The temperature dependence of the cation distribution in synthetic hercynite (FeAl$_2$O$_4$) from in-situ neutron structure refinements

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ABSTRACT

The temperature dependence of the cation distribution in synthetic hercynite (FeAl$_2$O$_4$) has been determined using in-situ time-of-flight neutron powder diffraction. The sample was synthesized from the oxides under controlled oxygen fugacity and then quenched in air. Neutron diffraction patterns were then collected under vacuum on heating from room temperature to 1150 °C, and the cation distribution was determined directly from site occupancies obtained by Rietveld refinement. The degree of inversion, x, decreased from 0.135(4) at room temperature to 0.112(4) at 600 °C. Thereafter the degree of inversion increases smoothly with increasing temperature, reaching a value of 0.219(5) at 1150 °C. The decrease in x on heating to 600 °C is a kinetic phenomenon caused by the system moving toward its equilibrium degree of order from the relatively disordered state maintained after quenching from the synthesis temperature. The equilibrium ordering behavior between 600 and 1150 °C has been analyzed using both the O'Neill-Navrotsky and Landau thermodynamic models. Although the data could be fitted with both models over the temperature range of the measurements, Landau theory predicts the incorrect curvature of the equilibrium x-T curve, leading to a significant discrepancy in the calculated behavior when the model is extrapolated outside the calibrated temperature range. The correct x-T curvature is predicted by the O'Neill-Navrotsky model, and values of the model coefficients α = 31.3 ± 1.1 kJ/mol and β = 19.7 ± 3.4 kJ/mol were obtained by least-squares fitting to the equilibrium data. This confirms the results of a previous study using quenched material, which suggested that the sign of the β coefficient in FeAl$_2$O$_4$ is opposite to that found in other 2–3 oxide spinels.

INTRODUCTION

The 2–3 class of oxide spinels, which includes FeAl$_2$O$_4$, is represented by the general formula unit AB$_2$O$_4$, where A is a divalent cation and B is a trivalent cation. The O anions form an approximately cubic close packed arrangement, and the cations distribute themselves over one tetrahedral site and two octahedral sites per formula unit (pfu), according to the general scheme:

$$A_{1-x}B_x(A_{x/2}B_{1-(x/2)})_2O_4$$

where parentheses represent cations on octahedral sites. The variable x is the inversion parameter. Two ordered configurations of the spinel structure can be adopted at low temperatures; the normal configuration with $x = 0$, and the inverse configuration with $x = 1$. At elevated temperatures the cations become increasingly randomly distributed over tetrahedral and octahedral sites. A value of $x = \frac{2}{3}$ corresponds to a completely random distribution of A and B over the three cation sites per formula unit. Because the order-disorder process in spinel is non-con-

vergent (there is no symmetry difference between an ordered and a totally disordered spinel), such a completely random distribution would only be anticipated at infinite temperature and is approached asymptotically on increasing temperature in real samples.

Hercynite (FeAl$_2$O$_4$) adopts the predominantly normal cation distribution at low temperatures (Bohlen et al. 1986; Chassagneux and Rousset 1976; Gaballah et al. 1975; Hill 1984; Larsson et al. 1994; Yagnik and Mathur 1968). The temperature dependence of the cation distribution is, however, less well defined. There are several inconsistencies between published high-temperature cation distributions for FeAl$_2$O$_4$. The origin of these inconsistencies is threefold. First, all studies to date have been performed on material quenched from high annealing temperatures. The kinetics of cation ordering in spinels is fast enough to allow some degree of cation redistribution during quenching, leading to a quenched-in cation distribution that differs from the equilibrium cation distribution at the annealing temperature (Larsson et al. 1994; Millard et al. 1992; Peterson et al. 1991; Redfern et al. 1996; Wood et al. 1986). Second, several studies report the

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presence of Fe^{3+} in their samples (Hill 1984; Bohlen et al. 1986). Such deviations from ideal stoichiometry can have a large effect on both the equilibrium and the kinetic properties of spinels (Redfern et al., in preparation). Third, many studies use Mössbauer spectroscopy to quantify the relative amounts of Fe^{2+} on octahedral and tetrahedral sites. Because the Mössbauer spectra are poorly resolved, with multiple peak contributions from both tetrahedrally and octahedrally coordinated Fe^{2+}, there is a large degree of uncertainty in their interpretation. This point is illustrated by the study of Larsson et al. (1994), which showed a significant difference between cation distributions determined by Mössbauer spectroscopy and X-ray diffraction (XRD) on the same samples.

The aim of this study is to determine the equilibrium high-temperature cation distribution in $FeAl_2O_4$ using in-situ neutron structure refinement and characterize the kinetics of non-equilibrium high-temperature order-disorder. Time-of-flight neutron scattering provides the ideal probe of cation ordering in this mineral due to the very large contrast between the neutron scattering lengths of Fe and Al (9.54 fm and 3.45 fm, respectively), the ability to perform the experiment in-situ under high vacuum (which prevents oxidation of Fe^{2+} to Fe^{3+}), and the ability to record the entire diffraction pattern rapidly (hence reducing the amount of time the sample is annealed at high temperature, which lowers the probability of introducing point defects). The high accuracy and precision of the results allow an effective comparison between different thermodynamic theories of the cation ordering process to be made and hence a new constraint on the high-temperature crystal chemical properties of $FeAl_2O_4$ to be derived.

EXPERIMENTAL PROCEDURES

Synthesis

The sample was synthesized from oxide powders under controlled oxygen fugacity (f_{O_2}). A 16 g stoichiometric mix of Fe_2O_3 (99.999%) and Al_2O_3 (99.99%) was weighed out and homogenized by grinding under acetone in an agate mortar. The oxide mix was then pressed into several pellets using a 0.5 inch diameter WC die. The pellets were sintered for a period of 22 h at 1400 °C under a flowing atmosphere of CO and CO_2 gases in the ratio $CO/CO_2 = 75/25$ (Nafziger et al. 1971). The pellets were then quenched by dropping them to the bottom of the furnace. XRD examination of a sintered chip from each of the pellets showed them to be single phase hercynite. The pellets were then reground, repressed, and reannealed at 1400 °C for 14.5 h, 1100 °C for 26.5 h, and 700 °C for 41 h, using a gas mixture of CO/CO_2 = 85/15 (which corresponds to the f_{O_2} for the quartz-fayalite-iron oxygen buffer). The f_{O_2} was monitored throughout the synthesis using an yttria-stabilized zirconia solid electrolyte probe (Sato 1971). The observed f_{O_2} was in agreement with the f_{O_2} calculated from the tables of Deines et al. (1974) to within 0.02 log units at

1100 °C. After the final annealing period at 700 °C, the sample was quenched by dropping the pellets from the furnace onto SiO_2 glass wool, which formed the lining of a previously evacuated metal beaker.

Neutron diffraction procedures

The neutron powder diffraction data were collected using the high-intensity POLARIS time-of-flight diffractometer at the ISIS spallation neutron source (Rutherford Appleton Laboratory, U.K.). All 16 g of sample pellets were stacked as a pile, held in a tantalum wire basket, and suspended inside a vanadium element furnace. The furnace was evacuated to a pressure of 10^{-6} mbar. The temperature was measured and controlled using type K thermocouples. The sample and furnace thermal mass ensured good thermal stability throughout each data collection. The neutron diffraction patterns were collected for flight times between 2.5 and 19.6 ms, corresponding to d-spacings between 0.4 and 3.2 Å. This range of data included around 250 independent Bragg reflections, giving 140 individual Bragg peaks in the powder diffraction pattern when accounting for different reflections having identical d-spacings. The data from individual detectors were corrected for electronic noise, normalized against standard spectra from a sample of vanadium, and focused using in-house software. No corrections were made for beam attenuation by the furnace or sample, because these were found to be negligible.

We found no evidence for oxidation of the sample, which is expected due to the relatively high vacuum of the sample chamber and the close proximity of tantalum and vanadium metal to the sample, both of which act as O getters. The color of the sample (light blue-green) was unchanged after the high-temperature heating experiments. The room-temperature lattice parameter measured after the experiment with an NBS Si internal standard was identical to the initial lattice parameter (8.1458 ± 0.0006 Å) to within 1 esd. Both these facts indicate that no change in stoichiometry had occurred. The room-temperature lattice parameter of the present sample is 0.006 ± 0.001 Å smaller than those reported by Larsson et al. (1994) for samples HC1 and BG2, indicating a small difference in stoichiometry. This difference could be explained either by ≈2 mol% solid solution of Fe_3O_4 (a_0 = 8.397 Å) in the Larsson et al. (1994) samples, or, alternatively, ≈2 mol% solid solution toward γ-$Al_{8/3}O_4$ (a_0 = 7.905 Å) in the present sample. We prefer the former explanation, implying that it is the present sample, rather than the samples of Larsson et al. (1994) that is more nearly stoichiometric $FeAl_2O_4$, because the lower lattice parameter found here agrees better with the extrapolation to end-member stoichiometric $FeAl_2O_4$ obtained from measurements of the lattice parameters of the binary $FeAl_2O_4$-Fe_3O_4 solid solution (O'Neill, unpublished data).

The crystal structures were refined assuming ideally stoichiometric total site occupancies using the GSAS Rietveld refinement software (Larson and Von Dreele
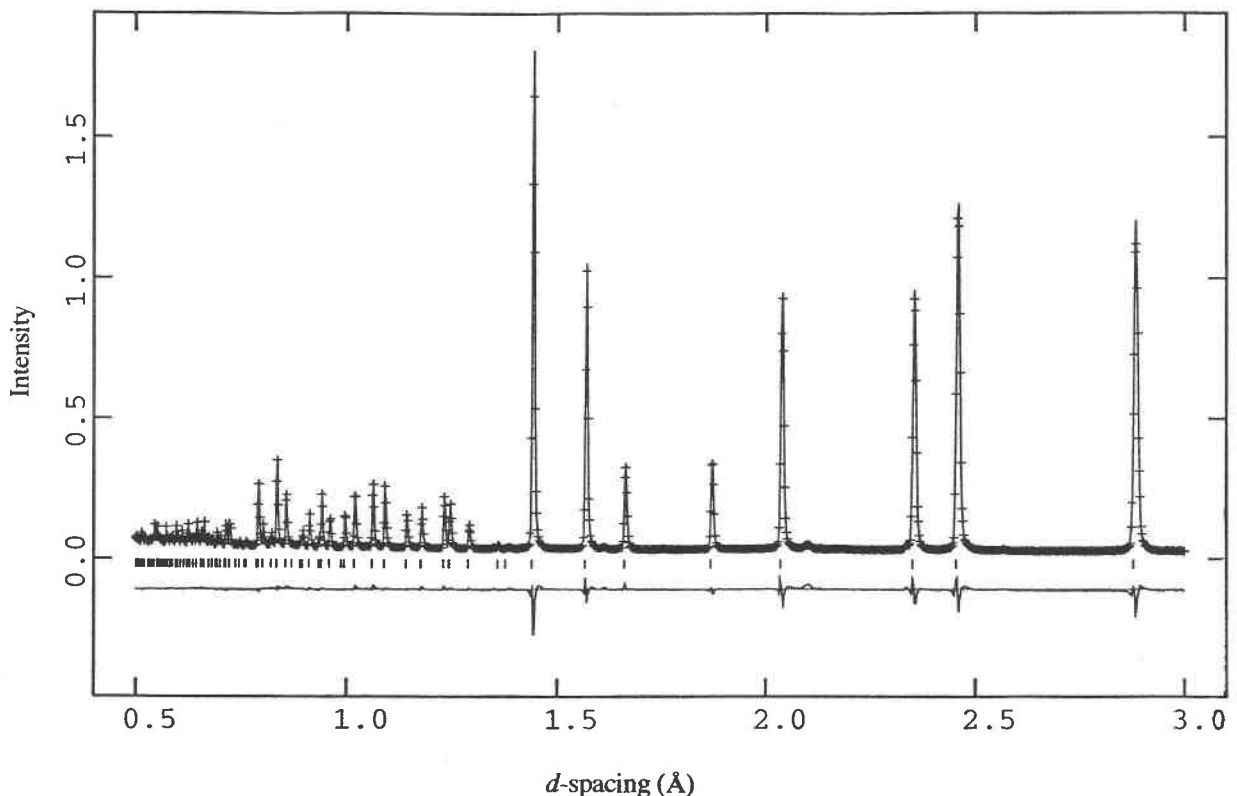
FIGURE 1. Time-of-flight neutron diffraction pattern for synthetic $FeAl_2O_4$ at room temperature together with the calculated pattern and difference plot from Rietveld refinement. Note the high quality of the neutron diffraction data at low d-spacings.

1994). The background signal was modeled using a 6th-order polynomial. The crystallographic variables were the unit-cell parameter, the coordinates of the O atom, the occupancies of the tetrahedral and octahedral sites, and the isotropic temperature factors. The cell parameter was independently calibrated by cross-calibrating against that determined from an aliquot of the same sample measured using X-ray diffraction with a Guinier camera and employing NBS Si as an internal standard. An example neutron diffraction pattern is shown in Figure 1, and the results of the Rietveld refinements are listed in Table 1.

RESULTS OF THE STRUCTURE REFINEMENTS

The change in the degree of inversion with temperature (Fig. 2a) is characteristic of all cation order-disorder processes in materials that are quenched rapidly to room temperature and then reheated (Harrison and Putnis 1996; Redfern et al. 1996). The degree of inversion observed at room temperature is 0.135(4), which corresponds to the degree of inversion that is retained after quenching the sample from the synthesis temperature. Because this cation distribution is disordered relative to the equilibrium cation distribution at room temperature (which is close to $x = 0$), there is a driving force for the system to order (i.e., for x to decrease). On heating from room temperature to 500 °C, only a small decrease in x is observed,

due to the slow kinetics of cation ordering over this temperature range. Between 500 and 600 °C, x decreases more rapidly, reaching a minimum value of 0.112(4) at 600 °C (this rapid approach to equilibrium on heating is often referred to as "relaxation" of the cation distribution). At this point the system has reached equilibrium, and as the temperature is increased further, the cation distribution disorders steadily along the equilibrium x-T curve (shown as the solid line in Fig. 2a). This cation relaxation process was quantified by Harrison and Putnis (1996) and Redfern et al. (1996) using the Ginzburg-Landau kinetic rate law. This theory is applied to the data in a later section.

The oxygen positional parameter is sensitive to the changes in the cation distribution (Fig. 2b), and follows a similar path on heating as the inversion parameter. The relationship between u and x is shown in Figure 3, and can be described by the 3rd-order polynomial:

$$u = 0.26488 - 0.00118x - 0.0289x^2. \qquad (1)$$

The lattice parameter, in contrast, is fairly insensitive to the changes in cation distribution (Fig. 2c). The same observation was made by Larsson et al. (1994) in their study of quenched $FeAl_2O_4$. The increase in a with temperature is dominated by thermal expansion, but shows a small increase in slope at 600 °C (as illustrated by the linear fits in Fig. 2c). The tetrahedral and octahedral site

TABLE 1. Refined structural parameters for $FeAl_2O_4$

$T(K)$	a (Å)	x	u	B_{tet}	B_{oct}	B_{oxy}	R_{wp}
298	8.145 78(3)	0.135(4)	0.264 252(3)	0.571(9)	0.387(12)	0.798(6)	3.33
473	8.156 12(3)	0.134(4)	0.264 238(3)	0.838(11)	0.542(15)	0.971(7)	3.05
673	8.169 49(3)	0.134(4)	0.264 223(3)	1.147(13)	0.744(17)	1.203(8)	2.75
723	8.172 98(3)	0.133(4)	0.264 210(3)	1.219(13)	0.785(17)	1.246(8)	2.70
773	8.176 57(3)	0.132(4)	0.264 202(3)	1.290(14)	0.823(18)	1.299(8)	2.64
823	8.180 21(3)	0.125(4)	0.264 279(3)	1.365(14)	0.872(18)	1.332(8)	2.57
873	8.183 90(3)	0.112(4)	0.264 380(3)	1.455(14)	0.912(19)	1.355(8)	2.54
923	8.187 81(3)	0.122(4)	0.264 311(3)	1.538(15)	0.967(20)	1.441(9)	2.50
973	8.191 77(3)	0.132(4)	0.264 219(3)	1.618(16)	1.037(20)	1.538(9)	2.46
1023	8.195 71(3)	0.143(4)	0.264 113(3)	1.697(17)	1.110(21)	1.624(10)	2.41
1073	8.199 88(3)	0.153(4)	0.263 994(3)	1.784(18)	1.170(22)	1.721(10)	2.40
1123	8.204 04(3)	0.166(4)	0.263 885(3)	1.858(18)	1.246(22)	1.816(11)	2.38
1173	8.208 26(3)	0.175(4)	0.263 791(4)	1.954(20)	1.315(24)	1.912(11)	2.39
1223	8.212 52(3)	0.185(4)	0.263 692(4)	2.044(21)	1.389(25)	2.003(12)	2.39
1273	8.216 80(3)	0.193(4)	0.263 599(4)	2.137(22)	1.459(26)	2.093(13)	2.38
1323	8.221 03(3)	0.201(5)	0.263 491(4)	2.234(23)	1.522(26)	2.186(13)	2.34
1373	8.225 25(3)	0.207(5)	0.263 366(4)	2.333(23)	1.595(26)	2.277(13)	2.27
1423	8.229 39(3)	0.219(5)	0.263 254(4)	2.416(24)	1.677(27)	2.365(13)	2.19

Note: $R_{wp} = \Sigma w(F_{obs} - F_{calc})^2 / \Sigma wF_{obs}^2$.

temperature factors (Fig. 2d) display a similarly small change in slope at 600 °C. The oxygen anion temperature factor appears to be more sensitive to the cation distribution and shows a distinct decrease at 600 °C in response to the rapid decrease in x that occurs at this temperature. The same relationship between B_{oxy} and x was observed in $FeAl_2O_4$ by Larsson et al. (1994) and also in the analogous $CoAl_2O_4$ spinel by O'Neill (1994).

The trend in x as a function of T is in very good agreement with the data measured by Larsson et al. (1994) on quenched material, using powder XRD structure refinement. The data from these two studies define parallel trends, with the x-T curve determined by Larsson et al. (1994) offset by +0.01 along the x axis relative to that measured in this study (see dashed line in Fig. 2a). This difference is <2 combined esd and can easily be accounted for by a small degree of non-stoichiometry in the sample used by Larsson et al. (1994). In the analogous $MgAl_2O_4$ spinel, an offset of $x = 0.02$ was observed using neutron diffraction between one sample with ideal stoichiometry and a slightly non-stoichiometric sample with formula unit $Mg_{0.99}Al_2O_4$ (Redfern et al., in preparation). In this case, a deficiency of just 0.005 Fe pfu in the sample used by Larsson et al. (1994) would be sufficient to account for the small offset between the neutron and X-ray diffraction data sets. An alternative explanation for the offset is the use of neutral atom scattering curves in the X-ray Rietvelt refinements of Larsson et al. (1994), rather than fully ionized or half-ionized curves. O'Neill and Dollase (1994) have demonstrated empirically that differences in the inversion parameter of similar magnitude to that observed here are obtained using data collected on $MgCr_2O_4$, refined with the three different sets of scattering curves (the difference in scattering between Mg and Cr is only one electron's worth larger than that between Fe and Al). These considerations do not effect our neutron refinements because neutrons scatter from the nucleus of the atom.

THERMODYNAMIC MODELING

Thermodynamics of cation ordering in spinels is the subject of many studies (Navrotsky and Kleppa 1967; O'Neill and Navrotsky 1983, 1984; Carpenter et al. 1994; Carpenter and Salje 1994a and 1994b). We present here only a brief account of the two most commonly used theories before applying them to the present data.

In the thermodynamic model proposed by O'Neill and Navrotsky (1983), the enthalpy of a spinel with an intermediate cation distribution, relative to the same spinel with the normal cation distribution, is expressed as a quadratic function of the degree of inversion ($\Delta H = \alpha x + \beta x^2$). Combining this with the configurational entropy of the intermediate cation distribution, the change in free energy relative to the normal spinel is obtained:

$$\Delta G = \alpha x + \beta x^2 + RT \sum_{i,j} N_j X_i^j \ln X_i^j \qquad (2)$$

where X_i^j is the fraction of cation i on site j, and N_j is the number of j-sites per formula unit. Setting the derivative of Equation 2 with respect to x equal to zero gives an expression relating x and T at equilibrium:

$$-RT \ln\left(\frac{x^2}{(1-x)(2-x)}\right) = \alpha + 2\beta x. \qquad (3)$$

This equilibrium relationship well describes the ordering behavior in a wide range of 2–3 spinels (Nell et al. 1989; O'Neill 1992, 1994; O'Neill et al. 1991, 1992; Wu and Mason 1981). In these studies the α parameter is found to be in the range +17 to +50 kJ/mol, and the β parameter lies in the range −15 to −25 kJ/mol, with an average value of $\beta = -20$ kJ/mol.

A multiple non-linear least-squares fit to our equilibrium data (between 600 and 1150 °C) yields values of $\alpha = +31.3 \pm 1.1$ kJ/mol and $\beta = +19.7 \pm 3.4$ kJ/mol, with a reduced χ^2 of 0.11. The data were weighted according to estimated standard deviations from the refinements quoted in Table 1, and an estimated uncertainty in the
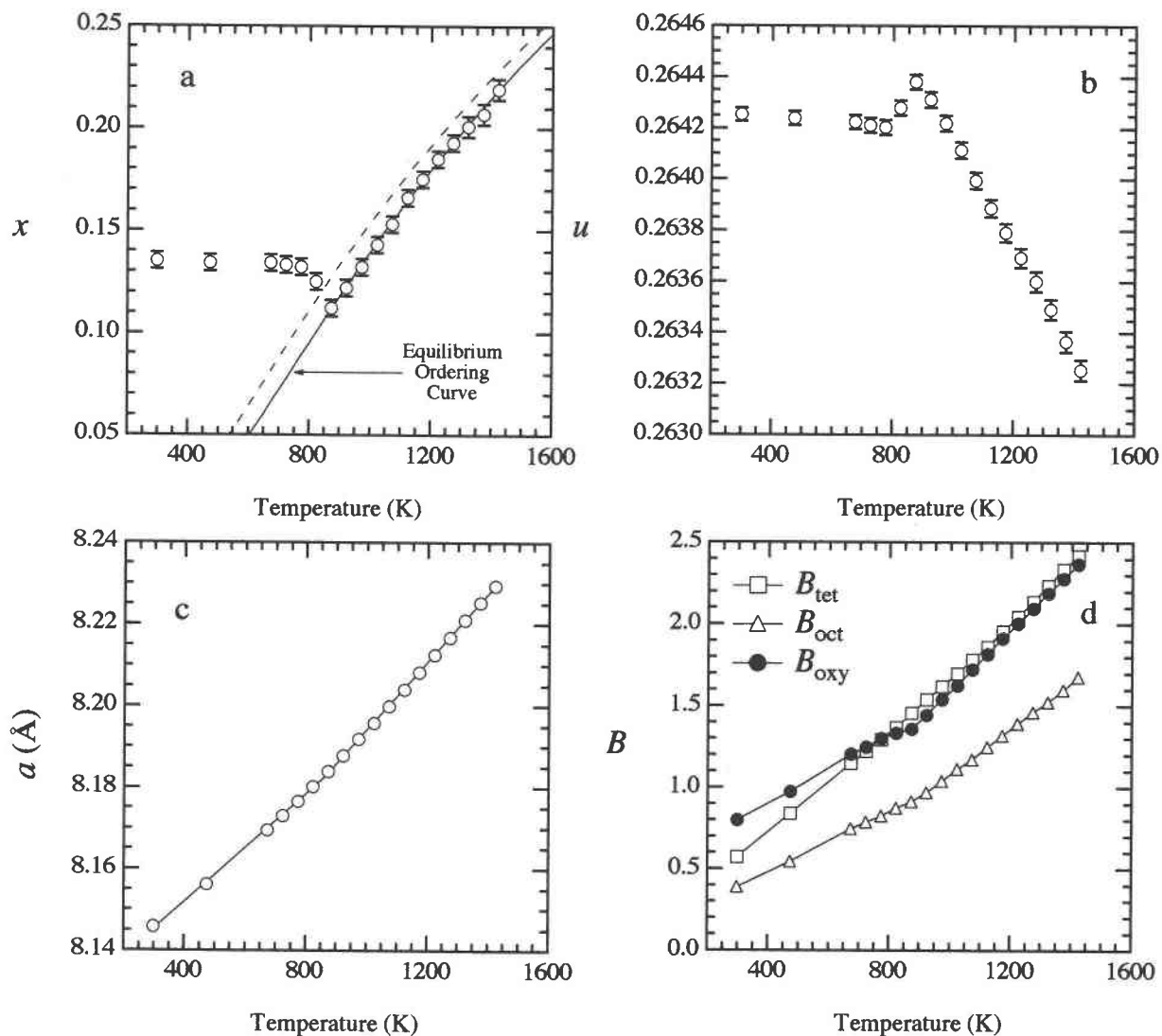
Figure 2. Temperature dependence of (**a**) inversion parameter (x); (**b**) oxygen positional parameter (u); (**c**) cell parameter (a); and (**d**) tetrahedral, octahedral, and oxygen temperature factors (B_{tet}, B_{oct}, and B_{oxy}). Solid line in (**a**) is a fit to the equilibrium data between 600 and 1150 °C using the O'Neill and Navrotsky (1983) thermodynamic model (Eq. 3), yielding α = +31.3 ± 1.1 kJ/mol and β = +19.7 ± 3.4 kJ/mol. Dashed line is an equivalent fit to the data of Larsson et al. (1994), shown for comparison.

temperature of ±5 °C (which turns out to be trivial in comparison to the uncertainty in x). The low value of the reduced χ^2 (0.11) reflects the over-estimate of the standard deviation in x made by the Reitveld refinement (0.004 to 0.005). This over-estimate is a consequence of the fact that minimization is performed on many parameters simultaneously during the refinement, some of which (e.g., the temperature factors) correlate with x. This leads to an increase in estimated standard deviations over that obtained by refining x alone. The internal estimate of the non-systematic component of the uncertainty in x for each datum (calculated as that required to produce a χ^2 of unity) is 0.001.

The result of the fit is shown as the solid line in Figure

2a. Although the model provides an excellent fit to the data, the sign of the refined β parameter is opposite to that found in other 2–3 spinels that have been analyzed using the O'Neill and Navrotsky (1983) model. This anomalous behavior was also observed by Larsson et al. (1994), who determined values for the thermodynamic parameters α = +27 kJ/mol and β = +24 kJ/mol. Their fit is shown as the dashed line in Figure 2a for comparison. It is particularly interesting to note that the value for β obtained here is opposite to that determined for $CoAl_2O_4$, which should display similar high-temperature crystal-chemical behavior to $FeAl_2O_4$ (O'Neill 1994). At present we can offer no explanation for this anomalous behavior.
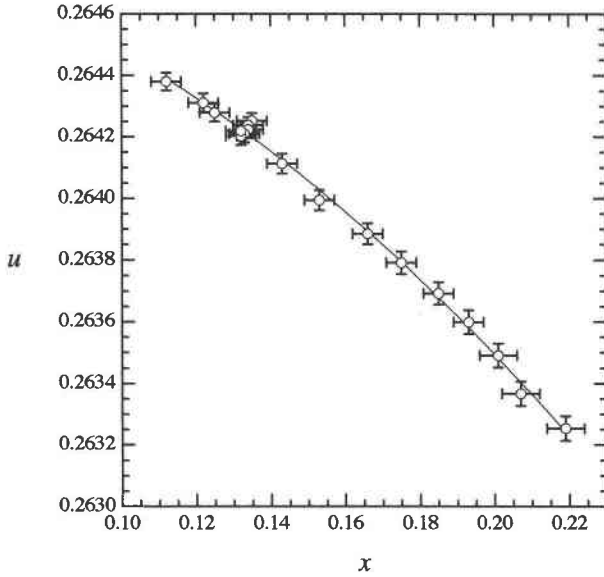
FIGURE 3. Oxygen positional parameter (u) as a function of the inversion parameter (x). Solid line, least-squares fit.

An alternative thermodynamic approach to ordering in spinels was proposed by Carpenter et al. (1994) and Carpenter and Salje (1994a), based on the Landau theory of phase transitions (Landau and Lifshitz 1980). In Landau theory, the free energy of an intermediate spinel is calculated relative to a hypothetical spinel with the fully disordered cation distribution. For this reason, an alternative order parameter, Q, is chosen to describe the cation distribution, such that $Q = 0$ corresponds to the state of complete disorder:

$$Q = X_B^{oct} - X_B^{tet} = 1 - \frac{3}{2}x. \qquad (4)$$

According to this definition $Q = 1$ for the normal cation distribution, and $Q = -0.5$ for the inverse cation distribution. The change in free energy, relative to the fully disordered state at the temperature of interest, is given by a potential of the form:

$$\Delta G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{6}cQ^6 \qquad (5)$$

where h, a, T_c, and c are constants. This free energy potential differs from that given in Equation 2 in two respects. First, the enthalpy change due to ordering in the Landau potential contains linear, quadratic, and 6th-order terms, whereas the enthalpy of ordering in the O'Neill and Navrotsky (1983) model includes just linear and quadratic terms. Second, the entropy change due to ordering in the Landau potential is a simple quadratic function of the order parameter. This differs from the O'Neill and Navrotsky (1983) model, which uses the exact form of the configurational entropy.

Setting the derivative of Equation 5 with respect to Q equal to zero, and applying the constraint that $Q = 1$ at

$T = 0$ K for a normal spinel gives an expression relating Q and T at equilibrium:

$$T = T_c + \frac{T_c}{(c' - 1)Q}(1 - c'Q^5) \qquad (6)$$

where $c' = c/h$ (Harrison and Putnis 1997). A least-squares fit to the equilibrium data between 600 and 1150 °C, weighted using the estimated standard deviations from the refinements for Q (0.006 and 0.0075) and an uncertainty of ±5 °C in T, yielded $T_c = 749 \pm 222$ K and c' $= 2.19 \pm 0.63$, with a reduced χ^2 of 0.73. However, if the precision of the data is taken as ±0.0015 in Q, as estimated from internal consistency, then the reduced χ^2 would be $\approx$7, indicating that the Landau model does not fit the data at this level of precision. This disparity can be seen in Figure 4, in that the curvature of the fitted curve is opposite to that suggested by the data themselves. This could lead to a significant discrepancy between calculated and observed behavior when the fit is extrapolated outside the temperature range of the experimental calibration.

Because the O'Neill and Navrotsky (1983) model reproduces the correct curvature of the observed data (dotted line in Fig. 2), we conclude that the origin of the discrepancy between the Landau model and the temperature-dependent form of the order parameter lies in the simplified form of the excess entropy due to ordering assumed in the Landau potential. Kroll et al. (1994) used a modified Landau potential to describe cation ordering in orthopyroxenes, which included the exact form of the configurational entropy, in addition to the traditional Landau entropy term (which then accounts for any non-configurational contributions). In this case the O'Neill-Navrotsky and Landau models differ only by the inclusion of a higher-order enthalpy term in the Landau model. Given the quality of the fit obtained with the O'Neill-Navrotsky model, the inclusion of such a higher-order term cannot be justified for $FeAl_2O_4$.

KINETIC BEHAVIOR

The process of cation distribution relaxation, which occurs when quenched materials are heated slowly to high temperatures, has been quantified by Harrison and Putnis (1996) and Redfern et al. (1996) using the Ginzburg-Landau rate law (Carpenter and Salje 1989; Salje 1988). The rate law is of the form:

$$\frac{dQ}{dt} = -\frac{\gamma \exp(-\Delta H^*/RT)}{2RT} \frac{\partial \Delta G}{\partial Q} \qquad (7)$$

where t is time, γ is a frequency factor, ΔH^* is the activation energy, and ΔG is the appropriate free energy potential describing the cation ordering process. Integrating Equation 7 under isothermal conditions we obtain:

$$t - t_0 = \int_{Q_0}^{Q} \frac{-2RT}{\gamma \exp(-\Delta H^*/RT)} \left(\frac{\partial \Delta G}{\partial Q}\right)^{-1} dQ \qquad (8)$$

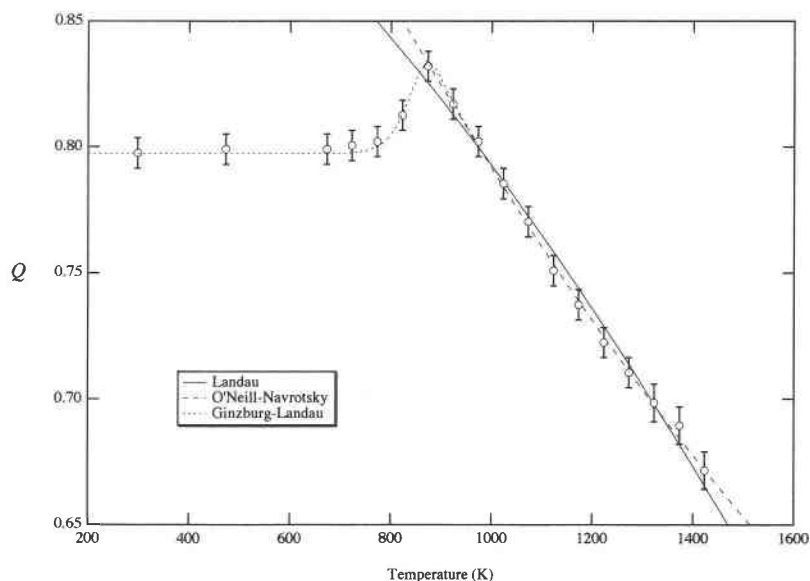where Q_0 is the initial value of Q at time t_0. This equation

FIGURE 4. The order parameter, Q (Eq. 4), as a function of temperature. The solid line is a fit to the data using the Carpenter et al. (1994) thermodynamic model (Eq. 6), yielding $T_c = 749 \pm 222$ K and $c' = 2.19 \pm 0.63$. The dashed line is the fit to the equilibrium data between 600 and 1150 °C using the O'Neill and Navrotsky (1983) thermodynamic model. The dotted line is the calculated behavior using the Ginzburg-Landau rate law (Eq. 7), with the thermodynamic driving force given by the O'Neill and Navrotsky (1983) model (Eq. 2).

allows the time taken for a given change in Q to be calculated. Alternatively one may calculate the change in Q for a given annealing time by evaluating Equation 8 numerically and varying the upper limit of integration in an iterative procedure until the correct annealing time is obtained. The evolution of Q vs. t during heating or cooling at a constant rate can be determined by approximating the constant heating or cooling rate by a series of discrete isothermal annealing steps separated by an instantaneous temperature change.

To apply the O'Neill and Navrotsky (1983) model to the Ginzburg-Landau rate law, the free energy due to ordering (Eq. 2) was recast in terms of Q, using the symmetric formalism of Holland and Powell (1996). An estimate for the frequency factor $\gamma = 1.354 \times 10^9$ s^{-1} was taken from the analysis of kinetics in MgFe$_2$O$_4$ spinel (Harrison 1997). The activation energy was then chosen in order to fit the experimental data. A value of $\Delta H^* = 215$ kJ/mol gave the best fit, although our confidence in this value can only be as high as our confidence in the choice of γ. The kinetic calculation was performed with a heating rate of 50 K/h, which was the approximate heating rate used during the neutron data collection. The constant heating rate was approximated to a series of isothermal annealing steps of 72 s duration, separated by an instantaneous temperature increase of 1 K. The calculation was begun at room temperature and $Q = 0.7975$ (i.e., the degree of order maintained after quenching from the synthesis temperature). The calculated evolution of Q vs. T during heating is shown as the dotted line in Figure 4. The dashed line is the equilibrium ordering curve, calculated using the O'Neill and Navrotsky (1983) model.

The combination of the Ginzburg-Landau rate law and the O'Neill-Navrotsky kinetic driving force provides an excellent description of relaxation process. The system rapidly approaches the equilibrium curve between 500 and 600 °C, because the kinetics of ordering become fast enough to allow Q to change on the time scale of the experiment at these temperatures. The calculated heating curve oversteps the equilibrium curve slightly as the temperature is raised above 600 °C. This effect is due to the fact that $dQ/dt = 0$ when $d\Delta G/dQ = 0$ (Eq. 7). The size of the overstep is negligible for a heating rate of 50 K/h, but can be more significant at faster heating rates (Harrison and Putnis 1996).

The kinetics of cation ordering in FeAl$_2$O$_4$ appear to be much faster than in other aluminate spinels (Larsson et al. 1994). For example, O'Neill (1994) failed to equilibrate a sample of CoAl$_2$O$_4$ that had been annealed at 700 °C for over 118 h. In comparison, the FeAl$_2$O$_4$ in this study reached equilibrium after heating to 600 °C over a period of just a few hours. The most likely explanation for the anomalously fast kinetics in FeAl$_2$O$_4$ is the presence of cation vacancies (point defects) caused by slight deviations from ideal stoichiometry (i.e., the oxidation of Fe^{2+} to Fe^{3+}).

THE SIGN OF β

This study is in good agreement with the XRD results of Larsson et al. (1994) and hence confirms that the β parameter in FeAl$_2$O$_4$ has a positive sign, rather than the negative sign observed in other 2–3 spinels. Explanations for this unusual behavior are speculative at this stage. Previously this observation had been interpreted as an experimental artifact caused by coupling between the kinetics of the ordering process and the concentration of point defects in the sample. This explanation can now be ruled out in the light of our in-situ measurements. Alternatively, the cation ordering behavior may be sensitive to the form used to describe the configurational entropy. If the entropy of intermediate FeAl$_2$O$_4$

differs significantly from the ideal configurational entropy (e.g., due to the presence of short-range ordered arrangements of Fe and Al on the octahedral and tetrahedral sites, instead of the statistically random arrangement dictated by the space group symmetry), then this might bias the fitted values of α and β in comparison to spinels that do not have short-range order. The existence of short-range order in the analogous $MgAl_2O_4$ spinel has been implied on the basis of high-temperature phase equilibrium experiments (Wood et al. 1986). Preliminary studies of $MgAl_2O_4$ using in-situ neutron diffraction also suggest that β is positive in this material (Redfern et al., in preparation).

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