constant scaling factor. For simplicity, this scheme was adopted in the fitting procedure described below.

Values for the Fe<sup>2+</sup>-Ti interaction parameters,  $J_1^1$ ,  $J_1^2$ , and  $J_1^3$ were determined by fitting to the equilibrium ordering data in end-member FeTiO<sub>3</sub>. According to the arguments above,  $J_1^1$  and  $J_1^2$  were assumed to be negative. A negative value of  $J_1^3$  was then required to stabilize the  $R\overline{3}$  ilmenite structure relative to alternative ordering schemes, in which Fe<sup>2+</sup> and Ti are ordered within the A- and B-layers (e.g., Fig. 3b). Fitting was performed manually by trial and error. The fitted parameters are listed in Table 3 and the calculated equilibrium ordering curve is in Figure 4d.

Values for the Fe<sup>3+</sup>-Ti interaction parameters,  $J_2^1$ ,  $J_2^2$ ,  $J_2^3$ , and the scaling constant, k, were determined by fitting simultaneously to the equilibrium ordering data in ilm70, ilm80, and ilm90. Fitting was performed using an automated conjugate gradient optimization routine. Data points close to  $T_c$  were not used as observables in the fit, because these lie within the order parameter fluctuation regime and require a supercell larger than that used in this study to be determined with any precision. The fitted parameters are listed in Table 3 and the calculated equilibrium ordering curves are shown in Figures 4a to 4c.

Although the experimental data are well described by the chosen set of interaction parameters, other combinations of  $J_p^q$  may describe the data equally well. The values listed in Table 3 should, therefore, be treated as candidate interaction parameters, which may be revised in the future if more specific experimental or theoretical constraints become available.

## Temperature-dependence of long- and short-range order

The results of the Monte Carlo simulations are compared to the degree of long-range order determined using neutron diffraction in Figure 4. Error bars represent the standard deviation in *Q* averaged over approximately 10 million Monte Carlo

 
 TABLE 3. Interaction parameters used in the Monte Carlo simulations

	19			q		
	$J_{\tilde{p}}$		1	2	3	
	(eV	)	N.N.	N.N.	N.N.N.	
			interlayer	intralayer	interlayer	
	1	Fe <sup>2+</sup> -Ti	-0.4167	-0.290	-0.1650	
р	2	Fe <sup>3+</sup> -Ti	-0.0954	0.0723	-0.0555	
	3	Fe <sup>2+</sup> -Fe <sup>3+</sup>	-0.0833	-0.0580	-0.0330	
Note $J^4$	es: N.N = J <sup>5</sup>	I. = nearest-ne	ighbor; N.N.N. =	next-nearest	t-neighbor;	$J_{p}^{3} =$



**FIGURE 4.** Results of the Monte Carlo simulations for (**a**) ilm70, (**b**) ilm80, (**c**) ilm90, and (**d**) ilm100. Open squares with error bars show the calculated degree of long-range order, Q, as a function of temperature. Error bars represent the standard deviation in Q during the simulation. Solid and dashed lines show the temperature-dependence of short-range order parameters  $\sigma_1$  (solid lines),  $\sigma_2$  (short-dashed lines) and  $\sigma_3$  (long-dashed lines). Closed circles are the results of in-situ neutron diffraction (Harrison et al. 2000). The arrows in (**a**) and (**b**) show the temperature ranges over which exsolution was observed in the Monte Carlo simulation.

steps for ilm80, ilm90 and ilm100, and approximately 300 million steps for ilm70. A larger number of steps was required for ilm70, because this composition involved mixing three cations in approximately equal proportions. The temperature-dependence of the short-range order parameters,  $\sigma_q$ , were obtained from:

$$P_{\text{Ti-Ti}}^{q} = X_{\text{Ti}}^{\text{A}} X_{\text{Ti}}^{\text{B}} (1 - \sigma_{a}) \text{ for } q = 1, 3, 4 \text{ and } 5$$
 (11)

and

$$P_{\text{Ti-Ti}}^{q} = X_{\text{Ti}}^{\text{A}} X_{\text{Ti}}^{\text{A}} + X_{\text{Ti}}^{\text{B}} X_{\text{Ti}}^{\text{B}} (1 - \sigma_{q}) \text{ for } q = 2$$
(12)

where  $P_{\text{Ti-Ti}}^{q}$  is the probability of a Ti-Ti pair occurring for a

given interaction type *q*. When  $\sigma_q = 0$ ,  $P_{\text{Ti-Ti}}^q$  is equal to the product of the point probabilities of finding Ti on the A- and B-layers (no short-range order). When  $\sigma_q > 0$ ,  $P_{\text{Ti-Ti}}^q$  is lower than the point probability (i.e., there is a tendency to avoid Ti-Ti neighbors). When  $\sigma_q < 0$ ,  $P_{\text{Ti-Ti}}^q$  is greater than the point probability (i.e., there is a tendency for Ti to cluster).

All calculations in Figure 4 were performed using the  $4 \times 4 \times 8$  supercell, so that the effect of exsolution on the degree of long-range order could be accounted for. As seen in Figure 2a, the degree of order in ilm70 deviates significantly from the macroscopic ordering model at temperatures below 700 °C. Harrison et al. (2000) suggested that this was caused by the development of chemical heterogeneities at temperatures below the solvus. This hypothesis is supported by the Monte Carlo

simulations. Exsolution is predicted to occur below 700 °C in ilm70. Below this temperature, the supercell contains a single lamella of disordered Fe2O3-rich material within a matrix of ordered FeTiO<sub>3</sub>-rich material. Because the disordered phase contains an equal amount of Ti on the A- and B-layers, the apparent degree of long-range order is reduced when Equation 1 is averaged over the whole supercell. This reduction in Q on cooling through the solvus counteracts the expected increase in Q due to increasing the degree of order in the FeTiO<sub>3</sub>-rich phase. Within a small temperature interval between 600 and 700 °C these two effects balance each other, and O remains essentially constant as a function of temperature. Ultimately, however, the composition of the exsolved Fe<sub>2</sub>O<sub>3</sub>-rich phase approaches that of pure Fe<sub>2</sub>O<sub>3</sub>, at which point all Ti is on the Blayer and Q = 1. Excellent agreement between the calculated and observed degree of long-range order is achieved between 500 and 700 °C in ilm70, even though only data points measured above 700 °C were used to constrain the values of  $J_p^q$ .

A small decrease in Q is predicted in ilm80 below 600  $^{\circ}$ C due to exsolution (Fig. 4b). This was not observed in the neutron experiments, however. Harrison et al. (2000) discuss the possible reasons why exsolution is less pronounced in this material than in ilm70. Firstly, the temperature of the spinode is lower than the kinetic closure temperature, which means that exsolution requires nucleation of the disordered phase, which in turn requires overcoming the nucleation energy barrier. Secondly, the density of transition-induced twin domain boundaries, which may act as nuclei for the disordered phase, is much lower in ilm80 than in ilm70 (Nord and Lawson 1989). No exsolution was observed in ilm90 and ilm100 at the temperatures simulated. The observed and fitted values of Q in both these samples are in excellent agreement. In ilm90, Q continuously decreases and the amplitude of order parameter fluctuations gradually increases as  $T_c$  is approached, suggesting that the character of the transition is either second-order or tricritical. In ilm100, Q discontinuously decreases and the amplitude of order parameter fluctuations suddenly increases above 1325 °C, confirming that the transition is first-order.

The temperature- and composition-dependence of the three short-range order parameters is complex. Several trends can be recognized, however, allowing us to make some general conclusions about the behavior of the solid solution. The largest short-range order parameter is  $\sigma_1$ , which describes the tendency to avoid nearest-neighbor interlayer Ti-Ti pairs (Fig. 4). The value of  $\sigma_1$  increases with decreasing Ti-content, which reflects the general principle that short-range order replaces long-range order as the dominant strategy of energy reduction as a system becomes increasingly dilute (Dove et al. 1996). This inverse relationship between long- and short-range order is also responsible for the pronounced peak in  $\sigma_1$  and  $\sigma_3$  at T = $T_{\rm c}$ . The next-nearest-neighbor interlayer short-range order parameter,  $\sigma_3 (\approx \sigma_4 \approx \sigma_5)$ , shows similar behavior to  $\sigma_1$  (Fig. 4). The rather dramatic changes in  $\sigma_1$  and  $\sigma_3$  which occur at low temperatures in Figures 4a and 4b have little effect on the enthalpy and entropy of the solid solution, because  $X_{Ti}^{A}$  tends to zero at high degrees of long-range order, and therefore large changes in  $\sigma_1$  and  $\sigma_3$  have only a small effect on  $P_{\text{Ti-Ti}}^1$  and  $P_{\text{Ti-Ti}}^3$ (Eq. 11).

The nearest-neighbor intralayer short-range order parameter,  $\sigma_2$ , shows different behavior to the interlayer parameters (dotted lines in Fig. 4). In ilm90 and ilm100,  $\sigma_2$  is zero below  $T_c$  but increases with increasing temperature above  $T_c$  (Figs. 4c and 4d). This indicates that a locally ordered configuration such as that in Figure 3b becomes thermodynamically stable at these temperatures. One might speculate that the existence of this ordering scheme contributes to the increasingly first-order character of the transition close to end-member FeTiO<sub>3</sub>. In ilm70 and ilm80,  $\sigma_2$  is small and positive above  $T_c$  (Ti-Ti avoidance) but becomes negative at temperatures close to  $T_c$  and below the solvus (Ti-Ti clustering) (Figs. 4a and 4b). The changes in  $\sigma_2$ below the solvus have more thermodynamic significance than the corresponding changes in  $\sigma_1$  and  $\sigma_3$ , because  $P_{\text{Ti-Ti}}^2$  does not tend to zero in the limit of full long-range order (Eq. 12).

#### Determination of the phase diagram

As described earlier, the apparent degree of long-range order is reduced at temperatures and compositions within the solvus. Exsolution occurs readily in simulations using the 4 ×  $4 \times 8$  supercell, whereas exsolution is suppressed in the  $8 \times 8 \times$ 2 supercell. Within the solvus, this leads to an obvious difference in *Q* calculated using the alternative supercells. Outside the solvus, both supercells yield precisely the same values of *Q*. This simple comparison allows the position of the solvus to



**FIGURE 5.** Calculated phase diagram for the Fe<sub>2</sub>O<sub>3</sub>-FeTiO<sub>3</sub> system. Triangles on the left limb of the solvus bracket the compositions at which long-range order was observed to break-down in the Monte Carlo simulations. Triangles on the right limb of the solvus bracket the compositions at which a clear difference in the degree of order was observed in the  $4 \times 4 \times 8$  and  $8 \times 8 \times 2$  supercells. The position of the high-temperature tricritical point (x = 0.92) has been calculated using the modified macroscopic model. The extent of the high-temperature miscibility gap is drawn schematically. Dashed lines have been drawn between the melting points of end-member Fe<sub>2</sub>O<sub>3</sub> and FeTiO<sub>3</sub>.

be determined (Fig. 5).

The  $\lambda$ -line for the  $R\overline{3}$  to  $R\overline{3}c$  transition intersects the solvus at a tricritical point at T = 800 °C and x = 0.6. This agrees quite well with the position predicted by Ghiorso (1990, 1997) (T =750 °C, x = 0.55), but differs somewhat from that predicted by Burton (1984 and 1985) (T = 714 °C, x = 0.5). Experimental evidence suggests that macroscopic exsolution may not occur until temperatures below 700 °C (Burton 1982). Due to the small size of the Monte Carlo simulation cell, it is likely that the temperature of the tricritical point is overestimated in this study. The solvus (Fig. 5) defines the temperature at which compositional clustering occurs in the simulation, and does not necessarily correspond to the temperature at which exsolution on a macroscopic scale is thermodynamically stable. Shortrange compositional heterogeneities play a crucial role in determining the magnetic properties of this system, and may also significantly affect the results of in-situ neutron diffraction experiments (Harrison et al. 2000). Therefore, Figure 5 provides a useful determination of the temperature-composition space where such clustering might occur.

The tricritical point marking the boundary between secondand first-order regions of the  $R\overline{3}$  to  $R\overline{3}c$  transition has been placed between ilm90 and ilm100, although the precise position of this point is difficult to determine using the Monte Carlo simulations. The macroscopic model predicted a tricritical point at x = 0.87. After accounting for the reduction in configurational entropy due to short-range ordering, the model predicts a tricritical point around x = 0.92 (see next section). The latter value is shown in Figure 5. The extent of the miscibility gap which develops on the Ti-rich side of the tricritical point is unknown, and the gap shown in Figure 5 should be regarded as schematic. For reference, the dotted lines in Figure 5 show a simple linear interpolation between the melting points of endmember Fe<sub>2</sub>O<sub>3</sub> and FeTiO<sub>3</sub> (1622 and 1367 °C, respectively).

## Energy and entropy of the solid solution

Figure 6 illustrates the variation in energy and entropy as a function of Q for a composition close to ilm80. Above  $T_c$ , the curves were obtained by performing a "constrained-swap" simulation, in which only intralayer and double-layer swaps were permitted. In this way, Q remains constant during the simulation (fixed by the choice of starting configuration) and the system equilibrates with respect to the degree of short-range order. Only temperatures above  $T_{\rm c}$  were investigated to avoid the formation of domain structures at small values of Q. The curves are well described by a fourth-order polynomial, as illustrated by the least-squares fits to the data using Equation 4. The size of the fourth-order term decreases with increasing temperature, as expected for pairwise interactions in the high-temperature limit. Equilibrium energies from an unconstrained Monte Carlo simulation lie close to the fourth-order polynomial curve calculated at temperatures close to  $T_c$ , providing justification for the energy model adopted in Part I.

The corresponding variation in entropy, *S*, as a function of *Q* in Figure 6b, was determined using Bogoliubov integration (Eq. 10). The ideal point entropy,  $S_{\text{point}}$ , was calculated under the assumption that Fe<sup>3+</sup> is equally distributed over the A- and B-layers (i.e., the macroscopic entropy model). At high degrees

of long-range order, *S* is larger than  $S_{point}$ , demonstrating that this assumption does not provide a good description of the Fe<sup>2+</sup>-Fe<sup>3+</sup> distribution in the simulation (see inset in Fig. 6b). The upper solid curve shows the upper limit of point entropy, calculated under the assumption that both Fe<sup>2+</sup> and Fe<sup>3+</sup> are distributed randomly over the A- and B-layers (see Table 1). For temperatures below  $T_c$ , *S* can be described reasonably well by the relationship  $S = f S_{point}$ , where *f* is a constant scaling factor and  $S_{point}$  refers now to the upper limit of point entropy. This is illustrated by the dashed line in Figure 6b, which was obtained by multiplying the upper solid curve by a factor f = 0.87. Values of *f* for other compositions within the  $R\overline{3}$  stability field were determined in a similar manner and are listed in Table 2.

The scaling factor, f, performs a similar function to the variable "*a*" in traditional Landau theory ( $\Delta S = 1/2aQ^2$ ), in that it provides an empirical means of accounting for the reduction in configurational entropy due to short-range ordering (Carpenter and Salje 1994; Harrison and Putnis 1997). The approach used here provides a better approximation to the configurational entropy at high degrees of long-range order, however. This is a key factor in determining the thermodynamic character of the transition, because the most discriminating changes in the *Q*-*T* curves occur at values of *Q* between 0.8 and 1, which is outside the region where the Landau approximation is valid. Values of *f* may be determined directly from Monte Carlo simulations or indirectly by fitting to calorimetric or phase equilibrium data (Carpenter et al. 1994; Carpenter and Salje 1994; Salje 1985).

The macroscopic model can now be modified to take account of the reduction in configurational entropy. The modified excess free energy is simply:

$$\Delta G = \Delta H - T f \Delta S_{\text{point}} \tag{13}$$

where  $\Delta S_{\text{point}}$  is the maximum excess point entropy for a given Q, calculated by substituting the values of  $X_i^j$  listed in Table 1 into Equations 2 and 3. Minimizing  $\Delta G$  with respect to Q, gives T as a function of Q and x at equilibrium. This function can be used, as before, to determine values for the enthalpy coefficients a and b. The values of a and b determined using the modified model are in Table 2 and shown in Figure 2b.

Energy and entropy calculations were performed as a function of temperature for several bulk compositions along the ilmenite-hematite join, allowing the excess energy and entropy of mixing to be determined (Fig. 7). All excess properties have been defined relative to Fe<sub>2</sub>O<sub>3</sub> and fully ordered FeTiO<sub>3</sub>. The diagram is divided into long-range disordered ( $R\overline{3}c$ ), long-range ordered ( $R\overline{3}$ ) and two-phase ( $R\overline{3}c + R\overline{3}$ ) fields. Ideally, the variation in energy and entropy as a function of composition within the two-phase field would be a straight line joining the two phases at the boundary. The curvature of the lines within this field in Figure 7 is an artifact due to the limited size of the supercell used in the simulations, which results in a finite energy contribution from the interface between the exsolved phases.

A striking feature of the energy of mixing (Fig. 7a) is the rapid decrease in energy close to the  $FeTiO_3$  end-member. The energy of  $FeTiO_3$  appears to lie significantly off the trend de-



**FIGURE 6.** (a) Energy as a function of long-range order for a composition close to ilm80. Open circles show the results of constrained-swap Monte Carlo simulations, in which Q is held constant by allowing only intralayer and double-layer swaps to occur. Solid lines show least-squares fits to the energies using a fourth-order polynomial (Eq. 4). Superimposed are the equilibrium energies from an unconstrained Monte Carlo simulation (filled circles). (b) Entropy as a function of long-range order for a composition close to ilm80. The shaded region shows the configurational point entropy, bounded by the two models described in Table 1. Superimposed are the equilibrium entropies from an unconstrained Monte Carlo simulation. Dashed line is a least-squares fit to the Monte Carlo entropies with an equation of the form  $S = f S_{point}$ , where f is a constant scaling factor and  $S_{point}$  is the upper limit of point entropy.

fined by the rest of the solid solution. This is due, in part, to the first-order nature of the transition in FeTiO<sub>3</sub>. However, the magnitude of the stabilization energy of FeTiO<sub>3</sub> relative to the rest of the solid solution may be exaggerated due to the way in which the interaction parameters were calculated. The interaction parameters for the solid solution were obtained by fitting to ordering data for three separate bulk compositions simultaneously, whereas those for pure FeTiO<sub>3</sub> were obtained independently. For this reason, there may be an offset between the energy of the end-member relative to the rest of the solid solution, and the absolute values in Figure 7a should be treated with some caution. Qualitatively, however, Figure 7a illustrates the general features that are required to reproduce the equilibrium phase diagram. Note, in particular, the significant changes in energy of the solid solution which occur within the longrange disordered field  $(R\overline{3}c)$ . Conventional thermodynamic models calculate the energy of mixing within the disordered phase using a single temperature-independent regular solution parameter, and, therefore, do not allow for changes in energy caused by short range ordering. For compositions close to x =0.6, the energetic effect of short-range ordering is of the same order of magnitude as that of long-range ordering, and leads to a smooth variation in energy across the phase boundaries.

The entropy of mixing is independent of any offset in the absolute energy of FeTiO<sub>3</sub> relative to the rest of the solid solution, and can, therefore, be compared directly with the ideal configurational point entropy. The upper limit for complete

disorder is given by Equation 2 with Fe<sup>2+</sup>, Fe<sup>3+</sup> and Ti cations randomly distributed over all (001) layers. The lower limit for complete order is given by Equation 2 with Ti fully ordered onto the B-layers and Fe<sup>3+</sup> equally distributed over the A and B layers. Again, the entropy varies significantly within the  $R\overline{3}c$ field due to short-range ordering. For compositions dilute in Ti (i.e., x < 0.1), the effect is negligible. For compositions between 0.2 < x < 0.4, however, the entropy is close to the ordered limit at low temperatures and only approaches the disordered limit at temperatures close to the melting point. Conventional thermodynamic models assume that the entropy of the disordered phase lies at the upper limit of the shaded area at all temperatures.

It is possible to account for the entropic effect of short-range ordering within the long-range ordered phase using a simple modification to a standard macroscopic thermodynamic model. At present, no similar approach to the long-range disordered phase exists. This is a serious shortcoming of current macroscopic models. It is well known from studies of alloy systems, for example, that failure to account for the effects of shortrange ordering produces incorrect phase diagram topologies. Similar errors in the calculation of phase diagrams in mineral systems are to be expected. Although the data presented in Figure 7 could be used to derive activity-composition relations for specific temperatures, it is more desirable to formulate a macroscopic model which reproduces the behavior for a general set of conditions and might be applied to other systems with



**FIGURE 7.** (a) Excess energy of mixing as a function of composition, determined using Monte Carlo simulation. Solid lines refer to the energy of mixing at temperatures of (from bottom to top) 800, 842, 888, 941, 1000, 1066, 1142, 1230, 1333, 1454, and 1600 K. Thick dotted lines show the approximate position of the phase boundaries from Figure 5. (b) Excess entropy of mixing as a function of composition, determined from the Monte Carlo simulations via Equation 10. Solid and dotted lines are defined as in **a**. Shaded region is bounded by the ideal configurational point entropy of the fully disordered and fully ordered solid solution.

similar phase diagram topologies. The effects of short- and longrange magnetic ordering on the phase diagram topology below 500 °C must also be included in any such model.

### **ACKNOWLEDGMENTS**

R.J.H. acknowledges the support of the Marie Curie Fellowship. U.B. appreciates the support of the Deutsche Forschungsgemeinschaft (Habilitationsstipendium 1952/1-1).

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MANUSCRIPT RECEIVED DECEMBER 6, 1999 MANUSCRIPT ACCEPTED JULY 18, 1999 PAPER HANDLED BY BRYAN CHAKOUMAKOS