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Articles

Excess Enthalpy of Formation in the $FeTiO_3$−Fe_2O_3 System: Insights via the Ionic Model

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Experimental data by Navrotsky and co-workers show that the excess enthalpy of mixing, $\Delta H_{xs}(x)$, in the system $(Fe^{2+}{}_x,Ti^{4+}{}_x,Fe^{3+}{}_{2-2x})O_3$ joining α-Fe_2O_3 (hematite) and $FeTiO_3$ (ilmenite) changes in an unusual way from positive to negative with increasing x. Calculations using an ionic model supplemented by short-range repulsion and van der Waals terms allow excellent qualitative agreement with the experimental data and numerical agreement to within a factor of 3. The oscillating behavior of the excess enthalpy of mixing with x is shown to be associated with the specific substitution pattern of the Fe^{3+} ions for Fe^{2+} and Ti^{4+}, which avoid the generation of close Fe^{3+}/Fe^{3+} pairs at high x, but is random at low x.

Introduction

The energetics of solid solutions of metal oxides have received relatively scant attention from electronic structure theorists. However, we recently showed[1] from tight-binding theory how excess enthalpy ($\Delta H_{xs}(x)$) plots for (M,Mg)O (M = Fe, Co, Ni) solutions as a function of composition could be either positive or negative over the range depending on the electronic configuration of the transition metal. The usual type of $\Delta H_{xs}(x)$ plot found for many solid solutions is roughly parabolic in shape with a maximum at a mole fraction of 0.5. This is the point where the local environments of both end members are displaced equally far from their equilibrium structure and thus where maximal enthalpic destabilization occurs. Negative values of ΔH_{xs} are quite rare in fact, and thus the form (Figure 1) of the recent experimental determination[2] by Navrotsky and co-workers of the ilmenite−hematite solution energetics is interesting. Particularly so is the fact that $\Delta H_{xs}(x)$ changes sign with composition. The ilmenite−hematite ($FeTiO_3/Fe_2O_3$) solid solution differs from those of (M,Mg)O noted above in the sense that the substitution is not an isovalent one. The 2+/4+ pair in ilmenite is replaced by a 3+/3+ pair in hematite. The ilmenite−hematite system is more complex, not only in this way but also in terms of the complexity of the crystal structure. Importantly however, there are experimental data[3] on the ordering patterns of the metal ions in the solid solutions for the ilmenite−hematite case. This has aided the interpretation of the form of the plot of Figure 1. In terms of the two dashed curves whose sum can lead to the observed solid curve, these authors suggest that the positive contribution at low x drives "unmixing" and the negative curve at high x drives ordering. In contrast to the quantum mechanical calculations[1] on (M,Mg)O, this paper describes a theoretical study which uses a simple pair potential to describe interatomic interactions and is able to reproduce the form of Figure 1 and give insights into the energetics at an atomistic level.

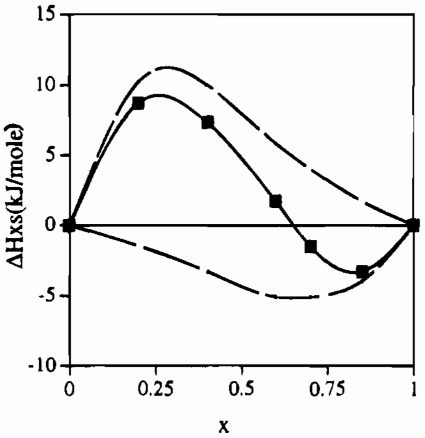

Figure 1. Solid curve: experimentally determined[2] excess enthalpy of mixing along the Fe_2O_3−$FeTiO_3$ solid solution join (x = ilmenite mole fraction). Dashed curves: see text.

Theoretical Approach

Ilmenite and hematite are a part of a important group of minerals, which with geikielite and pyrophanite are known as the rhombohedral oxides. α-Fe_2O_3 (hematite) has the corundum structure (Figure 2), and $FeTiO_3$, a simple derivative structure of it (actually known as the ilmenite structure).[2] The space group of hematite is $R\bar{3}c$, and that of ilmenite, a subgroup, $R\bar{3}$. The metal atoms occupy two-thirds of the octahedral holes of a nearly perfect hexagonal close-packing (...ABAB...) of oxide ions. In ilmenite the two different types of metal ion occupy alternate sets of octahedral holes in the layers parallel to (0001). The A sublattice contains the Fe^{2+} ions and the B sublattice the Ti^{4+} ions. In the substitution process, ilmenite → hematite, an Fe^{2+} ion is converted to an Fe^{3+} ion $(Fe^{2+}{}_x,Ti^{4+}{}_x,Fe^{3+}{}_{2-2x})O_3$. In the simplest terms therefore the oxide lattice remains fixed during the substitution of Fe^{3+} for Ti^{4+} as ilmenite → hematite (although, as we will see, the volume change plays a non-negligible role in the energetics).

One can envisage a multitude of different ways the three metal ions, Fe^{2+}, Fe^{3+}, and Ti^{4+}, are ordered for arbitrary x during the process ilmenite (x = 1) → (x = 0) hematite. In fact, we are considerably aided in our theoretical task by the availability

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(2) Brown, N. E.; Navrotsky, A. *Am. Mineral.* **1994**, *79*, 485.

(3) Brown, N. E.; Navrotsky, A.; Nord, G. L.; Bannerjee, S. K. *Am. Mineral.* **1993**, *78*, 941.

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Table 1. Occupation of A and B Sublattice Sites from Experiment and Those Used in This Work To Mimic It

	experiment sublattice sites					used in calculation sublattice sites			
	A		B			A		B	
mole fraction of $FeTiO_3$	Ti^{4+}	Fe^{2+}	Ti^{4+}	Fe^{2+}	mole fraction of $FeTiO_3$	Ti^{4+}	Fe^{2+}	Ti^{4+}	Fe^{2+}
1.0	1.0	0.0	0.0	1.0		1.0	0.0	0.0	1.0
0.8630	0.698	0.166	0.166	0.698	0.8333	0.667	0.167	0.167	0.66
0.6094	0.311	0.299	0.299	0.311	0.5833	0.333	0.250	0.250	0.33
0.4080	0.206	0.202	0.202	0.206	0.4167	0.208	0.208	0.208	0.20
0.2024	0.102	0.097	0.097	0.102	0.1667	0.083	0.083	0.083	0.08
0	0	0	0	0	0	0	0	0	0

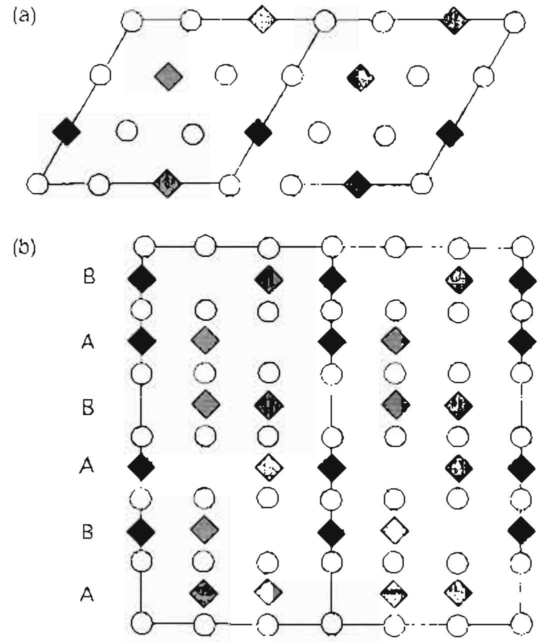

Figure 2. Plans of the corrundum structure of Fe_2O_3 showing scheme for replacement of 2 Fe^{3+} with Fe^{2+} and Ti^{4+}. A block consisting of two adjoining hexagonal unit cells provides the 24 metal atoms required for a total of 12 replacement steps along the Fe_2O_3−$FeTiO_3$ solid solution join. (a) Projection of the triply primitive hexagonal unit cell ($Z = 6$) of Fe_2O_3 onto [001]. Empty circles: oxygen atoms at $z = 0, {}^1/_3, {}^2/_3$. Stippled circles: oxygen atoms at $z = {}^1/_6, {}^3/_6, {}^5/_6$. Dark diamonds: iron atoms at $z = {}^3/_{12}, {}^5/_{12}, {}^9/_{12}, {}^{11}/_{12}$. Vertically hatched diamonds: iron atoms at $z = {}^1/_{12}, {}^5/_{12}, {}^7/_{12}, {}^{11}/_{12}$. Horizontally hatched diamonds: iron atoms at $z = {}^1/_{12}, {}^3/_{12}, {}^7/_{12}, {}^9/_{12}$. (b) Elevation of the doubled unit cell from (a) showing the occupation of two-thirds of the metal atom sites available in each layer between hexagonally packed layers of oxygen atoms. Placement of A (Fe^{2+}) and B (Ti^{4+}) sites is indicated for the completely ordered $FeTiO_3$ structure.

of experimental data[3] concerning site occupancies for $0 < x < 1$ which allow us to restrict the number of patterns we need to consider. Site occupation data for the two sublattices have been collected via saturation magnetism and microprobe analysis (see Table 1). The replacement process is not a random one. Although the ilmenite end-member is completely ordered (there are experimental data[4] for this up to temperatures in excess of 10000 °C) in the samples studied, there is considerablescrambling of Fe^{2+} and Ti^{4+} on the A and B sites as the substitution by Fe^{3+} proceeds.

The changes in formal charges with x indicated by the above suggest that an "ionic" model may be appropriate. Thus the pair potential $\Phi(r_{ij})$ between atoms i and j, as a function of their interatomic separation, r_{ij}, employed in this study is that[5,6] of eq 1. The first term is the Coulombic one, attractive for unlike ions and repulsive for like ions, the second is a short-range repulsion, and the third is the van der Waals attraction

$$\Phi(r_{ij}) = q_i q_j / r_{ij} + B_{ij} \exp(-r_{ij}/\varrho_{ij}) - C_{ij}/r_{ij}^{\,6} \qquad (1)$$

term. B_{ij}, ϱ_{ij}, and C_{ij} are adjustable parameters and are determined by fitting to the geometrical details of an experimentally determined structure. The van der Waals constant is set by the relationship $C_{ii} = 3I_i\alpha_i^2/4$, where I_i and α_i are the ionization potential and polarizability, respectively, for the atom i. The values B_{ij}, ϱ_{ij}, and C_{ij} where i ≠ j are estimated from those of the like atoms as

$$B_{ij} = \sqrt{B_{ii}B_{jj}},\quad C_{ij} = \sqrt{C_{ii}C_{jj}},\quad \varrho_{ij}^{\,-1} = (\varrho_{ii}^{\,-1} + \varrho_{jj}^{\,-1})/2 \qquad (2)$$

For the full structure the Coulomb term is multiplied by A_{ij}, the Madelung constant. The other terms are of short range, and only nearest neighbor interactions are included. The program METAPOX[5,6] was used for the computations. The parameters are listed in Table 2. Notice that the van der Waals term is only used for the O^{2-}—O^{2-} interaction. Even though such an "ionic" model is conceptually not completely correct, its virtue in estimating cohesive energies of both "ionic" and "covalent" systems is well-established.[7]

The calculations used a 24 metal atom cell of stoichiometry $M_{24}O_{36}$. This is twice the orthohexagonal cell. It provided 12 substitutions of a Fe^{2+}/Ti^{4+} pair for a Fe^{3+}/Fe^{3+} pair. It is a supercell large enough to be able to handle a variety of ordering patterns but one which leads, even in the worst case, to a readily accessible number of permutations. Computations were performed on all possible permutations of a given local ordering pattern within this cell, and a statistical average of the energy was obtained. From this $\Delta H_{xs}(x)$ is readily obtained. A similar method was used in our earlier study[1] of the (M,Mg)O system where 27 permutations were used. Three different modes of substitution were studied for ilmenite ($x = 1$) → ($x = 0$) hematite. The first (a) used a random replacement scheme of Fe^{2+}/Ti^{4+} by Fe^{3+}/Fe^{3+}; 48 structures needed to be included in the calculations. No scrambling of Fe^{2+} and Ti^{4+} sites was allowed. The second (b) is similar to (a) and avoided replacement of those close Fe^{2+}/Ti^{4+} pairs whose coordination octahedra share a common face (see Figure 2) by Fe^{3+}/Fe^{3+} pairs. Now 24 structures are needed. The third (c) employed the actual ordering pattern as a function of x established by Brown *et al.*[3] This is reported in terms of average site occupancy factors, and so the geometrical locations of the metal atoms in the 24 metal atom cell were chosen so as to best fit the experimental values (Table 1). The number of structures included here was 32.

Results

Figure 3 shows the results of four sets of calculations to determine $\Delta H_{xs}(x)$: Three ((a)−(c)) are described above. The

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(6) Parker, S. C.; Catlow, C. R. A.; Cormack, A. N. *Acta Crystallogr.* **1984**, *B40*, 200.

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Table 2. Potential Parameters[a]

interaction	A_{ij} (eV)	C_{ij} (eV/Å^6)	ϱ_{ij} (Å)
$Fe^{2+}-O^{2-}$	694.1		0.3399
$Fe^{3+}-O^{2-}$	1102.4		0.3299
$Ti^{4+}-O^{2-}$	754.2		0.3879
$O^{2-}-O^{2-}$	22764.3	27.063	0.1490

[a] Metal–oxygen parameters from ref 4; O–O interactions from ref 10.

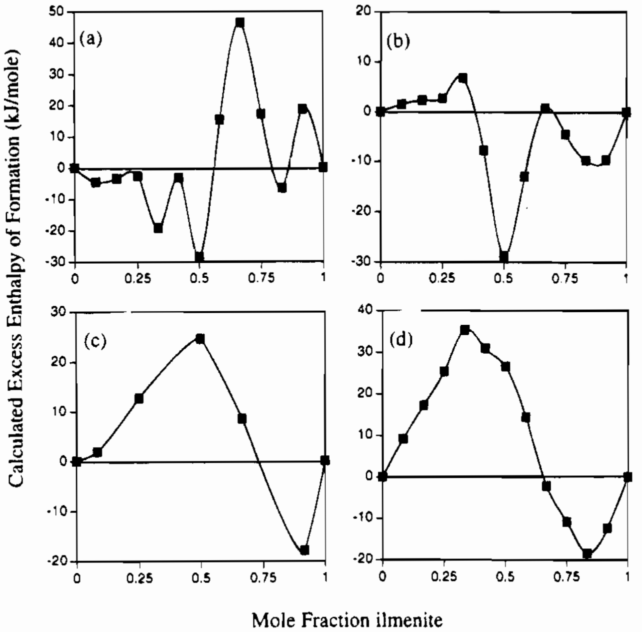


Figure 3. Excess energy of mixing calculated as a function of ilmenite mole fraction along the $Fe_2O_3-FeTiO_3$ join: (a) random replacement of 2 Fe^{3+} with Ti^{4+} and Fe^{2+}; (b) "close-pair" replacement of 2 Fe^{3+} with Ti^{4+} and Fe^{2+}; (c) ordered replacement of 2 Fe^{3+} with Ti^{4+} and Fe^{2+}, allowing for mixing of the three ions onto the two possible cation sites in the structure, according to experimental results established by Brown *et al.*[3]; (d) same calculation as in (c), but with a correction allowing for a Végard's law[8] volume change between Fe_2O_3 and $FeTiO_3$. The completely random substitution process leads to a parabola.

last (d) uses the ordering pattern as a function of x established by Brown *et al.*[3] but with a Végard's law[8] volume change imposed on the structures using the dimensions of the end-members. (There is evidence[9] that the changes in the dimensions of the structure are not linear with x. We have however ignored this here.) There are 13 points on each plot commensurate with the 24 metal atom cell chosen for the calculations. It is clear to see that the calculations which used an approximate to the observed ordering pattern fit the experimental $\Delta H_{xs}(x)$ data very well in many ways. Numerically, however, there is a factor of 3 between the amplitudes of the plots of Figure 1 and Figure 3d. The calculated $\Delta H_{xs}(x)$ plots for (a) and (b) are far from the experimental one. The completely randomly substituted system is expected to lead to a positive parabola for $\Delta H_{xs}(x)$ with a maximum at $x = 0.5$.

Table 1 shows the spatially averaged site occupancies of A and B sublattices. Clearly there is some scrambling of Fe^{2+} and Ti^{4+} between the two sites at intermediate stoichiometries. In fact, for $x < 0.6$ this appears to be nearly complete. Thus the observed curve (**1a**) of Figure 3d arises as a sum of the completely randomly substituted process for $x < 0.6$ (**1b**) and a differentially stabilizing feature for $x > 0.6$ (**1c**):

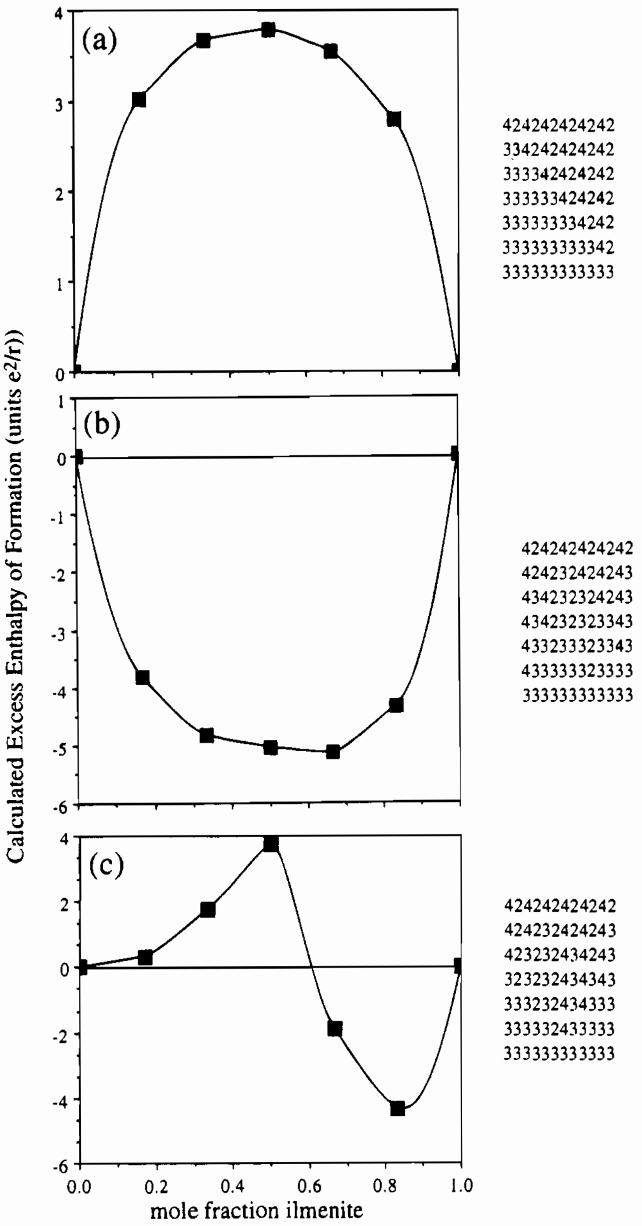
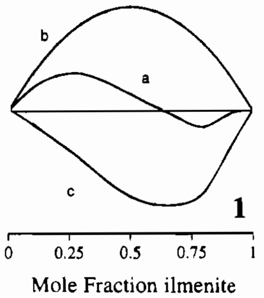


Figure 4. Calculated excess electrostatic energy curves for a series of "solid solutions" of the 12 atom chain which mimics ilmenite ("424242424242") and hematite ("333333333333"). The way the substitution proceeds is indicated at the right of each panel.



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The local details of the ordering patterns are impossible to derive from the experimental data, but we note that the close-pair avoidance (with the results shown in Figure 3b) leads to a negative value of ΔH_{xs} in this region. We can however, use a simple model which leads to some insights into this problem.

Figure 4 shows the calculated excess electrostatic energy curves for a series of "solid solutions" of a 12 atom chain of metal ions which only differ in their ordering patterns. We only evaluate the Coulombic energy of the chain, which, without

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(9) Lindsley, D. H. *Year Book—Carnegie Inst. Washington* **1965**, *64*, 144.
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cyclic boundary conditions, is just $\sum_{ij}q_iq_j/r_{ij}$. At the ilmenite-rich end this chain is described as "424242424242" and at the hematite end as "333333333333". Figure 4a shows the calculated excess enthalpy, $\Delta H_{xs}(x)$, associated with a substitution process in which (i) each adjacent "42" pair is replaced by a "33" pair and (ii) the substitution proceeds by replacement of adjacent "42" pairs (see the preceding diagram). $\Delta H_{xs}(x)$ is always positive. Figure 4b shows a plot for which $\Delta H_{xs}(x)$ is always negative. It corresponds to a substitution pattern where the "4" in the "worst" electrostatic situation and the "2" in the "best" electrostatic situation are replaced each time. The effect is a reduction in the effect of the large repulsive interactions associated with each "4" upon the substitution "4" → "3" which are not compensated by the increase in repulsive interactions associated with each "2" upon the substitution "2" → "3".

The plot of Figure 4c represents a substitution pattern where "4's" and "2's" are replaced by "3's", the latter being kept far apart, the exact opposite of Figure 4a. This $\Delta H_{xs}(x)$ plot has an oscillating shape, similar to that of both the observed hematite/ilmenite plot of Figure 1 and the calculated one of Figure 3d. Similar results are found for a model chain with the "31...31" arrangement of charges which eventually give "22...22" on substitution. Thus, initially on substitution of Fe^{2+} and Ti^{4+} by $2Fe^{3+}$ in both real three-dimensional and model one-dimensional examples, there is plenty of choice in site location to keep the 3+ ions (with their strong repulsion) apart. This leads to a negative value of ΔH_{xs}. As the replacement proceeds this becomes less true, the substitution pattern looks more "random", and the curve becomes positive. Thus, although by no means complete, the simple model supports the picture of diagram **1**. We cannot readily comment on the suggestion[11] that it is the positive (repulsive) intralayer Fe^{2+}/Ti^{4+} interactions which dominate at the hematite-rich end and negative (attractive) interlayer Fe^{2+}/Ti^{4+} interactions which dominate at the ilmenite-rich end. Recall that none of the substitutions can be performed arbitrarily; charge and stoichiometry need to be conserved. In addition, the averagings over a number of structural permutations for each composition in all of our three-dimensional studies make it difficult to attribute the dominant energetic behavior to one particular interaction.

One can ask why the model based on eq 1 overestimates the magnitude of $\Delta H_{xs}(x)$ by a factor of 3. One obvious adjustment is the introduction of a screening function for the electrostatic field, the largest contributor to $\Delta H_{xs}(x)$. Another is the introduction of orbital effects, of vital importance in the studies of ref 1. Both may indeed play a role, but the important point of this paper is that the ionic model is a useful way to capture the essence of the experimental data. It provides a much more transparent and atomistic picture than that of the thermodynamic models which have been used in this class of oxides (see ref 12 and references therein).

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