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Thermodynamics of Al/Al avoidance in the ordering of Al/Si tetrahedral framework structures

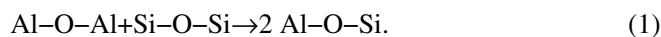
Received: 14 May 1997 / Revised, accepted: 2 June 1997

Abstract The main driving force behind Al/Si ordering in tetrahedral framework aluminosilicates is nearest-neighbour Al/Al avoidance. Computer simulation is used to explore the direct consequences of such Al/Al avoidance. The main result is that the order-disorder transition temperature T_c falls dramatically as the concentration x of Al in the structure is reduced, and if the only interactions are those associated with nearest-neighbour Al/Al avoidance, T_c becomes zero for x less than some critical value x_c , where $x_c=0.31$ for the feldspar framework and $x_c=0.34$ for cordierite. Also a large degree of short range order is found above T_c . Both results differ radically from the standard Bragg-Williams model. Plots of entropy and enthalpy of ordering are given as functions of x and T , which may be used to interpret experimental data or for extrapolation into ranges of x and T inaccessible to experiment.

Key words Loewenstein's rule · Al/Al avoidance · Al/Si ordering · Bragg-Williams

Introduction

Al/Al avoidance is very important in aluminosilicates, and is the main driving force behind order-disorder phase transitions in tetrahedral framework silicates. The Loewenstein energy J or J_1 is the energy cost associated with the formation of a nearest-neighbour Al–O–Al linkage; it is defined as the energy given out in the reaction



Energies J_2, \dots, J_r associated with interactions between more separated tetrahedra can be defined in a similar way. Computer simulations have been performed using

empirical interatomic pair potentials to determine values of J_1, J_2, \dots, J_r for sillimanite (Bertram et al. 1990), gehlenite (Thayaparam et al. 1994), and cordierite (Thayaparam et al. 1996). These simulations showed that J_1 is of the order of five times greater than next-nearest-neighbour interactions.

The main objective of this paper is to determine how Al/Al avoidance influences the formation of long range order below the phase transition temperature, T_c , and the formation of short range order above T_c . The motivation for this work follows our earlier computer simulation work on Al/Si ordering phase transitions (Dove et al. 1996) in which we identified the crucial rôle that Al concentration x (i.e., the concentration of Al on tetrahedral sites, with $1-x$ as the concentration of Si) plays in determining the transition temperature. In particular, it was suggested that when $x < 0.5$, T_c is much lower than the estimate given by the Bragg-Williams model because of the possibility of forming local configurations with complete Al/Al avoidance without precipitating long range order.

The main result of this paper is that there is a dramatic fall in the order-disorder transition temperature T_c with reduced Al concentration x . In fact, T_c becomes zero for x less than some critical value x_c . This dramatic fall in T_c is the "dilution" effect discussed by Dove et al. (1996). The other significant result presented in this paper is that there is a great deal of short range order even above T_c .

In this paper we also use the model to produce results for long and short range order and thermodynamic quantities such as the enthalpy and entropy as functions of x and T . These results can be used to interpret experimental data, and for extrapolation into regions of x and T where experiment is not possible.

Computational method

The Al/Al avoidance model

In our computer simulations, we define a network of sites with the same topological structure as the aluminosilicate

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being investigated; in this paper we specifically consider the feldspar and cordierite frameworks. To calculate the internal energy of a configuration, we associate an energy of J with each Al–O–Al linkage and zero with each Al–O–Si and Si–O–Si linkage, specifically excluding all other possible interactions. Thus in the model, the energy E of a configuration is

$$E = E_0 + J \sum_{\langle ij \rangle} \eta_i \eta_j, \quad (2)$$

where the sum is over all nearest-neighbour pairs, and η_i is 1 if atom i is Al and 0 if it is Si. Energy and enthalpy are equivalent for this model, since it does not include volume effects. Note that this model can be mapped onto the standard Ising spin model where σ_i is 1 for Al and -1 for Si by substituting $\eta_i = \frac{1}{2}(1 + \sigma_i)$.

The term E_0 is a constant, and has no consequences for the evolution of the computer simulation, so we can set it equal to zero. Therefore E will be zero for any state with complete Al/Al avoidance, and $N_{\text{Al-Al}}J$ for a state with $N_{\text{Al-Al}}$ Al–O–Al linkages.

We investigated the model using the Monte Carlo method for fixed values of x and T . We initially assigned Al and Si atoms to the sites with a distribution corresponding to a totally ordered state with concentration x , and then allowed the system to equilibrate at a given value of T . The reason for this was that if we had started in a disordered state (corresponding to $T=\infty$), domain structures might have formed at low temperatures, and these would not have been recognised as ordered. Equal length runs were used for equilibration and analysis.

Definitions of order parameter

We measure the degree of order of a configuration by a long range order parameter Q . The definition of Q is different for different frameworks. Most of the frameworks we considered can be divided into two sublattices A and B in such a way that all the nearest neighbours of atoms on the A sublattice are on the B sublattice and vice versa; we will refer to frameworks with this property as ‘‘ABAB frameworks’’. For ABAB frameworks, a state has long range order if one sublattice is preferentially occupied by Al atoms, and the definition of Q we use is

$$\frac{(\text{No. of Al atoms on A sublattice}) - (\text{No. of Al atoms on B sublattice})}{\text{Total number of Al atoms}} \quad (3)$$

Here Q can vary between 1 and -1 for any value of x .

This definition of Q does not apply, for example, to the cordierite framework, since it contains nine-membered rings and therefore is not an ABAB framework. In this case, we define Q in terms of the correlations between atoms which are as far apart as possible. Since we used periodic boundary conditions in our computer simulation, this distance was half the sample size. If we define

$$P_{\text{AA}} = \left\langle \eta_i \eta_{i+l_x/2} \right\rangle, \quad (4)$$

where l_x is the length of the sample in the x direction, then the definition of Q we used for cordierite was

$$Q = \frac{P_{\text{AA}}(\text{sample}) - P_{\text{AA}}(\text{random})}{P_{\text{AA}}(\text{ordered}) - P_{\text{AA}}(\text{random})}. \quad (5)$$

Here $0 \leq Q \leq 1$ for any value of x . This equation can be simplified if we write $P_{\text{AA}}(\text{random})=x^2$, and we can then calculate $P_{\text{AA}}(\text{ordered})$ as follows. If $x = \frac{4}{9}$, there exists at least one ordered state with total Al/Al avoidance and a repeat unit of one orthorhombic unit cell with 36 tetrahedra; for such a state $P_{\text{AA}} = \frac{4}{9}$. Ordered states with $x < \frac{4}{9}$ can be formed by removing randomly chosen Al atoms from an ordered state with $x = \frac{4}{9}$, and hence

$$P_{\text{AA}}(\text{ordered}) = \frac{4}{9} \cdot \left(\frac{9}{4}x \right)^2 + \frac{5}{9} \cdot 0 = \frac{9}{4}x^2. \quad (6)$$

Therefore (5) reduces to

$$Q = \frac{4}{5x^2} \left(\left\langle \eta_i \eta_{i+l_x/2} \right\rangle - x^2 \right). \quad (7)$$

Statistical analysis

Running simulations at constant x and T gave us $Q(x, T)$ and $E(x, T)$, where E is the internal energy per atom. We estimated $T_c(x)$ by running simulations at constant x over a range of T and determining where Q fell to zero. The results were checked by comparison with the calculation of the susceptibility

$$\chi(T) = \frac{\langle Q^2 \rangle - \langle Q \rangle^2}{T}. \quad (8)$$

$\chi(T)$ will diverge at T_c , so plots of $\chi^{-1}(T)$ provide an independent measurement of T_c , in a fully self-consistent manner. If necessary, this process was repeated over a smaller range of T to estimate T_c more precisely.

The free energy F of the model can be calculated by thermodynamic integration. The general principle of this method for any model is to separate the Hamiltonian H into a sum of a term H_0 that corresponds to an approximation to H that can be solved exactly, and a term $\Delta H = H - H_0$. The free energy can be obtained from this separated Hamiltonian using a result that follows from the Bogoliubov inequality (Yeomans 1992):

$$F = F_0 + \int_{\lambda=0}^1 \langle \Delta H \rangle_{\lambda} d\lambda, \quad (9)$$

where F_0 is the free energy corresponding to a system governed by the Hamiltonian H_0 , and $\langle \Delta H \rangle_{\lambda}$ denotes the average of $(H - H_0)$ obtained over a distribution function determined by the Hamiltonian

$$H_{\lambda} = H_0 + \lambda \Delta H. \quad (10)$$

In its practical implementation, the distribution function can be obtained by performing a Monte Carlo simulation subject to the Hamiltonian H_λ , and evaluating at each step the energy corresponding to the Hamiltonian H .

In our system the implementation of this approach was relatively straightforward. The Hamiltonian describing the system was equivalent to the energy given by (2). Our approximate Hamiltonian H_0 was that for a non-interacting system, i.e. $H_0=0$, in which at any temperature the Al and Si cations would be distributed at random in the structure. The free energy for this Hamiltonian, F_0 , is then obtained from the entropy of a completely random system with zero energy, and is therefore given by

$$F_0 = E - TS = k_B T (x \ln x + (1-x) \ln(1-x)). \quad (11)$$

The Hamiltonian H_λ is therefore identical in form to the Hamiltonian of the system as given by (2), except that the exchange constant J is replaced by the smaller value λJ . The average $\langle \Delta H \rangle_\lambda$ was evaluated for each value of λ at a fixed temperature by running the Monte Carlo simulation using the Hamiltonian H_λ . This had an average number of Al–O–Al linkages, from which the Hamiltonian H , required for the evaluation of $\langle \Delta H \rangle_\lambda$, could be calculated. In effect, since $H_0=0$, the energy given by the Monte Carlo simulation performed with the exchange constant λJ was simply divided by λ to give $\langle \Delta H \rangle_\lambda$. The process was repeated for many values of λ ranging from zero to unity, and the resultant $\langle \Delta H \rangle_\lambda$ was then integrated over λ to give the free energy using (9). The entropy of the model could then be calculated from the data for F and E .

Results for transition temperatures

Graphs of $T_c(x)$ for the feldspar and cordierite frameworks and the two-dimensional square lattice are shown in Fig. 1. The value of T_c drops rapidly with falling Al concentration x . This dramatic fall in T_c is similar to the experimental plot of $T_c(x)$ for feldspar over a narrow range of x shown by Carpenter and McConnell (1984), although the experimental T_c falls more rapidly. From Carpenter and McConnell (1984) we have $T_c(x=0.5) > 1823$ K (the melting point for pure anorthite) and also $T_c(x=0.4375) = 1663$ K. So the ratio

$$r = \frac{T_c(x=0.5)}{T_c(x=0.4375)} \quad (12)$$

has experimentally a value greater than 1.10, but the computer simulation gives $r=1.06$. However, our results for $T_c(x)$ are not very different from experiment, and are certainly much better than the Bragg-Williams prediction for $T_c(x)$, which is also shown for the feldspar framework in Fig. 1.

This dramatic fall in T_c occurs because frameworks with low coordination can have a lot of short range order without any long range order when the Al concentration is low; however, Bragg-Williams theory ignores short range

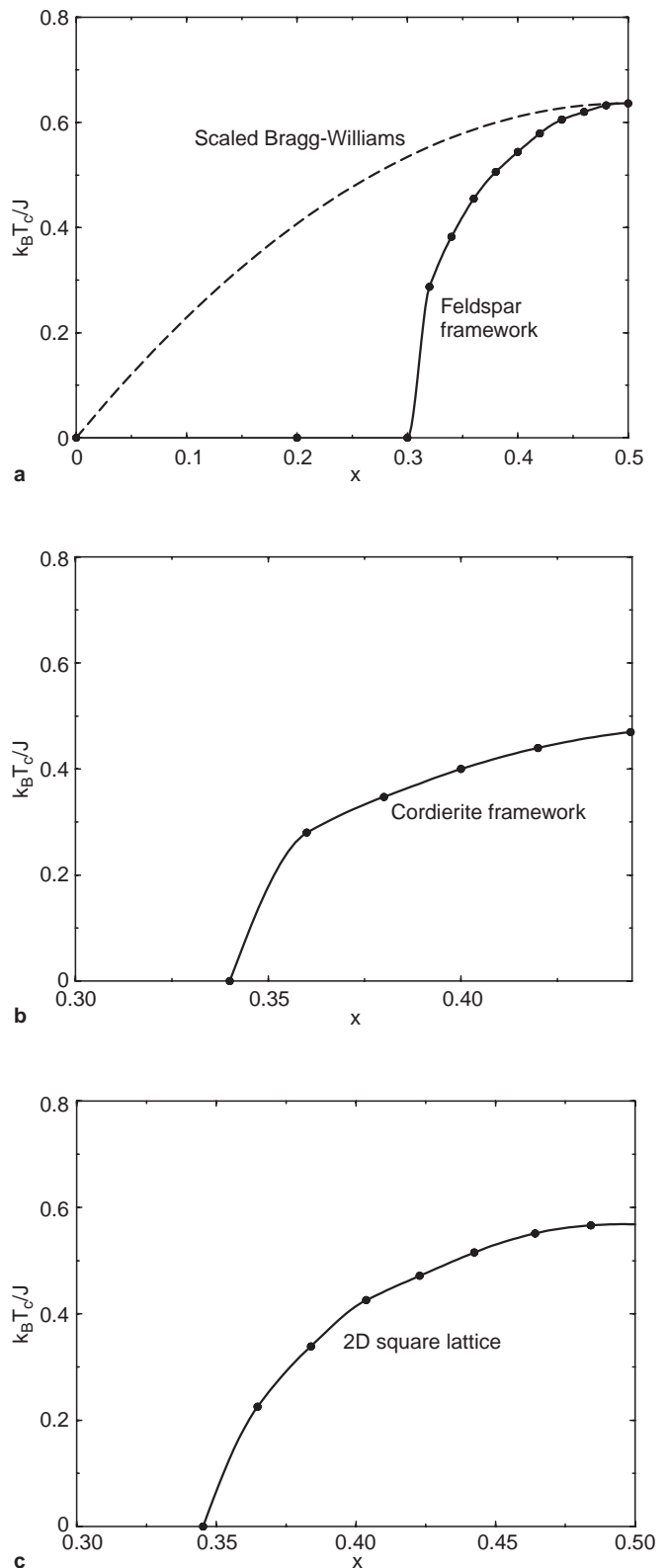


Fig. 1a $T_c(x)$ for the feldspar framework (solid line), compared with $T_c(x)$ for the Bragg-Williams model (dashed line). The latter has been scaled by a factor of 0.64 to give the correct T_c for $x=0.5$. **b** $T_c(x)$ for the cordierite framework. **c** $T_c(x)$ for the two-dimensional square lattice

Table 1 Values of the critical concentration x_c for various frameworks

Framework	x_c
Feldspar	0.31
Cristobalite	0.29
Nepheline	0.29
Cordierite	0.34
Body-centred cubic	0.18

order. The predictions of Bragg-Williams theory are better for frameworks with higher coordination, since it becomes exact in the limit of each atom having infinitely many neighbours.

We define x_c as the critical concentration at which $T_c(x)$ falls to zero. It was determined by plotting $Q(x)$ at $T=0$ and seeing where Q fell to zero, and, for confirmation, where the variance of Q was largest. We estimate that the error in x_c is ± 0.01 .

Table 1 shows x_c for various frameworks. Our values of x_c are high, i.e., these results are very different from the prediction of Bragg-Williams theory that $x_c=0$. This breakdown of the standard Bragg-Williams model is so pronounced because the coordination number of most of the frameworks we consider is only 4; note that x_c for the body-centred cubic framework is much lower than for the other frameworks because this framework has a higher coordination number. This is a different type of breakdown of Bragg-Williams theory from the one that occurs for the face-centred cubic framework, where it breaks down because of “frustration” in the sense of Wannier (1950). Of the frameworks we consider, only cordierite is frustrated, and therefore its value of x_c is slightly higher than those of the other tetrahedrally coordinated structures.

What are the physical reasons that there is no ordered state for $x < x_c$? Qualitatively, if x is sufficiently low then the Al atoms can be arranged more or less at random without any Al–O–Al linkages, i.e., the requirement of complete Al/Al avoidance does not lower the entropy very much. We can define an entropy $S_0(Q, x)$ for a system at $T=0$ with the order parameter constrained to some chosen value Q . Then the equilibrium value of Q will be such as to maximise $S_0(Q, x)$. This idea is discussed in more detail in the following paper (Myers 1998), where it is used to find an approximation for x_c .

Our results were anticipated, at least in a qualitative sense, by the large body of work on “percolation” (e.g. Stauffer and Aharony 1994). For a lattice with vacant sites, only for a concentration of occupied sites greater than some typical threshold will a single cluster extend throughout the whole lattice; for lower concentrations the system will break up into small clusters with no long range order. We have mapped our A and B sublattices onto a site-percolation model in order to obtain an estimate for the lowest value of x that will sustain long range order (unpublished work). We have found that this mapping does not give a very close lower bound for x_c , but it gives an alternative demonstration that $x_c > 0$.

Application to enthalpy and short range order

The short range order parameter σ is a measure of the degree of Al/Al avoidance. It must be unity for a structure with no Al–O–Al linkages, and zero for a totally random structure. We define it as:

$$\sigma = 1 - \frac{(\text{Proportion of Al-O-Al bonds in the sample})}{(\text{Proportion of Al-O-Al bonds in a totally random state})}. \quad (13)$$

This definition is the full short range order that would be measured experimentally by ^{29}Si NMR, for example. Below T_c it includes a component from the long range order, and so we also define a short range order parameter σ' that excludes the local ordering that arises from the long range order as

$$\sigma' = \frac{\sigma - Q^2}{1 - Q^2}. \quad (14)$$

Since the energy E of the model is directly proportional to the number of Al–O–Al bonds, E and σ are essentially different measures of the same quantity for this simple model, related by

$$E = \frac{1}{2} z J x^2 (1 - \sigma), \quad (15)$$

where z is the coordination number.

Unlike Bragg-Williams theory and Landau theory, the model gives us an approximation for σ both above and below T_c , and our Monte Carlo calculations show that there is a great deal of short range order even above T_c . Figure 2 shows how the short range order of the feldspar framework falls with increasing temperature for low and high x . Note that above T_c , σ is lower for higher values of x , because the difference in entropy between states with

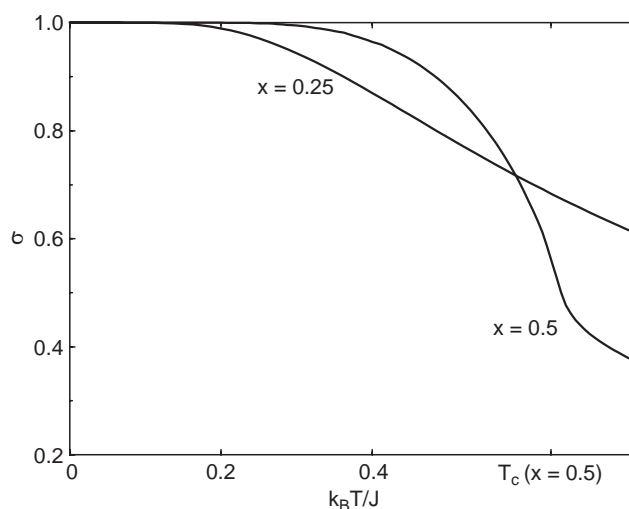


Fig. 2 Short range order versus temperature for different values of x for our computer simulation of the feldspar framework. Note that even when $T > T_c(x=0.5)$, σ is much greater than zero, although $\sigma \rightarrow 0$ as $T \rightarrow \infty$

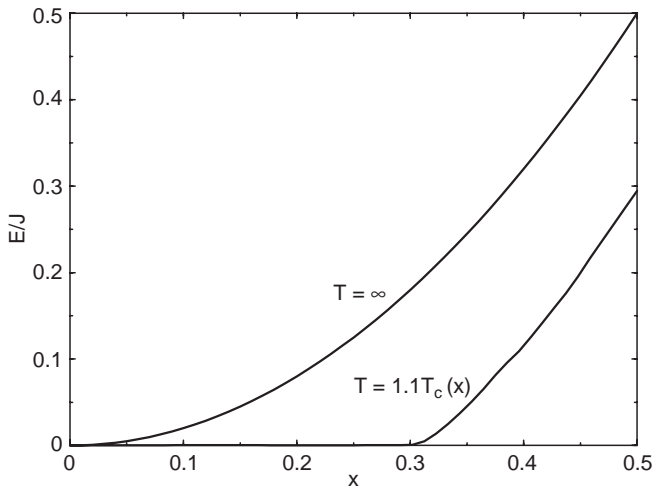


Fig. 3 Enthalpy of our computer simulation of the feldspar framework at $1.1 T_c(x)$, compared with the enthalpy at infinite temperature

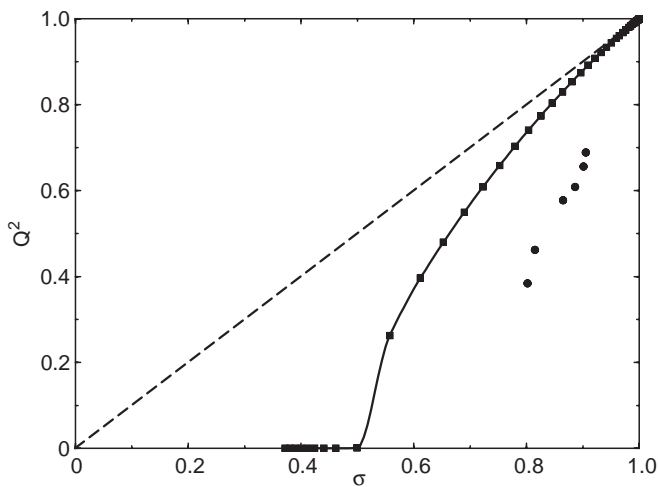


Fig. 4 Q^2 versus σ at $x=0.5$ for our computer simulation of the feldspar framework (solid line), as predicted by Bragg-Williams theory (dashed line), and experimental results obtained by annealing anorthite glass at 1400°C (filled circles)

much and little short range order is greater, but that σ is much greater than zero even for $x=0.5$ at high temperature.

Figure 3 illustrates that the enthalpy of the model at $T=1.1 T_c(x)$ is much less than at $T=\infty$, because of the large degree of short range order. This enthalpy, which is effectively an enthalpy of ordering, is approximately linear in x . We can compare it with experimental values of ΔH_{ord} of anorthite-rich feldspars (Carpenter 1994). For pure anorthite ($x=0.5$) the theoretical value of ΔH_{ord} is $0.294 J$ per atom, and Carpenter's experimental value is 37.3 kJ/mol , where one mole contains $4N_A$ Al and Si atoms. Thus we can calculate an approximate value for J :

$$J = \frac{37.3 \times 1000}{4 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \times 0.294} \text{ eV} = 0.33 \text{ eV}. \quad (16)$$

This value is within the range of $0.4 \pm 0.1 \text{ eV}$ obtained by Phillips et al. (1992). Therefore the model gives a reasonably good approximation to ΔH_{ord} at the anorthite end. However, the experimental enthalpy of ordering drops more steeply with falling x .

Figure 4 shows Q^2 versus σ over a range of temperatures for the feldspar framework with $x=0.5$ from our computer simulation, compared with the prediction of the Bragg-Williams model that $Q^2=\sigma$. The curve predicted by the computer simulation is much steeper than the Bragg-Williams curve, again because there is a great deal of short range order without any long range order.

The curve shown in Fig. 4 is for samples in equilibrium at various temperatures. Samples formed by incompletely annealing disordered anorthite glass must appear to the right of the curve, since short range order varies much faster than long range order. Experimental results from annealing anorthite glass at 1400°C (Phillips et al. 1992) confirm this, and are shown as dots in Fig. 4.

Results for entropy

It is not possible to measure S experimentally, but our Monte Carlo computer simulations enable us to estimate $S(x, T)$ for any chosen framework. Figure 5 shows the entropy per atom $S(x)$ of the feldspar framework for three different temperatures. Note that for low x , $S(x)$ is fairly high even at $T=0$. For example, when $x=0.25$, $S/k_B=0.4$ at $T=0$ compared with 0.562 for a fully disordered system. The high entropy at $T=0$ for low x arises because the atoms can easily be arranged so as to have complete Al/Al avoidance, as has already been discussed in connection with the absence of long range order for $x < x_c$.

Figure 6 shows how the entropy of the feldspar framework varies with T for x above and below x_c . For $x < x_c$, the temperature dependence of S is fairly weak, since the entropy is high even at $T=0$ (as discussed in connec-

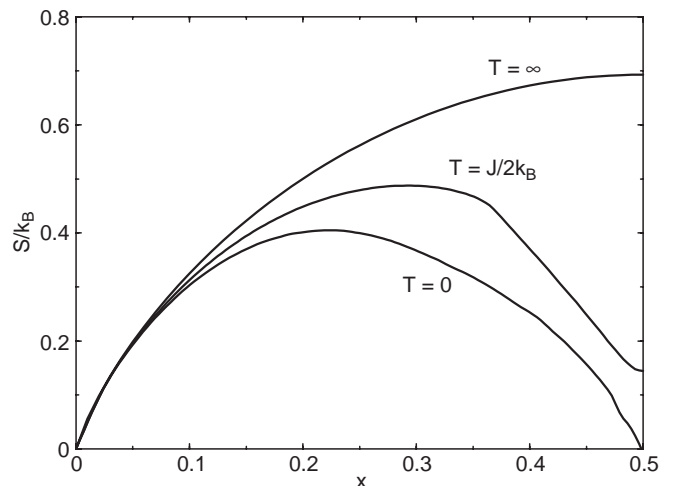


Fig. 5 Variation of entropy with composition for the feldspar framework at various temperatures

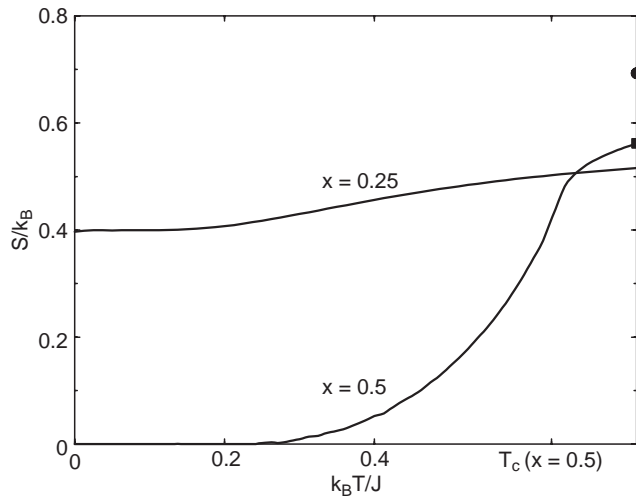


Fig. 6 Entropy of our computer simulation of the feldspar framework versus temperature for different values of x . The dots on the right-hand side represent the asymptotic values of $S(T)$ as $T \rightarrow \infty$ for $x=0.25$ (filled square) and $x=0.5$ (filled circle)

tion with Fig. 5). For $x > x_c$, the temperature dependence of S is much stronger, and $S(T)$ increases rapidly at T_c . It continues to increase above T_c , and is well below $S(T \rightarrow \infty)$ even at quite high temperatures, unlike $S(T)$ for low x .

Discussion and conclusions

Our model gives values of $T_c(x)$ for the feldspar framework which are considerably higher than its values of $T_c(x)$ for the cordierite framework or the two-dimensional square lattice. In the case of the cordierite framework, T_c is reduced by the frustration effect, and in the case of the square lattice, T_c is smaller because of the low dimensionality. Comparison of the graphs of $T_c(x)$ for the cordierite framework and the square lattice suggests that the frustration effect is more pronounced at higher concentrations, while the effect of low dimensionality is more pronounced at lower concentrations.

It seems plausible that the frustration effect would increase with x , since at low concentrations only small clusters of adjacent Al atoms are present in a random configuration, and these can be eliminated by small local adjustments that don't depend on the details of the structure. In other words, when x is low the entropy of a frustrated framework is about the same as that of an ABAB framework with the same coordination number, but when x is high the entropy of the frustrated framework is less for the same degree of short range order.

Low dimensionality reduces $T_c(x)$ because for a system to have long range order, there must be a non-zero probability that two atoms at any distance from each other are

Table 2 $1000|Q(x, T)|$ for the feldspar structure

$k_B T/J$	Percentage Al concentration																				
	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
0.000	279	615	726	798	848	885	914	936	953	966	975	983	989	993	996	998	999	1000	1000	1000	1000
0.025	30	601	724	798	846	885	914	936	953	965	975	983	989	993	996	998	999	999	1000	1000	1000
0.050	40	611	722	795	847	885	915	936	952	965	976	983	989	993	996	998	999	1000	1000	1000	1000
0.075	239	613	721	798	847	885	913	935	953	965	975	983	989	993	996	998	999	1000	1000	1000	1000
0.100	219	431	726	797	847	883	914	936	953	966	975	983	989	993	996	998	999	1000	1000	1000	1000
0.125	158	603	720	797	848	885	913	936	952	965	975	983	988	993	996	998	999	1000	1000	1000	1000
0.150	97	119	722	793	846	883	912	934	952	965	975	982	988	993	995	997	999	1000	1000	1000	1000
0.175	64	207	712	787	840	880	911	933	950	964	974	982	988	992	995	997	999	999	1000	1000	1000
0.200	29	289	705	780	837	874	906	929	948	961	973	980	987	991	995	997	998	999	1000	1000	1000
0.225	5	5	678	765	825	868	900	924	944	958	970	978	985	990	994	996	998	999	1000	1000	1000
0.250	61	219	653	746	810	853	890	917	938	954	966	976	983	989	993	995	997	999	999	1000	999
0.275	25	35	497	712	788	839	879	906	930	947	961	972	980	986	991	994	996	998	999	1000	999
0.300	0	65	240	675	760	820	862	895	920	939	955	966	976	983	988	992	995	997	998	999	997
0.325	7	5	143	613	722	789	840	878	907	928	946	960	970	979	985	990	993	995	997	998	995
0.350	9	11	89	436	667	754	813	856	889	915	935	951	963	973	980	986	990	993	995	996	992
0.375	3	7	14	65	588	704	776	828	868	897	921	939	953	965	974	981	986	990	992	993	987
0.400	7	2	8	45	197	623	729	795	839	873	903	924	941	955	965	974	980	985	988	989	980
0.425	1	3	6	5	36	83	667	742	802	845	879	905	926	942	954	964	972	978	981	981	972
0.450	6	3	4	10	11	65	357	674	751	806	849	879	904	924	939	951	960	967	971	971	960
0.475	0	2	4	2	20	23	41	145	685	756	806	846	878	901	919	933	945	953	957	956	944
0.500	1	5	3	1	5	7	9	15	442	675	749	800	839	870	892	910	923	933	938	936	924
0.525	2	1	2	3	9	7	12	69	72	305	662	734	786	826	855	878	894	905	911	910	897
0.550	1	1	1	6	6	4	9	15	0	177	148	631	712	765	804	832	853	868	874	871	861
0.575	0	0	3	0	1	7	5	3	11	7	21	221	579	669	725	765	793	813	822	821	812
0.600	0	1	0	2	1	4	2	3	5	11	4	13	17	405	162	664	703	732	747	750	741
0.625	0	0	1	0	3	1	2	3	7	2	4	15	7	16	43	78	191	586	618	632	630
0.650	0	1	0	0	1	1	1	0	4	3	2	2	2	7	11	27	51	75	66	192	41
0.675	0	1	1	1	1	2	2	0	1	2	2	2	4	2	7	12	14	3	3	5	2
0.700	1	1	1	1	1	0	0	0	1	2	2	3	2	2	2	1	0	5	2	10	2
0.725	0	0	0	1	1	0	1	1	1	2	1	2	0	3	0	4	2	1	2	1	2
0.750	1	0	1	0	1	1	0	1	2	1	2	0	2	3	1	1	2	2	4	1	1

Table 3 1000 $E(x, T)/J$ for the feldspar structure

$k_B T/J$	Percentage Al concentration																							
	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50
0.000	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
0.025	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
0.050	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
0.075	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
0.100	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
0.125	0	0	0	0	0	1	1	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	1	0
0.150	0	0	0	0	0	1	1	0	0	0	0	1	1	1	1	0	0	0	0	0	0	0	1	0
0.175	0	0	0	0	1	1	1	0	1	1	1	1	1	1	1	0	0	0	0	0	0	0	1	0
0.200	0	0	0	1	1	1	1	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1	0
0.225	0	0	0	1	1	1	1	1	2	2	2	3	3	3	3	2	2	1	1	1	1	1	1	0
0.250	0	0	1	1	1	1	2	2	2	3	4	4	5	5	4	3	3	2	2	1	1	1	1	1
0.275	0	0	1	1	1	2	2	2	3	4	5	6	7	7	7	5	4	3	3	2	2	1	1	1
0.300	0	0	1	1	2	2	3	3	4	5	7	8	9	10	9	7	6	5	4	3	2	2	1	3
0.325	0	1	1	1	2	3	4	4	6	7	9	10	12	13	13	10	9	7	6	4	3	2	2	5
0.350	0	1	1	2	3	3	5	5	7	9	11	13	15	17	17	14	12	10	8	6	5	4	3	8
0.375	0	1	1	2	3	4	5	6	8	10	13	15	18	21	22	19	16	13	11	9	7	6	5	12
0.400	0	1	1	2	3	5	6	8	10	12	15	18	21	25	27	25	21	18	15	12	10	8	8	18
0.425	0	1	2	3	4	5	7	9	11	14	17	21	25	29	32	33	28	24	20	17	14	12	12	25
0.450	1	1	2	3	4	6	8	10	13	16	20	24	28	33	38	40	37	32	27	23	20	18	18	34
0.475	1	1	2	3	5	7	9	11	14	18	22	27	32	37	43	47	48	41	36	31	28	25	27	45
0.500	1	1	2	4	5	7	10	12	16	20	24	29	35	41	48	54	59	54	47	41	38	36	38	60
0.525	1	1	2	4	6	8	11	13	17	22	27	32	39	46	53	60	68	69	61	55	50	49	54	77
0.550	1	1	3	4	6	9	11	14	19	23	29	35	42	50	58	66	75	83	80	71	66	66	73	98
0.575	1	2	3	4	7	9	12	16	20	25	31	38	45	53	63	72	83	94	101	94	88	88	97	124
0.600	1	2	3	5	7	10	13	17	21	27	33	40	48	57	67	78	90	102	115	123	117	116	127	155
0.625	1	2	3	5	7	10	14	18	23	29	35	43	51	61	72	83	96	110	126	142	153	156	166	194
0.650	1	2	3	5	8	11	15	19	24	30	37	45	54	64	76	88	102	118	135	153	174	195	215	250
0.675	1	2	4	6	8	12	16	20	25	32	39	47	57	68	80	93	108	124	143	163	187	213	243	280
0.700	1	2	4	6	9	12	16	21	27	33	41	50	60	71	83	97	113	130	150	172	196	225	257	294
0.725	1	2	4	6	9	13	17	22	28	35	43	52	62	74	87	101	118	136	156	179	205	234	268	305
0.750	1	2	4	6	9	13	18	23	29	36	44	54	65	77	90	105	122	141	162	186	213	243	276	314
∞	3	7	13	20	29	39	51	65	80	97	115	135	157	180	205	231	259	289	320	353	387	423	461	500

connected by an unbroken chain of Al–O–Si linkages, and there are more possible paths when the dimensionality is greater. The system will exhibit long range order if at least a certain proportion of the bonds are Al–O–Si; the required proportion is higher for a two-dimensional system than for a three-dimensional system. At low x , more of the bonds will be Si–O–Si even if there is total short range order. So it will take less short range disorder to induce long range disorder, and this effect will be much more pronounced in the two-dimensional system.

Our simplified model based on exploring the consequences of nearest-neighbour Al/Al avoidance while ignoring all other interactions gives fully quantitative results for enthalpy, entropy, and long and short range order. Moreover these are in semiquantitative agreement with experimental observations such as the data of Phillips et al. (1992) for Q^2 versus σ , and Carpenter and McConnell's (1984) plot of $T_c(x)$.

Landau theory and Bragg-Williams theory are often used to interpret and extrapolate experimental data because they give specific convenient functional forms for the free energy and other thermodynamic quantities (Carpenter 1992). Our model supplies computed results for all thermodynamic quantities which can be used to interpret data in a similar way. It should be significantly better than

the Landau or Bragg-Williams forms because the latter do not properly take short range order into account. For this purpose we include Tables 2, 3 and 4 of Q , E and S as functions of x and $k_B T/J$, from which the short range order parameters σ and σ' can be derived. Copies of these tables are available on the World Wide Web at

<http://www.esc.cam.ac.uk/deposit/myers97.html>,
and copies of our Monte Carlo programs are available at
<http://www.esc.cam.ac.uk/software/bogomc.html>
and

<http://www.esc.cam.ac.uk/software/isingmc.html>.
We have computed these for the feldspar framework but there seems to be little difference among four-fold coordinated frameworks of tetrahedra.

Acknowledgements Our calculations are performed on the Hitachi SR2001 located at Hitachi Europe's Maidenhead (United Kingdom) headquarters, and the Hitachi SR2201 located at the University of Cambridge High Performance Computing Facility. The research has been supported by grants from the National Environmental Research Council and the Engineering and Physical Sciences Research Councils of the UK, including a research studentship to E.M. All these are gratefully acknowledged.

Table 4 1000 $S(x, T)/k_B$ for the feldspar structure

$k_B T/J$	Percentage Al concentration																								
	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	
0.000	165	219	265	303	334	360	379	393	401	405	403	396	384	367	349	329	306	280	253	218	179	133	65	0	
0.025	165	219	265	303	335	360	379	393	402	405	403	396	384	367	349	326	306	271	253	218	182	123	78	0	
0.050	165	219	265	303	334	360	379	393	401	405	403	396	384	368	350	330	307	282	253	215	182	135	78	0	
0.075	165	219	265	303	334	360	379	393	402	405	403	396	384	367	350	329	307	283	251	220	184	140	83	0	
0.100	165	219	265	303	334	360	379	393	402	405	403	396	384	368	349	328	308	281	255	221	185	138	81	0	
0.125	165	219	265	303	335	360	380	393	402	405	403	397	384	368	350	329	308	282	254	223	184	140	81	0	
0.150	165	219	265	303	335	360	380	394	403	406	405	398	386	370	351	331	308	283	256	222	184	137	84	0	
0.175	165	220	265	304	335	361	381	395	404	408	407	400	389	373	353	332	309	285	257	223	185	139	84	0	
0.200	165	220	266	304	336	362	382	397	406	411	410	404	393	377	358	336	313	286	257	224	185	140	86	0	
0.225	165	220	266	305	337	363	384	399	409	414	414	409	399	383	363	340	315	289	258	225	186	141	85	0	
0.250	165	220	266	305	338	365	386	402	413	418	419	415	406	390	369	345	320	292	260	227	188	143	86	2	
0.275	165	220	267	306	339	366	388	404	416	423	425	422	413	399	377	352	325	297	266	230	189	144	88	2	
0.300	165	221	267	307	340	368	390	407	420	428	431	429	421	408	387	360	332	302	269	233	192	144	87	9	
0.325	165	221	268	308	341	369	392	411	424	433	437	436	430	419	398	369	340	309	275	237	195	149	88	16	
0.350	165	221	268	308	343	371	395	413	428	437	443	443	439	429	411	381	350	318	282	243	200	152	91	25	
0.375	166	221	269	309	344	373	397	416	432	442	449	450	448	440	424	395	361	327	290	251	207	157	99	37	
0.400	166	222	269	310	345	374	399	419	435	447	454	458	456	450	437	411	375	340	301	260	216	164	106	53	
0.425	166	222	270	311	346	376	401	422	439	452	460	464	465	460	450	429	391	354	314	271	226	173	117	69	
0.450	166	222	270	311	347	378	403	425	442	456	465	471	472	470	462	446	411	371	328	285	238	186	130	90	
0.475	166	222	271	312	348	379	405	427	445	460	470	477	480	479	473	461	436	391	348	302	254	203	149	115	
0.500	166	223	271	313	349	380	407	430	449	464	475	483	487	488	484	475	458	417	371	323	275	224	173	144	
0.525	166	223	271	313	350	382	409	432	451	467	479	488	494	496	494	487	475	448	398	350	299	249	202	178	
0.550	166	223	272	314	351	383	410	434	454	471	484	493	500	503	503	498	490	473	433	380	330	281	237	217	
0.575	166	223	272	314	352	384	412	436	457	474	488	498	506	510	511	509	503	492	471	420	368	321	280	263	
0.600	166	223	272	315	352	385	413	438	459	477	491	503	511	516	519	518	514	507	495	470	417	369	331	317	
0.625	166	224	273	315	353	386	415	440	461	479	494	507	516	522	526	527	525	520	513	501	476	433	395	380	
0.650	167	224	273	316	354	387	416	441	463	482	498	510	520	528	532	534	534	531	526	519	509	494	473	469	
0.675	167	224	273	316	354	388	417	443	465	484	501	514	525	533	538	541	543	541	538	534	528	522	516	514	
0.700	167	224	273	317	355	389	418	444	467	487	503	517	528	537	544	548	550	550	549	546	542	539	536	535	
0.725	167	224	274	317	355	389	419	446	469	489	506	520	532	542	549	554	557	558	558	557	554	552	551	550	
0.750	167	224	274	317	356	390	420	447	470	491	508	523	535	546	553	559	563	565	566	566	565	563	562	562	
∞	168	227	279	325	367	405	440	471	500	527	551	573	593	611	627	641	653	664	673	680	686	690	692	693	

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