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The phenomenon of low Al-Si ordering temperatures in aluminosilicate framework structures

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ABSTRACT

The enthalpy of ordering of Al and Si between tetrahedral sites in framework structures is now known from several studies to be in the range 0.3–1.4 eV per two Al-O-Si linkages, depending on the structure and type of linkage between tetrahedra. On the basis of this value a simple Bragg-Williams model predicts an ordering phase transition at a temperature, T_c, on the order of a few thousand degrees after adjusting the estimate to account for fluctuations in short-range order. However, there are several materials with T_c below 1800 °C (a typical melting point), with some having T_c so low that it cannot be observed because of the slowness of the ordering kinetics, e.g., gehlenite and leucite. We discuss two mechanisms that can reduce T_c substantially: low effective dimensionality and low Al concentration. The cases of sillimanite, gehlenite, cordierite, and leucite, and some simple demonstration systems, are treated quantitatively with the aid of Monte Carlo computer simulations. Other materials (kalsilite, anorthite, albite, and nepheline) are discussed qualitatively in terms of the same principles.

INTRODUCTION

The purpose of this paper is to deduce some of the important factors that determine the phase transition temperature for Al-Si ordering in aluminosilicate minerals. In particular, we want to understand why there is a wide variation of transition temperatures, ranging from values too low to be measured to values substantially higher than melting points, even though aluminosilicates have very similar structures. At one level the processes behind the Al-Si order-disorder phase transition are easily understood. At low temperatures the enthalpy dictates that an ordered state will be preferred. To a large extent this is simply related to the tendency for Al-O-Si and Si-O-Si linkages to be preferred over Al-O-Al linkages, the well-known rule of Loewenstein (1954). At high temperatures entropy favors disorder, and the balance between the enthalpic and entropic contributions to the free energy determines the temperature at which the phase transition occurs. To quantify these simple considerations, though, is far from a trivial exercise in statistical mechanics. The starting point is an equation for the ordering energies where we only need to consider nearest-neighbor interactions (Yeomans 1992):

$$E = E_0 + \frac{1}{4}\sum_{i,j} J_1\sigma_i\sigma_j \qquad (1)$$

where E is the total energy of the material, E_0 is the energy of the disordered state, i, j denote pairs of sites, and associated with each site is a variable $\sigma_i = +1$ or -1 when the site is occupied by an Al or Si, respectively. Equation 1 is subject to the constraint that $\Sigma\ \sigma_i$ has a constant value, for example, equal to zero when the numbers of Al and Si atoms are identical. The sum in Equation 1 is over all pairs of sites with each pair counted once. The coefficient J_1 is given by the energy of ordering:

$$J_1 = V_{AA} + V_{SS} - 2V_{AS} \qquad (2)$$

where V_{AA}, V_{SS}, and V_{AS} are the energies of the linkages Al-O-Al, Si-O-Si, and Al-O-Si, respectively. The generally large and positive value of J_1 is a quantitative statement of Loewenstein's (1954) rule: The energy required to form Al-O-Al linkages is sufficiently high that in practice the number of such linkages in an aluminosilicate is frequently very small. Equation 2 can be generalized if we consider interactions beyond the nearest-neighbor linkage and if we have more than one type of tetrahedral site in the disordered phase:

$$E = E_0 + \frac{1}{4}\sum_{i,j} J_r\sigma_i\sigma_j + \sum_i \mu_s\sigma_i \qquad (3)$$

where the coefficients J_r are now generalized for neighbors beyond the nearest-neighbor linkage, and μ_s has the nature of a chemical potential for the site of type s. The chemical potential accounts for the fact that certain sites may be preferentially occupied by Al or Si independent of the degree of long-range order.

A popular approach to solving for the equation of state from Equation 1 is the use of the Bragg-Williams (1934) approximation (see also Rao and Rao 1978; Putnis 1992), which leads to the prediction of a second-order phase transition at a temperature determined by J_1:

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$$k_B T_c = \frac{1}{4} J_{tot} \quad (4)$$

where J_{tot} is obtained by summing J_1 over all neighbors. Examples of the application of the Bragg-Williams model in mineralogy are given by Burton (1987) and Davidson and Burton (1987). The Bragg-Williams model is known to be quantitatively incorrect because it neglects fluctuations in the short-range order. The only short-range order is that determined by the degree of long-range order at temperatures below T_c. However, there have been so many studies of the statistical mechanics of Hamiltonians with the form of Equation 1 (e.g., Yeomans 1992) that we now have a reasonable idea of the effect on T_c from fluctuations of short-range order of similar form to the long-range order. The transition temperature is modified by a numerical factor, and for the paper the relevant factors are 0.676 for a structure with tetrahedral coordination (e.g., a diamond lattice), 0.752 for a structure with octahedral coordination (e.g., a simple cubic lattice), and 0.567 for a square lattice (these factors are listed in Table 33.4 of Ashcroft and Mermin 1976). To complete the picture we also must consider cases in which the number of Al atoms does not equal the number of Si atoms. Denoting the concentration of Al atoms by x, we can rewrite Equation 3 in a form which we called the adjusted Bragg-Williams (ABW) estimate for T_c:

$$k_B T_c(\mathrm{ABW}) = \begin{Bmatrix} 0.676 \\ 0.752 \\ 0.567 \end{Bmatrix} f(x) \cdot \frac{1}{4} J_{tot} \quad (5)$$

in which we have taken account of the normal fluctuations in short-range order as described above. The new factor $f(x)$ depends on the way we model the difference between the numbers of Al and Si atoms. From the theory of ordering in alloys, in which we expand about the point $x = \frac{1}{2}$, we have

$$f(x) = 4x(1 - x). \quad (6)$$

In this case it is assumed that x is not very different from $\frac{1}{2}$ and that there is ordering over equal numbers of two types of site. On the other hand, if we require that the number of sites of each type in the ordered phase must equal the number of atoms of each type, it is not difficult to obtain the result

$$f(x) = 4x^2 \quad (7)$$

for $x \leq \frac{1}{2}$. These two forms give different values for $f(x)$, but the differences are not significant in the examples that we will discuss in detail in this paper.

How good is the ABW estimate of T_c? Let us consider two cases in which the Al:Si ratio is 1:1 (i.e., $x = \frac{1}{2}$), anorthite and kalsilite. For anorthite, $CaAl_2Si_2O_8$, J_1 has been estimated from experiment to be 0.40 ± 0.12 eV (Phillips et al. 1992). Using the prefactor for tetrahedral coordination, and including four nearest-neighbor interactions in J_{tot}, we obtain an estimate for T_c from Equation 5 of 3140 ± 940 K. This is not very different from the estimates of 2280 ± 85 K given by Carpenter et al. (1990) and 2490 K by Carpenter (1992). In the case of kalsilite, $KAlSiO_4$, which from a topological point of view is not significantly different from anorthite, an estimate for J_1 of 0.33 eV from the electronic structure calculations of De Vita et al. (1994, and in preparation; see below for a further discussion of these calculations) gives an estimate for T_c of 2600 K. Given that no evidence of disorder has been obtained for temperatures below the melting point of 2010 K, this estimate appears reasonable. A similar situation holds for the related material nepheline.

Contrary to the "success" of the ABW estimate of T_c for anorthite and kalsilite, there are many cases in which the ABW estimate fails spectacularly, and these are the central focus of this paper. Recently we have deduced estimates of the ordering interactions J_r for sillimanite (Bertram et al. 1990), gehlenite (Thayaparam et al. 1994), leucite (Dove et al. 1993), and cordierite (Thayaparam et al. 1996). The values are reproduced in Table 1, and given the importance of these values in the present work we discuss them further in the next section. Using these parameters we estimated T_c(ABW), using Equation 5, for some of these examples. In the case of sillimanite, the experimental T_c is between 2000 and 2100 K and the estimated T_c(ABW) is 3766 K (Bertram et al. 1990; note that we incorporated the appropriate correction for short-range order). For cordierite, the experimental T_c is around 1750 K, and the estimated T_c(ABW) is 7830 K (see below). The important point in these examples is that the estimates of T_c from the ABW model are substantially higher than the actual transition temperatures; indeed, in the cases of leucite and gehlenite the observed transition temperature is so low that long-range order has not been observed.

In this paper we are concerned with the reasons why, in cases like the ones we have used as examples, the ABW model fails so badly. The problem surely lies in the neglect of fluctuations of short-range order; but since the ABW formula (Eq. 5) already includes a factor that usually accounts completely for fluctuations in short-range order we need to understand the nature of the fluctuations that can drastically reduce T_c below the estimated T_c(ABW). After all, the ABW estimate works reasonably well for anorthite and kalsilite. In principle it should be possible to develop a statistical mechanics calculation that considers all the effects of short-range order. For example, the Cluster Variational Model (CVM) (de Fontaine 1979, 1994) should be capable of giving reasonably accurate estimates of T_c. However, experience with the CVM model in mineralogy has not been satisfactory. Burton and Davidson (1988b) compared three models for ordering of octahedral cations in omphacite, which experimentally has a T_c value around 1123 K (Carpenter 1981). The models required values for J_r appropriate for the particular ordering processes. These were derived by Cohen and Burnham (1985). Monte Carlo simulations of the ordering (Cohen 1988) gave an estimate for T_c of 850 ± 250 K (the large error was not explained). The close

agreement between the Monte Carlo values and observed values shows that the ordering energies for omphacite deduced by Cohen and Burnham (1985) are reasonably accurate. The simple Bragg-Williams model, which was initially developed for omphacite by Davidson and Burton (1987), gave an estimate for T_c of 5154 K. This is substantially greater than the observed value. Burton and Davidson (1988a, 1988b) pointed out that a CVM calculation performed by Cohen (1986) did not yield an ordering phase transition at all because it did not contain all the relevant physical information. A more detailed CVM calculation by Burton and Davidson (1988b), which purported to contain all the essential physical ingredients, gave a value for T_c of 3820 K. This is lower than the Bragg-Williams estimate by a factor of 0.74, similar to the factors already cited in connection with the ABW estimates of Equation 5. Thus the CVM model of Burton and Davidson (1988b) captured only the usual effects of short-range order, i.e., those incorporated into the ABW estimate (Eq. 5), but the CVM estimate of T_c is still substantially above the observed value. Burton and Davidson (1988b) explained this by suggesting that the ordering energies derived by Cohen and Burnham (1985) were in error. But the agreement of the Monte Carlo T_c with the observed T_c indicates that the problem really lies in the CVM calculation, which overestimates the Monte Carlo T_c by a massive factor of 4.5.

What this discussion shows is that a proper CVM calculation must contain all the essential physics if it is to produce anything that is quantitatively meaningful, and simply making a CVM calculation complicated will not of itself guarantee that the essential physics will be properly captured. Instead it is essential to understand the basic physics behind the ordering process before developing a detailed statistical mechanics model. We also argue that a good statistical mechanics model should necessarily give a reasonably accurate estimate for T_c as a test calculation. In the present paper we aim to identify two essential physical features that arise in some cases of Al-Si ordering and that lead to a large reduction of T_c from the ABW estimate. It should be noted that, by comparing the experimental T_c with the ABW estimate rather than with the normal Bragg-Williams formula, we are already taking account of the normal fluctuations that lead to a reduction of T_c, and that a standard CVM calculation automatically considers. We focus on two important mechanisms that lower T_c, namely low effective dimensionality and low Al concentration. We note that frustration will also lead to a reduction of T_c, but we do not encounter this factor explicitly in the examples we discuss in this paper. In the last section we consider the case of cordierite, in which both factors operate at the same time.

Methodology

Calculations of the ordering interactions

In this paper we do not derive the ordering interactions J_r, but, since we use results from a variety of (consistent) sources, some comment about the methodology is appropriate. For the systems we study in this paper the ordering interactions have been obtained by two computational approaches. The first approach uses empirical interatomic pair potentials of the shell-model type described by Winkler et al. (1991) and Patel et al. (1991). Detailed studies using the shell model have been carried out for sillimanite (Bertram et al. 1990), gehlenite (Thayaparam et al. 1994), cordierite (Thayaparam et al. 1996), and, to a lesser extent, leucite (Dove et al. 1993). The methodology has been explained in detail in these papers. In essence, for a given material calculations of the lattice energy, with all atomic positions being relaxed, were performed for a large number of Al-Si configurations within a supercell. The energies of the different configurations were then fitted to Equation 3 by a least-squares procedure. Care was taken, in part guided by preliminary results of the fitting, to include a wide range of different types of configurations to span the full energy surface. For cordierite we included the chemical potential parameter μ to account for the existence of two distinct tetrahedral sites in the disordered phase. The results of the calculations of J_r for sillimanite, gehlenite, leucite, and cordierite are given in Table 1.

Table 1. Values of the ordering interactions J_r (in eV) per 2Si + 2Al atoms for the materials studied in this paper

		r = 1 (nearest-neighbor interaction)			
Sillimanite	1	J_{1ab} 0.98	J_{1c} 0.56		
Gehlenite	2	J_{1ab} ·(T2 − T2) 0.52	J'_{1ab} ·(T1 − T2) 0.44		
Leucite	3	0.65			
Cordierite	4	J_1 ·(T1 − T2) 0.84	J'_1 ·(T2 − T2) 1.34		
Kalsilite	5	0.43			
		r = 2,3 (second- and third-neighbor interactions)			
Sillimanite	1	J_{2abc} 0.17	J_{2ab} 0.14	J'_{2ab} 0.22	
Gehlenite	2	J_{2ab} −0.075	J_{3ab} −0.009	J_{1c} −0.066	J_{2c} 0.072
Cordierite	4	J'_2 0.092	J^{II}_2 0.136	J^{III}_2 0.336	J^{IV}_2 0.124
		J^{V}_2 0.172	J^{VI}_2 −0.008	J^{VII}_2 0.556	J_3 −0.264
		μ −0.269			

Note: The precise specifications of the different types of neighbor are given in the cited references, and in the present context are less important than the comparison of the range of values. References: 1 = Bertram et al. (1990), 2 = Thayaparam et al. (1994), 3 = Dove et al. (1993), 4 = Thayaparam et al. (1995), and 5 = De Vita et al. (1994, and in preparation).

The general experience is that although these potentials can predict bond lengths and cell parameters with reasonable accuracy for any given aluminosilicate (Dove 1989; Winkler et al. 1991; Patel et al. 1991), they are less accurate than quantum mechanical calculations for actual energies because the models were not developed taking account of binding energies. Therefore the second approach involved the complete ab initio solution of the

Schrödinger equation. The only substantial approximation is use of the local density approximation for the electron exchange and correlation energy, which is known to give very good accuracy in materials with strong ionic or covalent bonding. Because they are computationally far more demanding than the empirical shell-model calculations, the ab initio calculations were restricted to a small set of calculations of the ordering energies in kalsilite, $KAlSiO_4$ (De Vita et al. 1994, and in preparation). The experience gained from these calculations was then used in the calibration of the shell-model calculations. The total energy was calculated for a number of different configurations in a supercell of 16 tetrahedra, allowing full relaxation of all atoms to their equilibrium positions. The results were then interpreted in terms of J_1. The most important conclusion was that the value of J_1 is the sum of two contributions. The first, 0.2 eV, was due to the charge and chemical differences between Al and Si atoms (De Vita et al. 1994, and in preparation). The second contribution varied between zero and 0.4 eV and was due to the size difference between Al and Si atoms causing local strains when disordered; its magnitude depends very much on the local surrounding structure and distribution of Al and Si atoms. The total J_1 value therefore ranged from 0.2 to 0.6 eV, an average best estimate for general disorder being $J_1 \approx 0.33$ eV. The shell-model calculations were then performed using the same configurations for comparison. It was found that the two approaches gave broadly similar results for the local strain contribution to J_1 (De Vita et al. 1994, and in preparation), but the ionic contribution was overestimated by about 0.1 eV by the shell model, which is hardly surprising since it employs full ionic charges of +3 and +4 for Al and Si, respectively.

Monte Carlo simulations of ordering phase transitions

To help calibrate the calculated ordering interactions against experimental data, and also to enable us to gain a physical picture of the ordering processes, we performed a number of Monte Carlo simulations using the calculated ordering interactions and energies of the form in Equation 3 (Heermann 1986). These simulations were performed on a massively parallel processor, the Cambridge AMT DAP 610/20 with 4096 individual processors, which allowed 4096 unit cells arranged on a 16 × 16 × 16 grid. We wrote the Monte Carlo program in the formalism of Equation 3, and so changes in the occupancy of a site from Al to Si or vice versa were represented by flipping the sign of the individual σ_i values. The Metropolis algorithm was applied to the corresponding energy change ΔE_i calculated from Equation 3. The fact that the one-atom flips are unphysical does not invalidate the procedure if sampling the configurational phase space. However, it does not conserve the number of Al and Si atoms in the whole sample. This problem was overcome by adding an extra term to the energy:

$$E_{\text{control}} = -gQ' \tag{8}$$

where g is a control chemical potential, and

$$Q' = \Sigma\, \sigma_i = N_{\text{Al}} - N_{\text{Si}}. \tag{9}$$

N_{Al} and N_{Si} are the total numbers of Al and Si atoms, respectively. The summation is over all sites in the computer sample. The value of g was adjusted at each temperature until the correct value of Q' was obtained in the ensemble. Although this approach may seem to be more complicated than the usual process of swapping the values of σ_i on pairs of sites [which would necessitate the use of the Kawasaki (1972) rather than Metropolis update scheme], it has the advantage that it is easily and efficiently programmed for a massively parallel processor.

The magnitude of the ordering interactions J_r

Analysis of the ordering interactions

From the comparison in Table 1 of the results for J_1 values calculated for the four materials mentioned and kalsilite, it is seen that J_1 varies widely between the different structures and also between nearest-neighbor linkages of different type in the same material. Values in the range $J_1 \approx 0.4$–1.4 eV were obtained from the shell model. An energy of about 0.4 eV was determined by Bell et al. (1992) from calculations on some zeolite structures using the same potentials. The spread in values of J_1 can be interpreted as arising from local strain effects, in accordance with the results on kalsilite mentioned above and the fact that the distance and geometry between joined tetrahedra are nearly constant. There is no apparent correlation of J_1 with the T-O-T bond angle or the T-T distance, and so the variation of J_1 must be caused by local strain around the pair of sites when occupied by two Al, two Si, or one Al and one Si, respectively.

From Table 1 it can also be seen that the magnitudes of J_r to second and more distant neighbors are an order of magnitude smaller than the values of J_1, and they vary in sign. The variation in sign implies that the values of these distant interactions must be dominated by local strain effects.

It should be noted that the form of Equation 3, with J_r truncated after second or third neighbors, does not give a perfect representation of the energetics, indicating that the J_r ordering interactions have long-range tails owing to the Coulomb interactions and strain effects.

In this paper we use the values of J_r obtained from the shell model, recognizing that the values of J_1 should probably be reduced by about 0.1 eV as suggested by the ab initio calculations on kalsilite quoted above. It is not known what correction to apply to the more distant J_r.

Calibration of the calculated ordering interactions

Whereas the ab initio calculations provide one means of calibrating the ordering interactions calculated using the shell model, it is also important to calibrate against experimental data. Unfortunately the experimental situation is not satisfactory in this regard. Navrotsky et al.

(1982) have reported ordering enthalpies from calorimetry for some aluminosilicate glasses that, when interpreted in our terms, give J_1 values in the range 0.4–0.8 eV, consistent with the results in Table 1. We noted above that Phillips et al. (1992) have deduced a value of $J_1 = 0.40 \pm 0.12$ eV for anorthite. These results, however, cannot be directly used to judge the shell-model calculations, given the way that J_1 varies from structure to structure. We hoped to make a precise comparison for cordierite, for which Putnis (1994) combined the calorimetric measurements of Carpenter et al. (1983) with the NMR measurements of the number of Al-Al nearest-neighbor linkages as a function of annealing time (Putnis and Angel 1985; Fyfe et al. 1986) to give an estimate for J_1 of 0.35 eV. Unfortunately a reexamination of the NMR data showed that this is not possible because the calculated number of Al-Al linkages is extraordinarily sensitive to small measurement errors in the strengths of the NMR lines. Taking the data of Putnis et al. (1985) at face value, and extending the analysis of Putnis and Angel (1985) explicitly account for T1-T2 and T2-T2 linkages, gives negative values for the number of Al-Al linkages on neighboring T2 sites. From detailed Monte Carlo simulations (Thayaparam et al. 1996) and a reanalysis of the experimental data using a different Monte Carlo method (Dove and Heine 1996) it appears that this number should actually be very nearly zero for each data set, but the negative values arise from subtracting two large quantities with associated errors. The estimated value for J_1 given by Putnis (1994) for the enthalpy per Al-Al linkage must therefore be considered as a rough approximation. We have used a Monte Carlo method to obtain configurations, and hence the numbers of Al-Al linkages, that match the NMR spectra exactly (Dove and Heine 1996). This yielded an upwardly revised value for J_1 of ~0.4 eV. However, this procedure suggested that there should have been small peaks in the NMR spectra corresponding to Si with no Al neighbors, and these were apparently not observed by Putnis et al. (1985). By modifying the NMR data, and supposing that the intensities of these peaks are nonzero but small enough that they could have been missed in the raw data, we found that the calculated number of Al-Al linkages could be significantly increased (Dove and Heine 1996). We then reanalyzed the NMR data analytically by including the constraint that the number of Al-Al linkages on neighboring T2 sites is zero rather than negative (Thayaparam et al. 1996) and allowing there to be a small number of Si with no Al neighbors. We obtained an increase in the calculated enthalpy of ordering by a factor of two without altering the quality of the fit. This led to a revised value for the experimental enthalpy of ordering of 0.7 eV, although with a large uncertainty, and this is for linkages between T1 and T2 sites. The value for this interaction obtained from the shell-model calculations given in Table 1 is 0.84 eV. When we subtract 0.1 eV to take account of the overestimate in our calculations suggested by the comparison with the ab initio calculations discussed above, the agreement between our calculated value for J_1 and the experimental values is satisfactory. Nevertheless, we recognize that the experimental situation itself is far from satisfactory. Further NMR studies on cordierite may allow us to resolve these problems.

FIGURE 1. A linear chain of sites occupied alternately by Al (A) and Si (S) atoms, except for energetically unfavorable S–S and A–A linkages at a distance of ξ sites apart on average.

QUASI ONE-DIMENSIONAL STRUCTURES: SILLIMANITE AND GEHLENITE

General considerations

In describing materials as having a quasi one-dimensional structure we are not referring to their atomistic structure as a whole but rather that interactions between T sites are much stronger in one direction (say along z) than in the other (x,y) directions. Without any x,y interactions the T sites would form a set of purely one-dimensional chains, which cannot have long-range order at any temperature except 0 K. The basic reason is illustrated in Figure 1, showing Al (A) and Si (S) on a chain of T sites. Suppose we have one "wrong" linkage (i.e., A-A or S-S) on average every ξ sites. The energy of each wrong linkage is $\frac{1}{2}J_1$ higher than an A-S linkage, and it can occupy approximately ξ different positions, giving it an entropy of $k_B \ln \xi$. The free energy of the system per site is therefore

$$F(T) = \xi^{-1}(\tfrac{1}{2}J_1 - k_B T \ln \xi) \quad (10)$$

where we have ignored any J_r beyond nearest-neighbors. $F(T)$ can always be made negative by choosing a large enough value of ξ. Although the entropy always favors some disorder in a system, in the special case of one dimension a single wrong linkage destroys long-range order. The range ξ of short-range order can be obtained by minimizing Equation 10 with respect to ξ, giving

$$\xi \approx \exp(\tfrac{1}{2}J_1/k_B T) \quad (11)$$

which becomes very large for $T < \frac{1}{2}J_1/k_B$, i.e., for T below the estimate T_c(ABW) in Equation 5. We therefore expect T_c to be controlled largely by the weak x,y interactions and to be less than the estimate of T_c(ABW) from Equation 5, in which all interactions are given equal weight.

In sillimanite the T sites are linked into ladders parallel to the c axis (Fig. 2); the linkage from each tetrahedron to the left and the right of the ladder is to the pillars of edge-sharing AlO_6 octahedra in the structure, which do not participate in the Al-Si ordering. Thus in the absence of J_r beyond nearest-neighbors we have a set of isolated one-dimensional ladders, and the argument of Equations 10 and 11 can easily be extended to show again that there

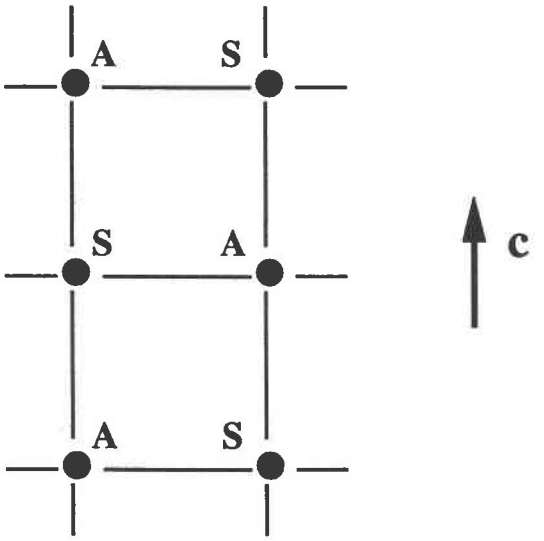

FIGURE 2. Al (A) and Si (S) atoms ordered on one ladder of tetrahedral sites in sillimanite parallel to the c axis. Note the linkages on the left and right edges of the ladder are connected to columns of AlO_6 octahedra not participating in the ordering process.

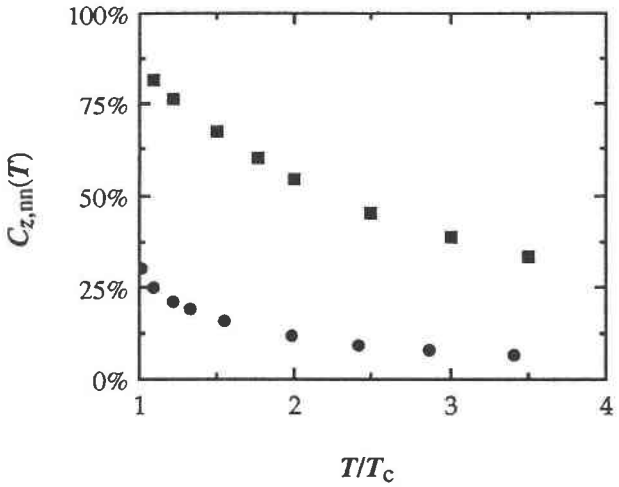

FIGURE 3. Correlation $C_{z,nn}(T)$ between nearest-neighbors in the z direction for the quasi one-dimensional system, Equation 12 (squares), as a function of temperature, compared with that for the isotropic model, Equation 15 (circles). Temperature is plotted relative to T_c in each case.

is no long-range ordering. In reality long-range ordering is ensured by the weaker interactions, J_r, between ladders; but their magnitude is considerably smaller than J_1 (Table 1), and T_c is correspondingly reduced.

An illustrative example

Before discussing sillimanite in more detail we demonstrate what happens in a simpler case and give a theoretical interpretation. Consider a simple cubic (or tetragonal) structure with equal numbers of A (Al) and S (Si) atoms and nearest-neighbor interactions with the parameters $J_z = 4$ and $J_x = J_y = 0.1$, giving $k_BT_c(\text{ABW}) = 1.58$ (in arbitrary units). From Equation 5, the value of $T_c(\text{ABW})$ is dominated by the value of J_z; the contributions of J_x and J_y are minor. Using the Monte Carlo simulations described above the real transition is at $k_BT_c = 0.82$, which is appreciably below the estimate of $k_BT_c(\text{ABW})$. Note that the equation for $k_BT_c(\text{ABW})$ included the numerical prefactor of 0.752 that is appropriate for the simple cubic structure (Eq. 5). The difference between the Monte Carlo T_c and $T_c(\text{ABW})$ contrasts with the situation in the simple cubic nearest-neighbor Ising model (with suitable parameters, in arbitrary units, for equal numbers of A and S atoms) where $J_x = J_y = J_z = 4$ and, by construction, $k_BT_c = k_BT_c(\text{ABW}) = 4.51$. More revealing is Figure 3 which shows the correlation $C_{z,nn}(T)$ between nearest-neighbors (i,j) in the z direction:

$$C_{z,nn}(T) = -\langle \sigma_i \sigma_j \rangle \tag{12}$$

where $\langle\ \rangle$ denotes a thermodynamic average over time and all sites. This quantity is unity for perfectly alternating ASAS . . . order in the z direction and gives the degree of short-range order above T_c. Figure 3 shows that with $J_x = J_y = J_z$, $C_{z,nn}(T) \sim 0.2$ near T_c, which is typical for normal three-dimensional systems, but the quasi one-dimensional system has much stronger short-range order above T_c.

We now give a theoretical interpretation of the behavior of the quasi one-dimensional model to give an approximate formula for T_c. The build up of correlation (short-range order) in the z direction follows Equation 11 for the reason already given, with each chain treated, as a first approximation, as independent of the other chains. As T decreases, correlated sections of chain become more or less perfectly ordered ASAS . . . or SASA . . . for a length ξ, which we can represent by a single Ising spin variable, ± 1. The long-range ordering then develops through the sideways interactions of these sections. Because of their length, their x,y interactions have magnitude $\xi J_x, \xi J_y$, which, if substituted into the Bragg-Williams form (Eq. 4) with a prefactor of ½ (justified below), gives

$$\begin{aligned} k_BT_c &\approx \frac{1}{2}\xi(T_c)(\tfrac{1}{2}J_x + \tfrac{1}{2}J_y) \\ &\approx \frac{1}{4}(J_x + J_y)\exp(\tfrac{1}{2}J_z/k_BT_c) \\ &\approx \frac{1}{2}(\tfrac{1}{4}\Sigma J_{ij\perp})\exp(\tfrac{1}{2}J_z/k_BT_c) \end{aligned} \tag{13}$$

where the last step gives a generalization. Equation 13 is in fact exact for the two-dimensional case, in which $J_y = 0$ and in the extreme anisotropic limit $J_x \ll J_z$ (Onsager 1944), which explains our choice of prefactor. Equation 13 must be solved numerically for our quasi one-dimensional model, giving $k_BT_c = 0.74$, in reasonable agree-

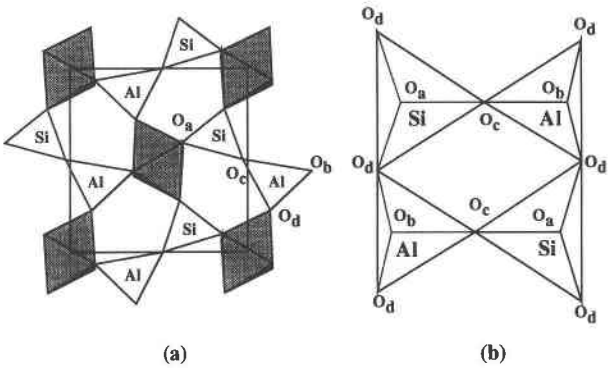

FIGURE 4. The structure of sillimanite projected onto the *a-b* plane. Shaded areas are columns of edge-sharing AlO_6 octahedra running parallel to the *c* axis (**a**). Between these are ladders (shown in **b**), also running parallel to the *c* axis, of pairs of tetrahedra joined by one T-O_c-T linkage in the *a-b* plane. The other three O atoms of each tetrahedron are shared with the columns of octahedra. One-half of the O atoms (labeled O_a,O_b) are attached to only one T site, whereas the others (O_d) are connected to two T sites vertically above one another in the *c* direction, and so the O_d provide T-O_d-T linkages in that direction.

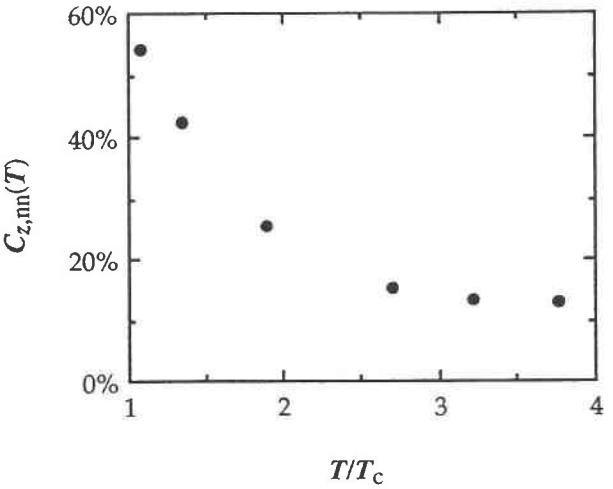

FIGURE 5. The correlation $C_{z,nn}(T)$ between nearest-neighbor T sites in the *c* direction in sillimanite from the interactions in Table 1.

ment with the Monte Carlo result. Equation 13 can be solved approximately as

$$k_B T_c \approx \tfrac{1}{2} J_z / \ln(4J_z/\Sigma J_{ij\perp}) \quad (14)$$

or

$$T_c/T_c\,(\mathrm{ABW}) \approx 1/\ln(4J_z/\Sigma J_{ij\perp}). \quad (15)$$

We see that T_c is indeed controlled by $\Sigma J_{ij\perp}$, but it depends on it only logarithmically.

Application to sillimanite

The sillimanite, Al_2SiO_5, structure is shown in Figure 4. As noted in connection with Figure 2, the T sites form ladders, with each ladder rung being a T-O_c-T linkage in the *a-b* plane and the ladder sides being T-O_d-T linkages in the *c* direction. The ladders are otherwise connected only to the columns of octahedra and not directly to one another. Thus in terms of the J_{ij} values the different ladders are connected by somewhat distant J_r only. The values of J_{ij} obtained by Bertram et al. (1990) are given in Table 1. J_{1ab} and J_{1c} are for the interactions involving the linkages in and perpendicular to the *a-b* plane, respectively; the other J_r values apply to second and further neighbors and are defined by Bertram et al. (1990). As we see from Table 1, the interactions between ladders are nearly an order of magnitude smaller than those within a ladder, and we have a quasi one-dimensional system. To map it directly onto the model given by Equation 13 we can suppose that J_{1ab} is sufficiently large near T_c that the two T atoms forming one rung of a ladder are nearly always either an Al-O_c-Si or a Si-O_c-Al combination, i.e., one rung can be represented as a single Ising spin variable connected by interactions $J_z = 2(J_{1c} - J_{2abc}) = 0.76$ eV, where the factor 2 arises from the two T atoms. Similarly the interaction between ladders can be expressed in terms of the more distant J_r giving $\Sigma J_{r\perp} = 0.16$ eV. Our estimate of T_c from a numerical solution of Equation 13 is 2032 K, which can be compared with the temperature 2670 K we have determined using Monte Carlo simulations. We also performed the Monte Carlo simulations after subtracting 0.1 eV from the values of J_{1ab} and J_{1c}, as discussed previously, and obtained a revised T_c of 2160 K. The nearest-neighbor correlation along the *c* axis is shown in Figure 5 and is large near T_c compared with the results for the isotropic Ising model shown in Figure 5.

Because sillimanite decomposes on heating at atmospheric pressure before it disorders, there is no direct experimental value of T_c for comparison with our calculation. However Holland and Carpenter (1986) and Greenwood (1972) have inferred a value of T_c between 1970 and 2070 K by extrapolation of high-pressure data. Our Monte Carlo value of $T_c = 2120$ K with the corrected values of J_1 agrees well with the experimental value, and we take this as a general endorsement of the calculation of the J_r values. The strong short-range order calculated above T_c (Fig. 5) becomes even stronger below T_c, which is consistent with the fact that there is very little noticeable disorder in natural specimens of sillimanite, as discussed by Stebbins et al. (1993).

In conclusion, we have shown how quasi one-dimensional systems in general, and sillimanite in particular, display substantially lower values of T_c than given by T_c(ABW) in Equation 5. The low T_c is accompanied by very strong short-range order governed by the J_1 terms.

Application to gehlenite

The structure of disordered gehlenite, $Ca_2Al_2SiO_7$, contains two formula units per tetragonal cell, as shown in

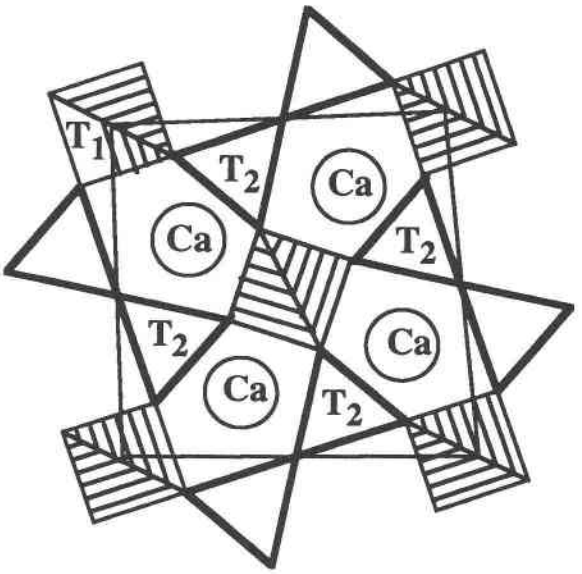

FIGURE 6. The unit cell of the gehlenite structure with T1 and T2 tetrahedra marked. Note that the T2 tetrahedra are not linked in the c direction, each having an apical O atom.

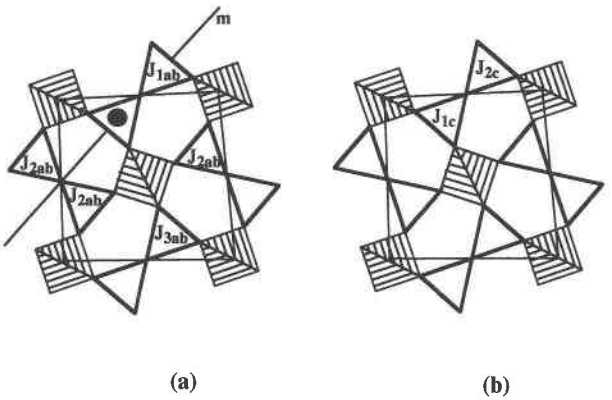

FIGURE 7. Definition of the interactions, J_r, between the T2 sites marked by the heavy dot and other T2 tetrahedra as marked: (**a**) in the a-b plane, (**b**) in the next layer in the $\pm c$ direction. Note the mirror plane m.

Figure 6. The T1 sites (Fig. 6 lined) are always occupied by Al, and so ordering takes place only among equal numbers of Al and Si atoms on the T2 sites. The T2 sites effectively consist of isolated pairs in the sense that in the a-b plane the T2 pairs are linked only through the Al T1 tetrahedra, i.e., there are no nearest-neighbor J_1 type of linkages between T2 sites except within each pair. There are also no nearest-neighbor linkages in the c direction through a shared O atom. The different interactions J_r are defined in Figure 7 and their values given in Table 1. The interactions J_{1c} and J_{2c} in the c direction are an order of magnitude smaller than J_{1ab} and J'_{1ab}.

We now consider the Al-Si ordering process, decreasing in temperature T from a completely disordered state at very high T. At a temperature $k_B T \leq \frac{1}{2}J_{1ab}$, T $\leq$ 3000 K, the interactions J_{1ab} and J'_{1ab} favor one Al in T1 and one Al and one Si in each T2-T2 pair. The disposition of the Al and Si atoms makes no difference energetically because the pairs are isolated from one another with respect to nearest-neighbor linkages.

We now suppose that each T2-T2 pair of sites is occupied by an Al-Si pair and consider its ordering, Al-Si or Si-Al, with respect to other pairs as the temperature is decreased further. It is important to realize that the J_{2ab} interaction gives zero effect in this regard. If the site marked with a dot in Figure 7a is occupied by an Al atom, because of the mirror plane m (Fig. 7a), there is no energy difference between the pair labeled J_{2ab}, J_{2ab} on the left of Figure 7a being occupied by Al,Si or Si,Al. This is a rigorous consequence of symmetry. Further ordering therefore is driven by the next largest interactions, namely J_{1c} and J_{2c}. These have opposite sign and reinforce one another in ordering Al-Si pairs above each other in the c direction in the same way. The relevant energy for this ordering is $|J_{1c} - J_{2c}| = 0.14$ eV, corresponding to a temperature of 1620 K. At and below this temperature one-dimensional order is expected to develop in chains parallel to the c direction. We have confirmed this by Monte Carlo simulations. The only interaction between chains comes from the very small J_{3ab}, resulting in three dimensional order at T_c = 640 K as determined by our Monte Carlo simulations. This is too low to be verified experimentally. Louisnathan (1971) reported that a natural gehlenite sample showed a slight spontaneous strain, indicative of some degree of long-range order, but this has not been found by other workers checking a wide range of samples (M.A. Carpenter, personal communication). The value of J_{3ab} is so small that its magnitude, and even its sign, must be regarded as quite uncertain. Thus our estimates of T_c and of the ordered structure are also uncertain but we can nevertheless conclude that T_c must be small.

Low Al concentration: Leucite and albite

General considerations

A second type of situation causing a low T_c is a low Al concentration, i.e., $x < \frac{1}{2}$. Examples are $x = \frac{1}{4}$ in albite and $x = \frac{1}{3}$ in leucite. The ABW formula, Equation 5, contains an appropriate reduction factor $f(x)$, but we show in this section that this does not give a sufficient reduction of T_c. Therefore with only four linkages from each T site, there are too few Al atoms to interact fully enough through the nearest-neighbor J_1 coupling to give long-range order. Consider the planar square lattice in Figure 8 populated with Al (A) and Si (S) atoms in the ratio 1:3. The lowest energy is achieved when there are no A-A nearest-neighbor linkages, but this can be realized in many ways without long-range order, as shown in Figure 8. The ground state has a finite entropy and no long-range order, and no ordering phase transition is possible if there are only first-

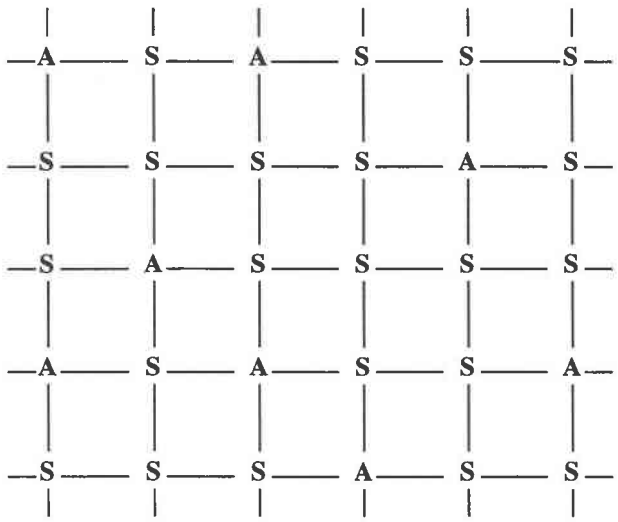

FIGURE 8. One of many arrangements of Al (A) and Si (S) atoms on a planar square lattice with the proportion of Al atoms $x = 0.25$, in which each Al atom has 4 Si nearest neighbors, showing no long-range order. Each such configuration has no Al–Al linkages and has the same energy ignoring all interactions beyond nearest-neighbors.

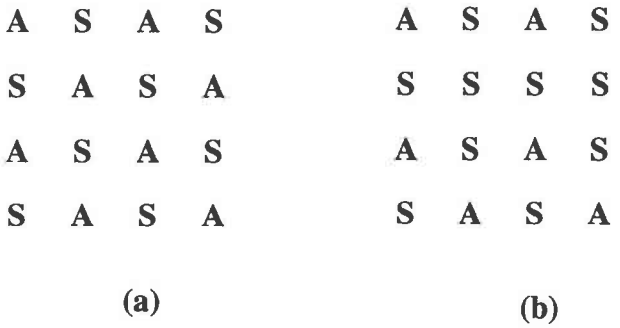

FIGURE 9. Ordered arrangements of Al (A) and Si (S) atoms on a planer square lattice with an Al concentration (a) $x = 0.5$ and (b) $x = 0.25$.

neighbors interactions. The important point is that with a low concentration of Al atoms it becomes possible to have complete Al-Al avoidance arising from short-range order without the establishment of long-range order.

An illustrative example

Consider the simple model of the square lattice with an Al:Si ratio equal to 1:3 and only nearest-neighbor interactions J_1. We start from an ordered arrangement with Al concentration $x = ½$ as shown in Figure 9a. Perfect order means that there are no Al-Al linkages, but any rearrangement that leads to the reduction in long-range order necessarily leads to some Al-Al linkages. To reduce the concentration to $x = ¼$ we replace half of the Al atoms by Si. The replacement can be selected at random without any cost in energy; this gives rise to a nonzero entropy in the ground state. Actually there is still some vestige of long-range order in this arrangement because the Al atoms occupy only a subset of the total number of sites. However, true long-range disorder can be created by moving some of the Al into the original Si sites but without creating any Al-Al linkages, as shown in Figure 8, resulting in even greater entropy. Thus the free energy is minimized by disordering at any infinitesimal temperature above 0 K without any increase in energy, i.e., without creating any Al-Al linkages. This demonstrates that complete Al avoidance can be achieved as a result of short-range order without the need to establish any long-range order.

Of course in real materials there are more distant interactions J_r beyond first neighbors. We therefore develop the model further (still with Al concentration $x = ¼$) by adding a second neighbor interaction $J_2 = J_1/10$, which is on the order of magnitude found by the shell-model calculations. The energy is minimized by each Al having all Si second neighbors, giving the ordered structure of Figure 9b. We evaluated the correlation function

$$C_z(T) = -[\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle] \qquad (16)$$

between second-neighbor sites by Monte Carlo simulation, shown in Figure 10. Short-range order is driven by J_1 and becomes larger below T_c(ABW), but long-range order is driven by the smaller J_2 giving a much lower T_c of $0.069T_c$(ABW).

Application to leucite

We now apply these ideas to leucite, $KAlSi_2O_6$. The crystal structure consists of four-membered rings of linked tetrahedra, and it is possible to populate the sites with equal numbers of Al and Si atoms in an ordered arrangement such that each Si atom has only Al neighbors and

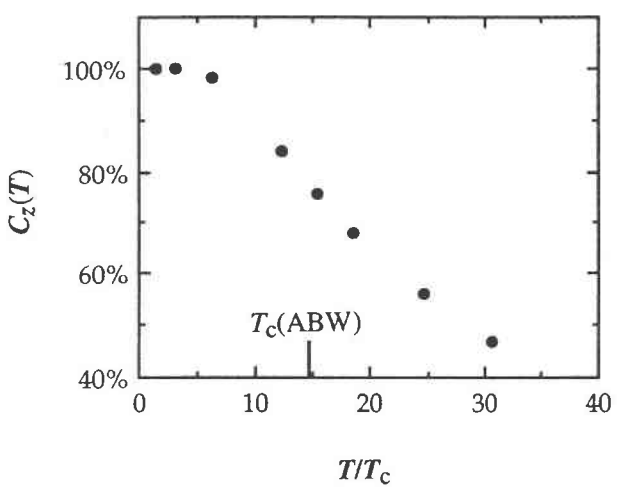

FIGURE 10. The short-range correlation $C_z(T)$ between second-neighbor sites on the square lattice of Figure 9b (i.e., in a diagonal direction), for $J_2 = 0.1J_1$ and Al concentration $x = 0.25$. Note how T_c is much less than T_c(ABW).

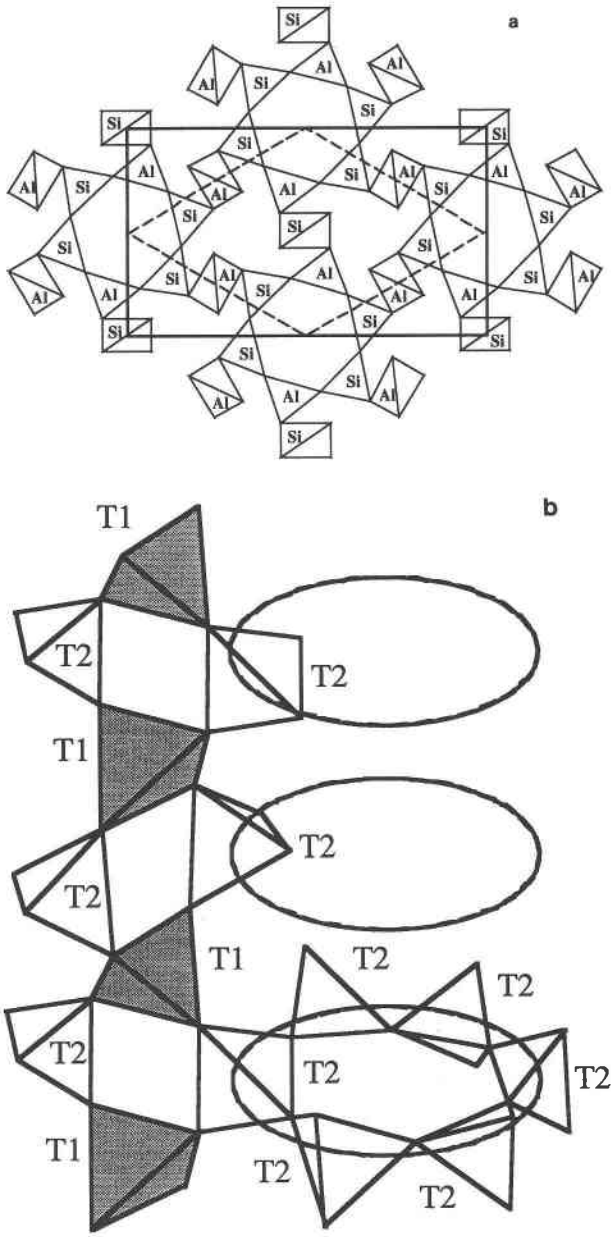

FIGURE 11. The cordierite structure. (**a**) Hexagons of T2 sites in an *a-b* plane are linked by T1 sites lying half-way between successive planes of T2 sites. The ordering and orthorhombic unit cell are shown. (**b**) A chain of square rings parallel to the *c* axis consist of T1 sites linking adjacent hexagons of T2 sites in one *a-b* layer and hexagons in adjacent layers.

vice versa. (Ordered arrangements of this kind are always possible when the structure consists of even-membered rings but impossible when there are odd-membered rings.) Following our treatment of the square lattice above we replace one third of the Al atoms by Si to reduce the Al:Si ratio from 1:1 to the required value 1:2. This can be done in many ways, and then the remaining Al atoms can be moved around leading to a zero-point entropy as before. This sort of disorder has been confirmed experimentally in cubic Cs-exchanged leucite and the related cubic analcime (Phillips and Kirkpatrick 1994; Dove and Heine 1996). Thus in the presence of J_1 only, there would be no ordering at any temperature, compared with T_c(ABW) = 4530 K using J_1 = 0.65 eV from Table 1. In the case of leucite only J_1 has been calculated (Dove et al. 1993), and so we assume that $J_2 \approx 0.1J_1$ by analogy with the other materials we have studied. We take the estimate of T_c/T_c(ABW) = 0.069 from the 1:3 diluted square lattice above (noting that the difference in dimension between the two cases is taken into account by the adjustment prefactors in the equation for T_c(ABW), Equation 5, and that the number of nearest-neighbors is the same in leucite and the square lattice), and with J_1 = 0.65 we obtain T_c = 310 K. This is a very low value, as in gehlenite, too low to be studied experimentally because of the slowness of the ordering kinetics at such temperatures, and it explains why long-range Al-Si ordering is not found in leucite.

Application to albite

We consider albite, $NaAlSi_3O_8$, as a further application. The T sites in feldspars are arranged in linked four-membered rings and can be occupied by a perfect alternation of Al and Si atoms as in anorthite. The replacement of one-half the Al by Si in albite leads to a large entropy as argued above. In the first section the value $T_c \approx$ 2300–2500 K was suggested for anorthite, and with a value for x of ¼ instead of ½ in Equation 6 for $f(x)$ we can use the anorthite T_c to give a rough estimate of T_c(ABW) ~ 1800 K (Eq. 5) for albite, assuming that the J values are similar in both cases. The actual T_c for albite is complicated by the fact that the $C2/m$-$C\bar{1}$ transition is a combination of Al-Si ordering and lattice displacement. Analysis has shown that the displacive part of the transition occurs first on lowering the temperature from the disordered state, pulling the Al-Si ordering with it at lower temperatures, and that the latter would occur at 833 K by itself (Salje 1990). The actual ordering T_c is again substantially below the ABW estimate as a result of the low Al concentration, similar to the case of leucite.

Al-Si ORDERING IN CORDIERITE

Cordierite, $Mg_2Al_4Si_5O_{18}$, has a somewhat complex ordering pattern (Fig. 11), and it shows both of the factors noted in the preceding sections. T_c for Al-Si ordering has been estimated as 1750 ± 30 K (Putnis, personal communication), from the TTT diagram on annealing (Putnis et al. 1985). This value is just below the melting point. It is not very low in the sense of T_c for gehlenite or leucite, but it is significantly lower than T_c(ABW). The cordierite structure has two types of tetrahedra, with 24 T2 sites per orthorhombic ordered cell arranged in hexagonal rings that are linked by 12 T1 sites. In the ordered structure each hexagonal ring has 2 Al and 4 Si T2 tetrahedra, whereas two-thirds of the T1 tetrahedra are Al. Thus for the basic unit of 3T1 + 6T2 sites, there are 12 T1-T2

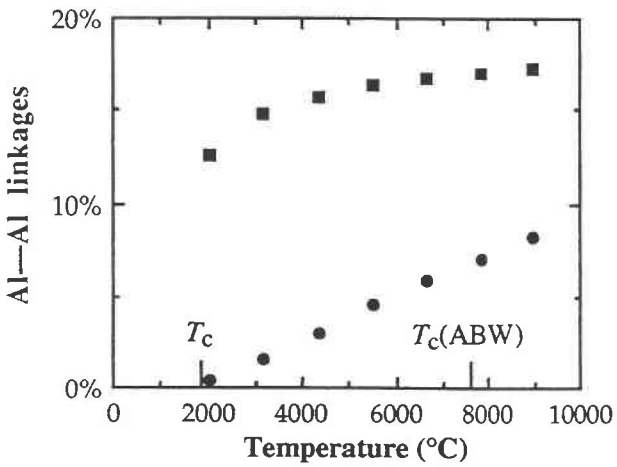

FIGURE 12. The percentage of Al-Al linkages among T1-T2 (squares) and T2-T2 (circles) linkages as a function of temperature from the interactions J_r of Table 1. Complete randomness would give $(\frac{4}{9})^2 = 19.8\%$.

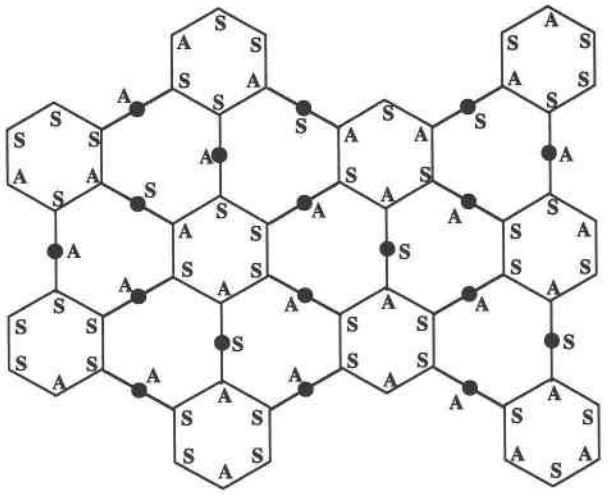

FIGURE 13. The topology of the T sites and their linkages in an *a-b* layer of cordierite, showing a disordered arrangement of Al (A) and Si (S) atoms but with no Al-Al nearest-neighbors. The T2 sites are the corners of the small hexagons, and the T1 sites are denoted by dots linking the hexagons, giving nine-membered rings.

nearest-neighbor links and 6 of type T2-T2. The corresponding interactions J_1 and J_1', respectively, are given in Table 1. For J_{tot} in Equation 5 we take a weighted average (ignoring the smaller more distant J_r)

$$J_{tot} = 4J_1(\text{average}) = 4\ (\tfrac{2}{3}J_1 + \tfrac{1}{3}J_1') = 4.04\ \text{eV} \quad (17)$$

which (with the atomic concentration $x = \frac{4}{9}$) gives T_c(ABW) = 7830 K. This is quite high because of the relatively large values of J_1 and J_1'. There are seven inequivalent second-neighbor interactions, J_2^i to J_2^{vii}, whose precise definitions are immaterial here and are given by Thayaparam et al. (1996). Only one type of third-neighbor interaction was included, corresponding to a diagonal across the hexagonal rings: It might be significant for the ordering among the T2 sites.

Consider now the equilibrium degree of order with decreasing temperature, notionally with the structure remaining solid. Below T_c(ABW) strong short-range order sets in, driven by J_1 and J_1'. It is therefore not surprising that crystalline cordierite formed from cordierite glass at 1670 K already has strong short-range order when this is measured within a few minutes of formation, with only a few percent of nearest-neighbor linkages being between two Al atoms (Putnis and Angel 1985; Dove and Heine 1996).

Figure 12 shows the percentage of Al(T1)-Al(T2) linkages and Al(T2)-Al(T2) linkages in equilibrium determined by our Monte Carlo simulation. The proportions are quite small near T_c, which in the case of the T2-T2 linkages, is helped by the large value of J_1' and by the energy preference of Al for the T1 sites over the T2 sites (which is reflected in the value of μ, Table 1). The T1 sites all lie in chains of four-membered rings in the *c* direction consisting of two T1 and two T2 sites. Perfectly alternating SiAlSiAl ordering is possible on these with all the T1 sites in a chain occupied by either Al or Si. Thus there is no barrier to easy short-range ordering in these rings and hence in their chains.

However long-range order is more difficult to attain in this structure. A Monte Carlo simulation of the ordering transition using the interaction parameters in Table 1 gave T_c = 2110 K, in reasonable agreement with experiment and substantially below the estimate T_c(ABW). The fact that T_c (both the experimental and simulated values) is so much lower than T_c(ABW) indicates that the long-range ordering is driven more by the second- (and higher-) neighbor interactions than by J_1 and J_1'.

We can understand why long-range order only sets in at such a low T_c as follows. The chains of four-membered rings are one-dimensional, and, as in sillimanite and gehlenite, do not result in long-range order in themselves. The ordering between the chains acts through the hexagons of T2 sites, and the low Al concentration of $\frac{1}{3}$ gives considerable freedom of arrangement. More precisely, two Al can be placed on a hexagon of six sites in nine different ways without being nearest-neighbors. And since the number of Al atoms on any one hexagon can vary from zero to three without necessarily causing any unfavorable Al-Al linkages on the hexagon, there can be even more possible configurations. Thus the hexagons do not give any strong ordering link between the chains. In fact it is not difficult to draw structures with perfect order in the chains in the *c* direction but disorder in the *a-b* plane while having no Al-Al linkages. One such structure is shown in Figure 13, which is a piece of a larger drawing extending over 56 hexagons. Indeed we developed a systematic way of extending the pattern indefinitely, and by counting the number of choices we could estimate an entropy of about $(\frac{1}{8})k_B$ ln 2 per chain. This tends to zero

per site if the chains are considered to be infinitely long; but since the ordered regions within any chain must be of finite size (as a result of ordering not being possible in one dimension, as discussed in the first section) this entropy may be significant in lowering T_c.

To summarize, in cordierite we have an interplay of the two mechanisms described in the previous two sections. The small dilution of the Al:Si ratio from 1:2 to 4:9 is enough to allow there to be configurations with no long-range order in three dimensions but with sufficient short-range order for there to be no Al-Al linkages. But this short-range order involves quasi one-dimensional ordering along the T1-T2 chains, which cannot lead to long-range order at nonzero temperatures; so there must be some breaks in the order and hence a nonzero number of Al-Al linkages along the chains. This picture is broadly in agreement with the NMR data (Putnis and Angel 1985; Dove and Heine 1996). Complete long-range order is only obtained by second- and third-neighbor interactions across the T2 hexagons. Since these interactions are weaker than the nearest-neighbor interactions, the resultant T_c is substantially below an estimate based on the strength of nearest-neighbor interactions.

Conclusions

Long-range order, short-range order, and the transition temperature

Although the transition temperature T_c is not the most basic item of information about an ordering transformation, it has a pivotal significance. We have highlighted the fact that T_c for Al-Si ordering varies over a rather wide range from a few hundred degrees to inferred values of several thousand. This is a striking result. Since many of the structures considered are tetrahedrally coordinated frameworks with very similar local structure, we might expect that the same basic Bragg-Williams treatment would apply equally well (or equally badly) to each structure. Instead the Bragg-Williams model works really well in some cases (e.g., anorthite and kalsilite), but in other cases it significantly overestimates T_c, even when the usual fluctuations in the short-range order have been accounted for (e.g., sillimanite, gehlenite, leucite, cordierite).

The free energy in the Bragg-Williams model, from which T_c is estimated, has two contributions. The first contribution is the enthalpy, which is calculated assuming that the dominant interactions are the nearest-neighbor interactions. At first sight this is reasonable, since the nearest-neighbor interactions are typically ten times stronger than the interactions between more-distant neighbors. For a state with less than perfect order, as found for temperatures near T_c, the enthalpy is calculated using a simple statistical argument. Any interaction between the atoms on two tetrahedral sites is considered to be a weighted average of the relevant Al-Al, Si-Si, and Al-Si interactions; the weighting reflects the probabilities of both sites being occupied by either atom type. The second contribution to the free energy is from the entropy, which is calculated using a similar statistical treatment to that used in the calculation of the enthalpy. Given the probabilities of each crystallographic site being occupied by an Al or Si, the entropy is evaluated simply by counting all the configurations that are consistent with these probabilities. The assumptions in both cases are essentially that every configuration for a given degree of order is energetically equivalent. This approximation becomes exact in the limit of a large number of nearest neighbors.

It is known that in the general case short-range order modifies the behavior close to T_c, and the corrections to the Bragg-Williams treatment that arise from critical fluctuations are well understood (e.g., Rao and Rao 1978). Indeed, we have incorporated these into our adjusted equation for T_c, Equation 5. Our examples where T_c is significantly below our estimates of T_c(ABW) point to deeper flaws in the Bragg-Williams model. One of these is low effective dimensionality, which arises from certain topological considerations. This is easy to see in the sillimanite and gehlenite structures but it also features in the ordering process in cordierite. The effect of low dimensionality is that there can be considerable short-range order along one direction, and long-range order is driven by weaker interactions between the chains. Another important factor is dilution. This is probably the most common factor because it relates to chemistry rather than topology. Even in cordierite, in which the Al:Si ratio is 5:4, the effects of dilution are of considerable importance. The existence of some dilution allows Al avoidance to be fully satisfied as a result of short-range order, without the need for long-range order. With complete Al avoidance, the driving force for long-range order must come from distant neighbors. Thus both of the central ideas of the Bragg-Williams model are negated: The nearest-neighbor interactions produce short-range order rather than long-range order, long-range order is then driven by distant-neighbor interactions rather than the stronger nearest-neighbor interactions, and the entropy is greatly reduced by the existence of short-range order.

On our calculations of the nearest-neighbor interactions

An important aspect of our enquiry lies in the question of whether there is any way in which the interactions J_r from computer simulations can be compared directly with experiments. The broad sweep of values of J_1 in Table 1 compare well with the measurements of Navrotsky et al. (1982) for a range of glasses and with the value of J deduced for anorthite (Phillips et al. 1992); but since they are different materials one cannot say anything more quantitative. Our study of cordierite was initiated with the expectation that a direct comparison would be possible with the enthalpy of ordering per Al-Al linkage annealed out of the material, but as we have discussed here and elsewhere (Dove and Heine 1996; Thayaparam et al. 1996) there are problems with the experimental data that lead to significant uncertainties. In any case, it is now clear that the experimental data yield only J_1 and not J'_1.

Cordierite is nevertheless a good model system for experiment, and we hope that further measurements are made.

The only hard numbers we have are the T_c values of sillimanite and cordierite and the comparison between the experimental values and our computations using Monte Carlo simulations. In both cases there would be no long-range order under the influence of the nearest-neighbor interactions only. The long-range order is ultimately driven by the interaction of more distant neighbors, which is unsatisfactory since these are small and therefore have greater uncertainty. In the quasi one-dimensional case of sillimanite the dependence on the more distant interactions is logarithmic (Eq. 13) and rather weak, which helps. The same is probably true also for cordierite. Under these circumstances the agreement of T_c from simulation with the observed T_c for sillimanite and cordierite is better than we hoped. In any event, these tests tell us little about our calculated values of J_1.

We can turn the question of the validity of the calculated J_r values around: Instead of emphasizing the similarity of the local structure of linked tetrahedra in all the minerals studied, we can ask why J_1 varies between them to the degree that is shown in Table 1. In particular, why is J_1' so large in cordierite? After all, the calculations for the different structures were performed using the same potential model, which is known to be transferable between different aluminosilicates with a consistent level of accuracy. We might therefore have anticipated that the values of J_1 would be more similar between different structures than they have proved to be, and so we could have hoped that J_1 would itself be transferable between different (but similar) structures. However, a clear conclusion from our work is that the value for J_1 found for any structure, whether from experiment or calculation, cannot be transferred to any other structure. We have no complete answer to this problem except to refer to our argument in the second section that the largest contribution to the J_1 terms is from local strain induced by the size difference between Al and Si tetrahedra when these are disordered. The strain energy is large if the structure, as a three dimensional whole, is cross-braced and rigid or small if the structure is more floppy in the sense that local difference in tetrahedron size can be accommodated by changes in the T-O-T bond angles, which have rather weak force constants. The degree of such rigidity can, of course, be very anisotropic in a given material.

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