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The use of Monte Carlo methods to determine the distribution of Al and Si cations in framework aluminosilicates from ^{29}Si MAS NMR data

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ABSTRACT

A Monte Carlo method was developed to determine the distribution of Al and Si cations from ^{29}Si MAS NMR data for framework aluminosilicates. The method was used to analyze data obtained from Cs-exchanged leucite in its high-temperature cubic phase and from cubic analcime samples. It was also used to determine the number of Al-O-Al linkages in cordierite for different degrees of Al-Si order. The results for cordierite were correlated with the calorimetric data of Carpenter et al. (1983) to estimate the energy for the reaction (Al-O-Al) + (Si-O-Si) → 2(Al-O-Si) of ~40 kJ/mol.

INTRODUCTION

The ^{29}Si MAS NMR technique has proven to be extremely useful as a probe of Al-Si cation ordering in framework aluminosilicates (Putnis et al. 1985; Putnis and Angel 1985; Fyfe et al. 1986; Brown et al. 1987; Murdoch et al. 1988; Phillips et al. 1989; Phillips and Kirkpatrick 1994). Resonance peaks are observed for Si in different crystallographic sites (reflecting long-range order, whether convergent or nonconvergent) and for equivalent sites with different numbers of Al neighbors (reflecting mostly short-range ordering); in some cases these different sets of peaks are nicely separated in the MAS NMR spectra, but in other cases they overlap making identification difficult. Putnis and Angel (1985) showed that, in principle, the ^{29}Si MAS NMR spectra contain all the information required to determine the number of Al-O-Al linkages. However, our own analysis of the data of Putnis et al. (1985) and Putnis and Angel (1985) showed that there are problems in extracting this information from the experimental data (Thayaparam et al. 1996). The main problem is that the end result is obtained by subtracting two large quantities, which means that it is extremely sensitive to small errors in the experimental data. More specifically, in cordierite there are two tetrahedral sites that can be partly occupied by Al: T1 and T2. Putnis and Angel (1985) obtained an equation for the total number of Al-O-Al linkages that included both the T1-O-T2 and T2-O-T2 linkages. Our own analysis (Thayaparam et al. 1996) showed that when both types of linkages are separately accounted for, the number of Al-O-Al linkages of the form T2-O-T2 is calculated from the experimental data as a negative quantity. This number can be made to be zero by a small amount of tinkering that does not significantly compromise the experimental data. Indeed, with this tinkering the calculated number of Al-O-Al linkages for the most ordered samples could differ from the values given by Putnis and Angel (1985) by a factor of 2. We concluded that another type of analysis is required.

This problem has assumed some importance following our recent work on the driving force for long-range Al-Si ordering in aluminosilicates (Bertram et al. 1990; Dove et al. 1993, 1996; Thayaparam et al. 1996). In the spirit of the formalism of the Bragg-Williams model (Putnis 1992), it is usually assumed that the driving force for ordering is the nearest-neighbor interaction that prefers to have two (Al-O-Si) linkages rather than (Al-O-Al) + (Si-O-Si) linkages: the so-called Al-avoidance principle. We recently argued that when the Al:Si ratio departs from 1:1 Al avoidance produces short-range order but not long-range order (Dove et al. 1996). This leads to a low temperature for long-range ordering, although the nearest-neighbor interaction associated with Al-O-Al linkages sets the temperature scale for the onset of short-range order. The ^{29}Si MAS NMR spectra could show this effect quite nicely . Phillips and Kirkpatrick (1994) obtained data for Cs-exchanged leucite in its disordered cubic phase and for cubic analcime samples at room temperature. They did not analyze their spectra to obtain the number of Al-O-Al linkages, but by comparing their spectra with calculations based on random disorder with complete Al avoidance they showed that the number of Al-O-Al linkages in their samples must be small. In the case of cordierite, the ^{29}Si MAS NMR spectra suggest that the number of Al-O-Al linkages is not zero in the disordered phase (Putnis et al. 1985; Putnis and Angel 1985). By correlating the ^{29}Si MAS NMR data with calorimetric data (Carpenter et al. 1983) it was shown that it is possible to determine the energy required to form an Al-O-Al linkage (Putnis 1992). This energy is required to calibrate our recent calculations of this quantity (Bertram et al. 1990; Dove et al. 1993; Thayaparam et al. 1996).

In this paper we present a new method to determine

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the number of Al-O-Al linkages from ^{29}Si MAS NMR spectra. This method is based on the traditional Monte Carlo method of statistical mechanics. We apply this method to analyze the ^{29}Si MAS NMR spectra of cubic Cs-exchanged leucite and cubic analcime samples obtained by Phillips and Kirkpatrick (1994) to show that the number of Al-O-Al linkages in each case is extremely small, and to the spectra of cordierite obtained by Putnis et al. (1985) to determine the number of Al-O-Al linkages in cordierite as a function of annealing time.

METHOD

The problem in using ^{29}Si MAS NMR spectra to determine the distribution of Al and Si cations is well defined. The important experimental quantity is g_n^j, which gives the relative number of Si cations on the site of type j that have n Al neighbors. This is normalized such that $\Sigma\, g_n^j = 1$ (summing over both j and n) and is easily measured because the intensities of the peaks in the ^{29}Si MAS NMR spectra are proportional to g_n^j. Thus, the objective is to determine a distribution of Al and Si cations that best fits the set of experimental values of g_n^j. Our approach is to use a sample containing several unit cells of tetrahedral sites and to redistribute the Al and Si cations over the tetrahedral sites using the experimental values of g_n^j as a guide. Specifically we define the quantity

$$\epsilon = \sum_n \sum_j [g_n^j(\mathrm{obs}) - g_n^j(\mathrm{calc})]^2/\sigma^2$$

to define how closely the distribution of cations in the simulations resembles the experimental distribution, where obs and calc denote the experimental and calculated values, respectively, and σ is an average error on the experimental values of g_n^j. The best distribution of the Al and Si cations is the one that gives the smallest value of ϵ. In the Monte Carlo method, two cations are selected at random, and their positions are switched if this action lowers the value of ϵ. Otherwise, their positions are switched with a probability $\exp(-\beta\epsilon)$, where β is a parameter that is selected by the user. The link with the standard Monte Carlo method is clear: ϵ plays the role of an energy, and β plays the role of the reciprocal of the temperature. The procedure of proposing and testing random switches of the positions of the Al and Si cations is repeated until ϵ oscillates about a minimum mean value. This method produces the most random distribution of Al and Si cations that is consistent with the experimental data (i.e., the entropy is maximized). Of course, added to the experimental data is the fuzzy experimental condition that the number of Al-O-Al linkages of all types must be positive, and in this sense we are doing more than simply fitting the experimental ^{29}Si MAS NMR spectra. From the equilibrated configurations it is an easy matter to calculate the number of Al-O-Al linkages. This method is analogous to "simulated annealing," applied to finding the optimum relative positioning of objects such as transistors on a silicon chip, and the reversed Monte Carlo method for determining the local structure of a disordered solid or liquid that best reproduces the total scattering (or diffuse scattering) in an X-ray or neutron scattering experiment. A few technical details are given in the Appendix.

RESULTS

Cubic Cs-exchanged leucite and analcime

The mineral leucite, $KAlSi_2O_6$, undergoes a phase transition at 960 K. There has been considerable discussion about the driving force for this transition. For example, Hatch et al. (1990) suggested that the phase transition involves Al-Si ordering, but this has been argued against by Palmer et al. (1989, 1990) and Palmer and Salje (1990) on experimental grounds, and by Dove et al. (1993) from the results of model calculations. Indeed, the phase transition can be fully explained on the assumption that it is a displacive phase transition without any accompanying Al-Si ordering (Dove et al. 1995). This then prompts the question as to why long-range Al-Si ordering occurs only at relatively low temperature (Dove et al. 1993, 1996).

There have been a number of ^{29}Si MAS NMR and ^{27}Al MAS NMR studies of Al-Si ordering in leucite at room temperature (Brown et al. 1987; Murdoch et al. 1988; Phillips et al. 1989). Unfortunately, it has been difficult to interpret the data owing to the existence of three similar tetrahedral sites at room temperature with overlap of the spectral lines associated with the three sites. More recently Phillips and Kirkpatrick (1994) studied the Cs analog of leucite. This is an interesting case because the cubic-tetragonal phase transition occurs at a much lower temperature than in the K case (Palmer and Dove in preparation), and it is therefore easy to heat into the high-temperature phase. The cubic symmetry of the high-temperature phase requires that the Al and Si cations cannot have long-range order. Our recent work associated with the problem of Al-Si ordering in leucite (Dove et al. 1993) and other materials (Bertram et al. 1990; Thayaparam et al. 1994, 1996; Dove et al. 1996) suggested that it is possible to have short-range order in the high-temperature phase involving complete Al avoidance without any long-range order. In this case, the ^{29}Si MAS NMR data for Cs-exchanged leucite are extremely useful. The mineral analcime, $NaAlSi_2O_6 \cdot H_2O$, is also of interest because it has a cubic structure that is similar to that of the high-temperature phase of leucite and therefore also has no long-range ordering of the Al and Si cations. However, in analcime the Si content is variable, and ^{29}Si MAS NMR data have been obtained for samples with different amounts of Si (Murdoch et al. 1988; Phillips and Kirkpatrick 1994).

The results of our simulations for Cs-exchanged leucite and the analcime samples are given in Table 1. We used a cubic supercell of 2 × 2 × 2 unit cells, containing 384 tetrahedral sites. The simulation of Cs-exchanged leucite shows clearly that there is short-range order leading to a complete absence of Al-O-Al linkages. This is consistent with the proposition that Al avoidance can be completely accommodated without driving any long-range order

(Dove et al. 1993, 1996). Thus, any long-range order is driven by weaker distant interactions and accordingly sets in at a relatively low temperature. On the other hand, our simulations show that the analcime samples do have a small number of Al-O-Al linkages, but when compared with the number there would be if there was a completely random distribution of the Al and Si atoms (~⅔ formula unit) it is clear that there is still a considerable degree of short-range order. The NMR spectra of the analcime samples have significant differences, which we have completely accounted for in our simulations.

Table 1. Experimental and calculated ^{29}Si MAS NMR spectral data for cubic Cs-exchanged leucite and various analcime samples

	N_{Si}	g_0	g_1	g_2	g_3	g_4	$N_{Al\text{-}Al}$
				Cs-leucite*			
Exp.	2.0	0.038	0.221	0.427	0.277	0.037	
Calc.		0.047	0.227	0.430	0.273	0.023	0
				Analcime (Mont-Saint-Hilaire)*			
Exp.	1.95	0.010	0.122	0.695	0.157	0.016	
Calc.		0.024	0.122	0.693	0.154	0.008	0.09
				Analcime (UIUC 1904)*			
Exp.	2.18	0.023	0.239	0.619	0.119	0.0	
Calc.		0.027	0.243	0.616	0.114	0.0	0.05
				Analcime (Barstow)*			
Exp.	2.53	0.077	0.365	0.463	0.090	0.005	
Calc.		0.076	0.367	0.462	0.091	0.004	0.02
				Analcime (Mojave)*			
Exp.	2.52	0.058	0.402	0.446	0.087	0.008	
Calc.		0.062	0.404	0.447	0.084	0.004	0.05
				Analcime (Murdoch)**			
Exp.	2.13	0.020	0.234	0.597	0.148	0.0	
Calc.		0.023	0.234	0.594	0.149	0.0	0.03

Note: The last column gives the number of Al-O-Al linkages per formula unit.

* Experimental data are from Phillips and Kirkpatrick (1994). Average errors are ±0.005.

** Experimental data are from Murdoch et al. (1988). Average errors are ±0.003.

Cordierite

Cordierite, $Mg_2Al_4Si_5O_{18}$, is easily formed by annealing from a glass of the appropriate composition. The initial product has a hexagonal structure, and there is necessarily long-range disorder. In the hexagonal structure there are two nonequivalent tetrahedral sites, T1 and T2. The T2 sites are connected in six-membered rings, and the rings are connected through linkages to the T1 sites. The complete framework then forms chains of linked T1 and T2 tetrahedra along [001]. This structure is described in detail by Putnis (1992). The ^{29}Si MAS NMR data (Putnis et al. 1985) and diffraction data (Meagher and Gibbs 1977) show that the six T1 sites contain more Al than Si (the Al:Si ratio is approximately 2:1) and that the 12 T2 sites contain less Al than Si (the Al:Si ratio is approximately 1:2). This partitioning is an example of nonconvergent ordering. The tendency to have more Al in the T1 sites than in the T2 sites probably arises from the close proximity of the T1 sites to the Mg^{2+} cations. On annealing, the sample progressively orders, as seen in the ^{29}Si MAS NMR data (Putnis et al. 1987), with the structure transforming to a state with a characteristic tweed microstructure until an orthorhombic structure is formed with long-range Al-Si order (Putnis 1992). The ^{29}Si MAS NMR data change continuously through these transformation processes (Putnis et al. 1987), showing no signs of either the formation of the tweed microstructure or the transition to the orthorhombic phase.

The results of our simulations for different annealing times are given in Table 2, and the results of the analysis of the simulation configurations are given in Table 3. We used a supercell made from a block of 2 × 2 × 2 orthorhombic unit cells containing 288 tetrahedra. The changes in the partitioning of the Al cations between the T1 and T2 sites on annealing are clearly seen. The more interesting point is that there are virtually no Al-O-Al linkages of the form T2-T2. This result was anticipated from our previous analysis of the ^{29}Si MAS NMR data, in which we obtained a negative number for this quantity in each case (Thayaparam et al. 1996). Indeed, in our interpretation of the ordering behavior in cordierite we proposed that there is a tendency toward one-dimensional long-range ordering along the T1-T2 chains, and that the formation of Al-O-Al linkages is avoided by short-range ordering within the rings of T2 tetrahedra. It is possible to stack ordered T1-T2 chains in different ways to avoid the formation of Al-O-Al linkages, which means that the stacking of these chains does not lead to any long-range order (Dove et al. 1996; Thayaparam et al. 1996). However, complete one-dimensional ordering at a finite temperature is not possible, and so there must be some degree of disorder in the T1-T2 chains, which leads to the formation of the Al-O-Al linkages within the chains.

As we stated in the introduction, our main aim is to determine the number of Al-O-Al linkages as a function of annealing time for comparison with calorimetric data. In Table 3 we compare our calculated number of linkages with the number computed directly from the experimental data by Putnis and Angel (1985). The agreement is reasonably good for short annealing times, but for longer annealing times the number given by Putnis and Angel (1985) is consistently lower than the value obtained in our simulations. This trend is expected because we found that the numbers of Al-O-Al linkages obtained directly from the experimental data each contain a significant negative contribution from the T2-T2 linkages, which is larger for the longer annealing times. The simulations exclude this negative contribution to the number of Al-O-Al linkages. In Figure 1 we plot the number of Al-O-Al linkages calculated in our simulations as a function of the logarithm of the annealing time. The plot is linear within the experimental errors, with a gradient of $\partial N/\partial \log_{10}(t) \approx -0.25$. The calorimetric data of Carpenter et al. (1983) show that the enthalpy of ordering at the same annealing temperature also varies as the logarithm of the annealing time, with $\partial H/\partial \log_{10}(t) \approx -10$ kJ/mol. Comparing these

TABLE 2. Experimental and calculated ^{29}Si MAS NMR spectral data for cordierite with different annealing times

	g^1_0	g^1_1	g^1_2	g^1_3	g^1_4	g^2_0	g^2_1	g^2_2	g^2_3	g^2_4
2 min										
Exp.	0.0	0.006	0.042	0.053	0.020	0.0	0.049	0.347	0.408	0.075
Calc.	0.0	0.006	0.044	0.050	0.025	0.0	0.050	0.350	0.406	0.069
6.5 min										
Exp.	0.0	0.0	0.032	0.053	0.033	0.0	0.065	0.343	0.397	0.077
Calc.	0.0	0.0	0.031	0.056	0.031	0.0	0.063	0.344	0.394	0.081
23 min										
Exp.	0.0	0.0	0.038	0.058	0.037	0.0	0.052	0.308	0.428	0.079
Calc.	0.0	0.0	0.038	0.056	0.038	0.0	0.056	0.306	0.425	0.081
6 h										
Exp.	0.0	0.011	0.022	0.043	0.080	0.0	0.020	0.203	0.513	0.108
Calc.	0.0	0.006	0.019	0.050	0.094	0.013	0.025	0.200	0.506	0.088
23.5 h										
Exp.	0.0	0.013	0.012	0.039	0.098	0.0	0.022	0.177	0.568	0.069
Calc.	0.0	0.006	0.013	0.044	0.100	0.013	0.025	0.175	0.563	0.063
48.5 h										
Exp.	0.0	0.003	0.010	0.023	0.114	0.0	0.020	0.143	0.625	0.061
Calc.	0.0	0.0	0.013	0.025	0.125	0.006	0.025	0.144	0.613	0.050
96 h										
Exp.	0.0	0.008	0.015	0.029	0.117	0.0	0.013	0.111	0.645	0.062
Calc.	0.0	0.006	0.013	0.038	0.125	0.013	0.019	0.106	0.638	0.044
408 h										
Exp.	0.0	0.008	0.016	0.018	0.131	0.0	0.014	0.056	0.672	0.084
Calc.	0.0	0.0	0.019	0.025	0.150	0.013	0.025	0.050	0.663	0.056
2000 h										
Exp.	0.0	0.0	0.014	0.027	0.144	0.0	0.0	0.059	0.698	0.058
Calc.	0.0	0.006	0.013	0.031	0.150	0.013	0.006	0.056	0.694	0.031

Note: Experimental data are from Putnis et al. (1985).

results leads to a value for the energy associated with the reaction (Al-O-Al) + (Si-O-Si) → 2(Al-O-Si) of ~40 kJ/mol. This is a little above the value of 35 kJ/mol given previously (Putnis and Angel 1985; Putnis 1992); and given the problems associated with the earlier determination of the number of Al-O-Al linkages, this new value is to be preferred. This value, however, is significantly lower than the value we obtained from our calculations (Thayaparam et al. 1996), even allowing for the calibration of our empirical models against ab initio electronic structure calculations. However, the present analysis neglects the chemical potential associated with the tendency of the Al to prefer the T1 sites even in the disordered phase. This effect is evident at short annealing times, with the excess of Al in T1 over the expected occupancy of ⅔. Given that the partitioning of the Al cations over the T1 and T2 sites changes with annealing time as the number of Al-O-Al linkages changes, the changes in enthalpy include this contribution. Because this contribution is expected to be of opposite sign to the energy of formation of Al-O-Al linkages, our estimate of this energy probably

TABLE 3. Analysis of the simulated ensembles of cordierite

Annealing t	Al site occupancy T1	Al site occupancy T2	Number of Al-O-Al linkages T1-T2	Number of Al-O-Al linkages T2-T2	Number of Al-O-Al linkages Putnis
2 min	0.79	0.27	1.53	0	1.51
6.5 min	0.80	0.27	1.41	0.13	1.49
20 min	0.78	0.28	1.34	0	1.33
6 h	0.72	0.31	0.84	0	0.74
23.5 h	0.73	0.30	0.81	0	0.74
48.5 h	0.73	0.30	0.63	0	0.56
96 h	0.70	0.32	0.59	0	0.47
408 h	0.68	0.33	0.38	0	0.26
2000 h	0.67	0.33	0.38	0	0.18

Note: The data in the last column are from Putnis and Angel (1985) and include both the T1-T2 and T2-T2 linkages.

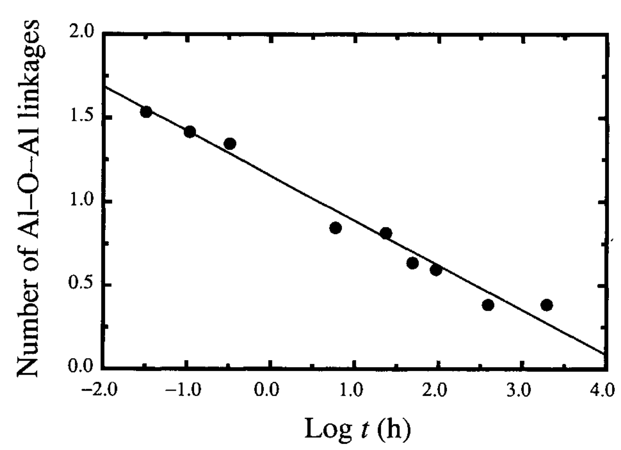

FIGURE 1. Plot of the number of Al-O-Al linkages of the form T1-O-T2 in cordierite against the logarithm of time as deduced in this study.

TABLE 4. Calculated ^{29}Si MAS NMR spectral data for cordierite annealed for 2000 h

	g^1_0	g^1_1	g^1_2	g^1_3	g^1_4	g^2_0	g^2_1	g^2_2	g^2_3	g^2_4
					$\alpha = 0$					
Data	0.0	0.0	0.014	0.027	0.144	0.0	0.0	0.059	0.698	0.058
Calc.	0.0	0.006	0.013	0.031	0.150	0.013	0.006	0.056	0.694	0.031
					$\alpha = 0.01$					
Data	0.009	0.009	0.021	0.034	0.140	0.009	0.009	0.063	0.644	0.061
Calc.	0.006	0.006	0.019	0.038	0.144	0.019	0.013	0.063	0.644	0.050
					$\alpha = 0.02$					
Data	0.017	0.017	0.028	0.040	0.137	0.017	0.017	0.066	0.598	0.065
Calc.	0.013	0.013	0.025	0.038	0.138	0.019	0.025	0.069	0.600	0.063

Note: Experimental data modified for a background correction as described in the text.

reflects a lower bound. From our empirical calculations (Thayaparam et al. 1996) we predicted that the magnitude of the chemical potential is about ⅓ of the energy required to form Al-O-Al linkages. Given that the excess of the occupancy of the T1 sites by Al is only slightly over ⅔ down to the shortest annealing times, it is quite possible (but impossible to prove) that the contribution of the chemical potential to the ordering enthalpy is small. It is possible that the effects of the chemical potential might be isolated with data collected at different annealing temperatures.

Finally, we explored the effects of systematic errors in the ^{29}Si MAS NMR data. In the above analysis we assumed that the errors are random. However, there is a hint in our results that there may be some systematic errors. For many of the cordierite experiments we calculate that $g^2_0 \neq 0$, contrary to the experimental data. Because the calculated values of g^2_0 are small compared with some of the other peaks in the spectra, it is quite possible that this peak could have been missed in the analysis of the raw data. The effect of neglecting this peak, and also g^1_0, is to increase slightly the baseline on the spectra. We simulated this effect by correcting the values of g^j_n by a constant value α and normalizing:

$$g^j_n(\text{corrected}) = \frac{g^j_n(\text{initial}) + \alpha}{1 + 10\alpha}.$$

We then performed a Monte Carlo simulation for two sets of corrected data for $\alpha = 0.01$ and $\alpha = 0.02$ using the data for an annealing time of 2000 h, and the results are given in Tables 4 and 5. The agreement between the corrected data and the simulations is better with $\alpha = 0.02$ than with $\alpha = 0$ (the uncorrected data). This mostly follows from the improved fitting of g^2_0. The major effect of the corrections to the data is to change the number of Al-O-Al linkages (Table 5), actually quite significantly. Another effect is to move some of the Al from the T1 sites to the T2 sites, which is not consistent with our understanding of the structure of the fully ordered phase. From this brief analysis we conclude that to be confident in the determined number of Al-O-Al linkages it is better to have more definite data for the two spectral peaks g^1_0 and g^2_0. Otherwise, the implication from the results in Table 5 is that the calculated value of the number of Al-O-Al linkages is extremely sensitive to small errors in the data, which casts further doubt on the estimated value of the ordering energy.

TABLE 5. Analysis of the simulated ensembles of cordierite for the 2000 h data corrected for the background

		Al site occupancy		Number of Al-O-Al linkages	
α	Quality of fit	T1	T2	T1-T2	T2-T2
0.0	1.0×10^{-3}	0.67	0.33	0.38	0
0.01	2.8×10^{-4}	0.65	0.34	0.47	0.06
0.02	1.4×10^{-4}	0.63	0.35	0.63	0.06

Note: The quality of fit is defined here as $\Sigma\,[g^j_n(\text{data}) - g^j_n(\text{calc.})]^2$.

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Appendix

The computer program NMRFIT was specifically written for this study using standard FORTRAN 77 to run on a DEC Alpha processor under OpenVMS. Because no part of the program was written using system-specific routines, the code should be easily portable. Indeed, the program was successfully tested in a UNIX environment. The random number generators are from the widely available NAG libraries, but alternative routines based on the FORTRAN random number generators are included.

The running of NMRFIT is controlled by three short files. The first contains the crystallographic data (space group symbol, unit-cell parameters, and fractional coordinates of the independent tetrahedral sites), the second contains control data (such as the size of the supercell, the value of β, and the number of steps in the Monte Carlo procedure), and the third contains the NMR data in the form of experimental values of g^j_n. The output files contain the calculated values of g^j_n, the number of Al-O-Al linkages partitioned into different sites, and the proportion of Al on each site. The final configuration is also saved at the end of a run. This can be used to start a new simulation, either to continue a run or to start a new run with a similar NMR spectrum.

We typically find that $\beta = 1$ leads to a good convergence of the problem in <1000 steps (counting a step as a successful switch rather than an attempted switch). The convergence depends on the specific structure. If there is no long-range order, then starting from a random configuration leads to convergence reasonably quickly. On the other hand, if there is long-range order in the system (as for example in some of the cordierite samples), the simulation converges much more quickly if the starting configuration is fully ordered. This reflects a well-known problem in lattice simulations in which there is a phase transition: To avoid problems related to the formation of domains and associated false minima in the free energy, it is frequently easier to start from an ordered structure. The program NMRFIT allows the use of both ordered and random initial configurations, and both were used in the simulations of cordierite. The number of required tetrahedral sites depends on the accuracy of the experimental data. Although a small number of tetrahedra limit the number of configurations that can be produced, which therefore affects the calculated values of g^j_n and the numbers of Al-O-Al linkages, we find that even with relatively small samples the effects of sample size are not significant compared with the errors in the experimental data. A typical run might take from a few minutes to a few hours, depending on how many attempts are required to achieve a successful switch. This itself is a function of the degree of order in the sample: the greater the degree of order, the fewer the number of configurations that fit the experimental data.

The program NMRFIT was not written in a very efficient way. For example, it calculates the g^j_n quantities from scratch at each step rather than updating the existing values. For the purist, the programming required to update g^j_n values would involve only careful bookkeeping and would not be difficult.

It is worth noting that there are some similarities with a method used by Murdoch et al. (1988) to analyze MAS NMR spectra on the basis of earlier work by Vega (1983). This method also used a statistical approach to deduce the form of short-range order on the basis of comparison of the computed and experimental MAS NMR data. However, unlike in the present case, the method used by Murdoch et al. (1988) specifically forced Al avoidance into their configurations, and without the use of a Monte Carlo update procedure the method of Murdoch et al. (1988) does not have a built-in ability to avoid false minima in the fitting procedure. In the program NMRFIT Al avoidance occurs in the configurations because the experimental data require it. The program NMRFIT is available by anonymous FTP (details are available from martin@minp.esc.cam.ac.uk) and from WWW URL http://www.esc.cam.ac.uk/mineral_sciences/nmrfit.html.