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AN ACCURATE SOLUTION FOR THE TWO-DIMENSIONAL MODEL OF ALBITE USING STATISTICAL MECHANICS

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Abstract

A two-dimensional model of Al, Si ordering in alkali feldspar is formulated and used to calculate accurately the configurational entropy for the model. For this purpose, a new method called Independent Basic Unit or **IBU** is introduced. To compare the results with the exact values, this method is applied to the one-dimensional model of albite. The results given by **IBU** are found to be accurate to the extent that the deviation in free energy is less than 0.8%. The reduced configurational entropy is calculated to be 1.065 corresponding to 8.854 J K^{-1} mol^{-1} for the two-dimensional model. This value is within 6% of standard values obtained by using approximate calculations for the same model.

Introduction

Al, Si ordering of albite and other alkali-feldspars is analysed in its most simple form as a lattice-gas model in which the occupancy of sites by Al is mapped onto an Ising-type variable. Models of this type go back to the 1970's (e.g., Mazo, [1]; Andersen and Mazo, [2]; Senderov, [3]) and yield reasonable approximations for the excess entropy as being identical to the configurational entropy.

In this paper, the original approach of Andersen and Mazo [2] of a 2D model is taken up again. An improved technique is used to solve the statistical mechanics of the Al, Si distribution under the usual constraints of Al-Al avoidance and charge neutrality. Within this model, an accurate solution can be found. The difference between this work and previous calculations (Andersen and Mazo, [2]; Rajabali, [4-5]) is that no explicit approximation will be made in this work for the calculation of the configurational entropy of the model. Such a difference is expected to have only a minor effect on the entropy at low temperatures, but it becomes important at high temperatures because of the aluminum avoidance rule, and especially at intermediate temperatures because of both the phase transition and the aluminum avoidance rule. Before we present these solutions it is useful to recall that the nearest-neighbor Ising models represent only a rough approximation, even for the excess entropy; in other words, the model is approximate even though the solution is accurate.

Keywords: Albite; Independent basic unit; Entropy

Na-feldspar shows a large elastic excess energy due to the Al, Si ordering process, (Salje *et al.*, [6]). The coupling between the cation position is partly due to lattice distortions. If such lattice distortions are explicity taken into account, the effective Hamiltonian related to such distortions can be written as [7]:

$$H = H_o + \frac{1}{2}\sum_{RR'}^{ij} A^{ij}(R-R')\,u^i(R)\,u^j(R')$$

$$-\frac{1}{2}\sum_{RR'} F^i(R-R')u^i(R)\,S(R')$$

where A^{ij} is a dynamic matrix, R is a set of lattice coordinates, $F(R)$ is a set of spin-lattice forces, S is the iso-spin (i.e. occupancy) and u is the strain

coordinate which describes the displacement of an atom from its ideal lattice site. Subject to constraints for the translational and rotational invariance of the lattice, the effective Hamiltonian can be written in terms of a space-dependent exchange constant $J(R)$ [7]. Marais *et al.* [8] have argued that this Hamiltonian is formally identical to an Ising Hamiltonian. Salje [7] has shown that $J(R) \propto 1/R^3$ in the case of zone-center instabilities with an oscillatory behavior for small values of R. In a classical Ising model, this effect is effectively ignored and $J(R)$ is replaced by one average number which is chosen to reproduce the experimental observations.

To include the lattice distortions in the model of Na-feldspar, the long-range crystal interactions (governed by Coulomb forces) have to be a function of Al, Si ordering in the lattice (Mazo, [1]; Senderov, [3]). The exact function for the site preference energy in terms of p (the fraction of T_{1O} sites occupied by Al atoms) is not known. However, Senderov [3] assumed a linear expression for such a function, and Mazo [1] used a similar linearity to get a reasonable agreement with the experiment. For such a function, we may either use a linear expression or even some other expressions that might give a better agreement with the experiment. This task remains for the future.

Independent Basic Unit

In order to calculate the exact configurational entropy of our model the following steps are taken:

(i) All sites are artificially divided into two arbitrary, alternating groups of "solid" and "nonsolid" in such a way that the nearest-neighbor sites of each solid site are all nonsolid sites and vice versa.

(ii) A nonsolid site with its nearest-neighbor sites is called a basic unit. Basic units are classified into several groups. Each group belongs to a specific configuration of solid sites of the basic unit.

(iii) The number of ways to distribute atoms among solid sites is calculated. This is equal to the number of ways for distributing independent basic units. An independent basic unit is considered to be a basic unit that has no common sites with other basic units.

(iv) The number of ways to distribute atoms among specific types of nonsolid sites is calculated; a specific type of nonsolid site belongs to the basic units with a specific configuration. The total number of ways to distribute atoms on all sites is then calculated.

(v) The total number of distributions (on solid and nonsolid sites), is used to calculate the configurational entropy.

Application of IBU to Two-Dimensional Model of Na-Feldspar

We use a two-dimensional model of Na-feldspar which was introduced by Andersen and Mazo ([2]). This model is simply a square lattice in which each square has three identical sites denoted by "b" and another site denoted by "a". Each unit has one of four different configurations A, B, C and D (Figure 1). Local charge neutrality holds because only one aluminum atom is allowed in each configuration

We now consider another square lattice in which each site is occupied by an A, B, C or D unit. In the Independent Basic Unit (**IBU**) approach, each site is either "solid" or "nonsolid". Therefore, from now on, by a site we mean a position which is occupied by an atom (Al or Si) and a "solid" ("nonsolid") site is a position which is occupied by a unit (A, B, C, or D). The basic unit contains four solid sites on its corners and one nonsolid site in its center (Figure 2) with $4^4 = 256$ possible configurations. Since solid sites are not nearest neighbors to each other, the aluminum avoidance rule is always obeyed. As shown in Figure 2, a basic unit can have five different configurations, Z_0, Z_1, Z_2, Z_3 and Z_4, excluding the configurations for its nonsolid site. If the Boltzmann probability for the basic unit with Z_i configuration is denoted by Q_i, where the subscript i shows the number of A units on the solid sites of the basic unit, then there are $\lambda_i Q_i N/2$ of basic units in the lattice with Z_i configuration, where λ_i is the multiplicity for Z_i configuration. Note that there are N/2 basic units in the lattice, where N is the total number of units. All configurations for a basic unit, along with their multiplicities and their numbers in the lattice are shown in Figure 2.

Now we consider the configurations for the nonsolid sites which are located at the centers of the basic units. The nonsolid sites may also be occupied by A, B, C or D units. In the distribution of units among these sites, the aluminum avoidance rule is taken into account. According to this rule, some units are not allowed to be located on some nonsolid sites. Let us first consider those basic units with the

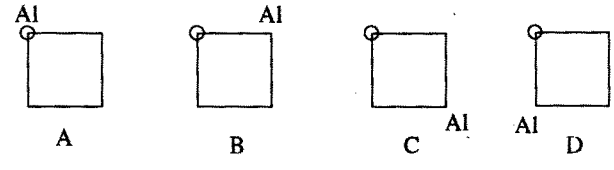
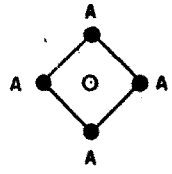
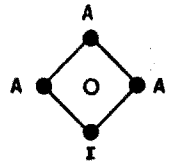
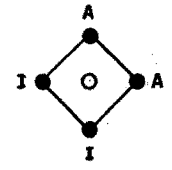
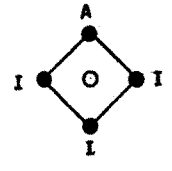
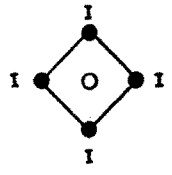


Figure 1. Four different configurations for a unit. The circles represent "a" sites and the other corners of squares represent the "b" sites. The position of only the Al atom is specified in each configuration, the other three corners are the positions of Si atoms.

configuration denoted by Z_4 in Figure 2. The nonsolid sites belonging to this type of basic unit are not available either for *B* units or for *D* units. Therefore, they may only be occupied by either *A* or *C* units. The probability of having either *B* or *D* units on this type of nonsolid site is set to zero, according to the aluminum avoidance rule. This constraint is shown as a broken line in Figure 3. A broken line connecting two units then means that such a configuration is not counted. Similarly, the nonaccessibility to this type of nonsolid site for *D* units is due to its interaction with the *A* unit located on the solid site on the bottom of the basic unit. All allowed and disallowed configurations and their multiplicities are tabulated in Figure 3 for Z_4 configurations. A similar set is given in Figure 4 for Z_3 configurations where disallowed configurations are on the left side and the remaining allowed ones are on the right side. Allowed and disallowed configurations, along with their multiplicities, are shown in Figures 5, 6, and 7 for the basic unit Z_2, Z_1 and Z_0 configuration, respectively.

Each unit on a nonsolid site gives disallowed

Basic unit	Configuration*	Multiplicity	Number of configuration
Z_4		$\lambda_4 = 1$	Q_4 N/2
Z_3		$\lambda_3 = 4 \times 3 = 12$	$12Q_3$ N/2
Z_2		$\lambda_2 = 6 \times 3 \times 3 = 54$	$54Q_2$ N/2
Z_1		$\lambda_1 = 4 \times 3 \times 3 \times 3 = 108$	$108Q_1$ N/2
Z_0		$\lambda_0 = 3 \times 3 \times 3 \times 3 = 81$	$81Q_0$ N/2

* The nonsolid unit sites are not occupied in this figure (see the other figures),

Figure 2. All different configurations for a basic unit. Full circles are solid sites and the open circle is a nonsolid site. Those units that are shown by *I* can be any of *B*, *C*, *or D* units.

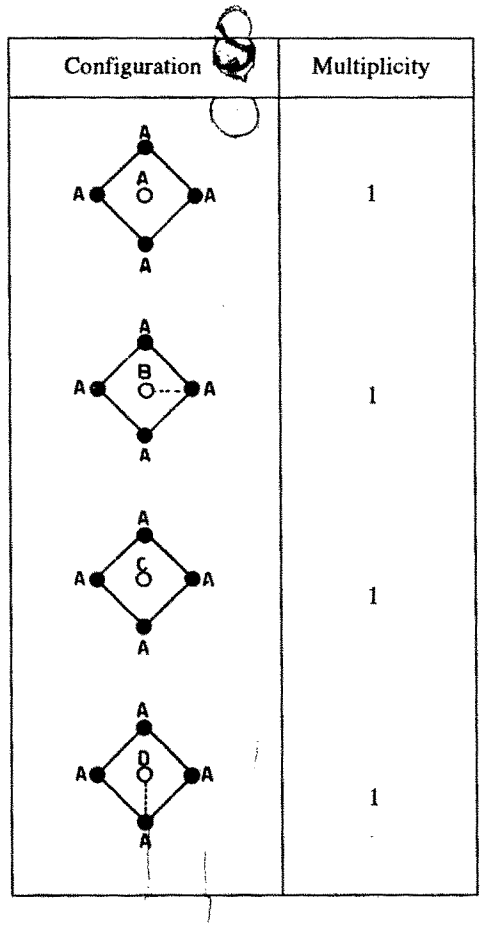


Figure 3. Configurations and multiplicities for the basic units with Z_4 configuration. The broken line that connects two units represents an infinite repulsion between these units, due to the aluminum avoidance rule.

configurations (due to the aluminum avoidance rule) with two units which are located on the solid sites. For instance, an *A* unit on the nonsolid site of a basic unit is not allowed if either the solid site on its top is occupied by a *D* unit or if the solid site on its left-hand side is occupied by a *B* unit (see the first row in Figure 4). Each of these disallowed cases has $4 \times 4 \times 4 \times 1 = 64$ configurations; where 1 is for the specific unit that makes disallowed configurations with the unit on the nonsolid site, and 4 is for the remaining solid sites that may be occupied by any unit (*A*, *B*, *C* or *D*). Therefore, it seems that each unit on the nonsolid site of a basic unit results in $2 \times 64 = 128$ disallowed configurations. However, these two groups of configurations have 16 configurations in common. Then, each unit on the nonsolid site of a basic unit gives a total number of 128 - 16 = 112 disallowed configurations. Therefore, the total number of disallowed configurations, must be equal to $4 \times 112 = 448$. There is a 2, 22, 94, 186, and 144 disallowed configurations, which are given in Figures 3, 4, 5, 6, and 7, respectively. These numbers sum up to a total of 448 disallowed configurations. There is a total of $4^5 = 1024$ configurations for a basic unit, including the configurations for its nonsolid site, of which 1024 - 448 = 576 are allowed. This number is the same as the total number of allowed configurations given in Figures 3 through 7.

Calculation of Configurational Entropy

In **IBU**, we have to specify the independent basic units of the lattice. For our square lattice model, they are shown in Figure 8 as a set of connected lines. As shown in this figure, these basic units have their own sites, which are not shared with any other independent basic units. There is a total of N/8 such basic units. Since these basic units are not really different from N/2-N/8 of the remaining basic units of the lattice, we shall devote 25 percent of basic units with each configuration to the independent basic units. The number of distributions on solid sites , $g(S)$, is actually equal to the number of ways to distribute 25 percent of basic units among the independent basic units, owing to the fact that these basic units include all solid sites. Since such basic units do not share any of their solid sites, $g(S)$ is simply given by:

$$g(S) = \frac{(N/8)!}{\Pi_i [(Q_i N/8)!]^{\lambda_i}} \qquad (1)$$

where the values for λ_i are given in Figure 2. There is one exception, due to the aluminum avoidance rule, that is $\lambda_1 = 106$ (not 108) which will be discussed.

In **IBU**, the general approach for calculating the number of ways for the distribution of units on the nonsolid sites, $g(N)$, is to calculate the distribution on each specific type of nonsolid site separately, exactly in the same way as in the Extended Sequential Construction Method (ESCM) approach given by Parsafar ([9]). The product of these individual terms gives $g(N)$. In order to use the **IBU** approach for this specific case, the number of distributions on those nonsolid sites belonging to Z_0, Z_1, Z_2, Z_3, and Z_4 is calculated with $g(N) = g_0 g_1 g_2 g_3 g_4$, where g_i is the number of distributions on the nonsolid sites belonging to the basic units with Z_i configuration.

We start with the Z_0 configuration. There are 81 $Q_0 N/2$ of basic units with Z_0 configuration (see Figure 2) and the same number of nonsolid sites belonging to Z_0. The fact that all of these nonsolid sites are not available for occupation by all units is taken into account when the number of ways for the distribution of the units among this type of nonsolid site, g_0, is

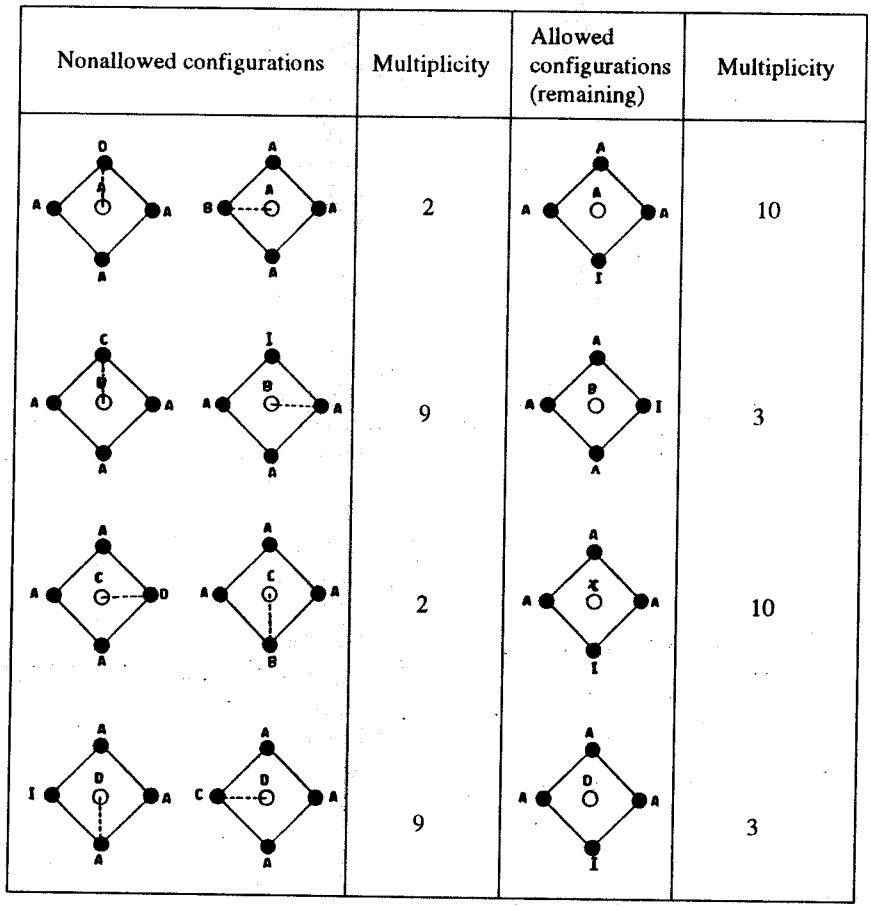


Figure 4. Allowed and disallowed configurations and the multiplicities for the basic unit with Z_3 configuration. The broken lines have the same meaning as in the previous figure caption ($I = B, C, D$).

calculated. For example, of the 81 $Q_0N/2$ such nonsolid sites, only 36 $Q_0N/2$ are available for A units (Figure 7). The available nonsolid sites of this type are 54 $Q_0N/2$, 36 $Q_0N/2$, and 54 $Q_0N/2$ for B, C and D units, respectively (see Figure 7). The fact that not all such nonsolid sites are available for the units is the major difficulty for the calculation of g_0, and of course is due to the aluminum avoidance rule. It is precisely because of this fact that the combinatorial factor g_0 cannot be simply expressed as a multinomial coefficient.

As shown in Figure 7, there are 36+54+36+54 = 180 allowed configurations for Z_0. These configurations may be classified by the units allowed on their nonsolid sites (Table I). The general configuration of the basic unit is denoted by "*KLMN*" in the second column of Table I, excluding the configuration of the unit located on the nonsolid site, where K, L, M, and N represent the unit located on the top, right side, bottom, and left side of the nonsolid site, respectively. The numbers of such configurations, λ_{0j}, are given in the third column. The units which are allowed on the nonsolid sites of these configurations are given in the last column. For example, as shown in Table I, there are four configurations in the first row (*BBCD*, *BBDD*, *BCCD*, *BCDD*) for which the nonsolid sites may be occupied by A, B, C or D units. Similarly, in each of the other rows of this table different configurations for Z_0 are specified, for which the allowed units on their nonsolid sites are given in column 4. The number of allowed configurations is denoted by λ_{ij} where i is the same subscript used for Z_i and Q_i (for this case i = 0), and j simply shows the row in Table I. The sum of the allowed configurations must be equal to 180:

$$\sum_{j=0}^{15} n_{0j}\lambda_{0j} = 180 \qquad (2)$$

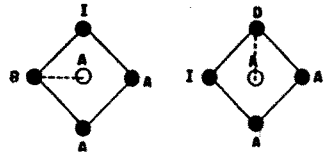
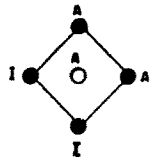
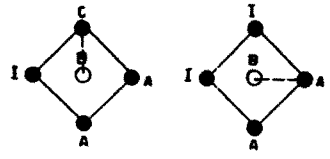
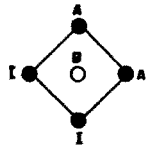
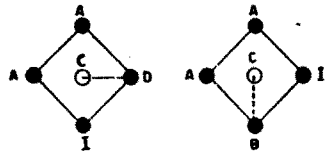
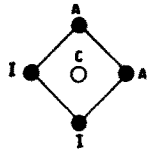
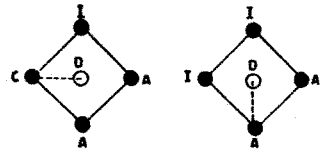
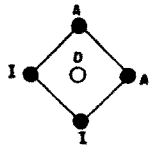
Nonallowed configurations	Multiplicity	Allowed configurations (remaining)	Multiplicity
	17		37
	30		24
	17		37
	30		24

Figure 5. Allowed and disallowed configurations and the multiplicities for the basic unit with Z_2 configuration ($I = B, C, D$)

where n_{oj} is the number of allowed units on the nonsolid site of each basic unit with special configurations given in row j of this table, for instance, $n_{01} = 4$, $n_{02} = n_{03} = n_{04} = n_{05} = 3$. The constraint (2) is consistent with Table I, because

$$4(4) + 3(4 + 5 + 4 + 12) + 2(5 + 4 + 5 + 4 + 15 + 4) + 1(5 + 5 + 0 + 5) = 180$$

The nonsolid sites belonging to Z_0 are then divided into 14 different groups, based on the units which are allowed to be located on the nonsolid site. There are 81 $Q_0N/2$ nonsolid sites belonging to the Z_0 configuration, of which $4Q_0N/2$ are available for A, B, C and D units (see the first row in Table I). Suppose that the probability of such nonsolid sites being occupied by A, B, C or D units is denoted by A_{01}, B_{01}, C_{01} and D_{01}, respectively. There are then $4Q_0A_{01}N/2$ of A, $4Q_0B_{01}N/2$ of B, $4Q_0C_{01}N/2$ of C and $4Q_0D_{01}N/2$ of D units which must be distributed on $4Q_0N/2$ of such nonsolid sites. The number of ways for such a distribution is given by g_{01}, where

$$g_{01} = \frac{(4Q_0N/2)!}{(4Q_0A_{01}N/2)!(4Q_0B_{01}N/2)!(4Q_0C_{01}N/2)!(4Q_0D_{01}N/2)!} \quad (3)$$

There are $4Q_0N/2$ nonsolid sites belonging to Z_0 that can be occupied by A, B, and C units (see j = 2 in Table I). Suppose that the probability of these sites being occupied by A, B, or C is denoted by A_{02}, B_{02}, and C_{02}, respectively, then the number of ways to distribute the units among these nonsolid sites, g_{02}, is given by

$$g_{02} = \frac{(4Q_0N/2)!}{(4Q_0A_{02}N/2)!(4Q_0B_{02}N/2)!(4Q_0C_{02}N/2)!} \quad (4)$$

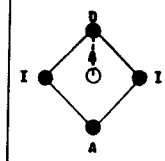
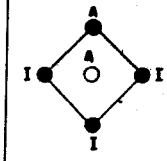
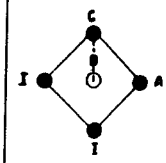
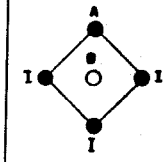
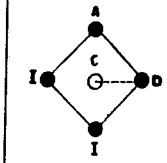
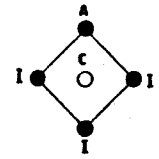
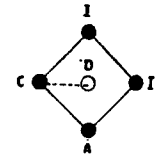
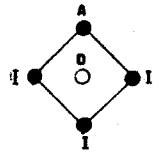
Nonallowed configuration	Multiplicity	Allowed configurations (remaining)	Multiplicity
	48		60
	45		63
	48		60
	45		63

Figure 6. Allowed and disallowed configurations and the multiplicities for the basic unit with Z_1 configuration ($I = B, C, D$)

Similarly, the number of ways to distribute the allowed units on the nonsolid sites of basic units with special configurations, given in each row of Table I, is calculated. In general, the number of ways for the distribution of allowed units on the nonsolid sites of the allowed basic units given in the row j of Table I, g_{0j}, is given by

$$g_{0j}=\frac{(\lambda_{0j}Q_0N/2)!}{\Pi_m\,(\lambda_{0j}m_{0j}Q_0N/2)!} \qquad (5)$$

where each m_{0j} is the probability of such special nonsolid sites being occupied by one of the special allowed units. For the cases that only one type of unit is allowed to be located on special nonsolid sites, there is only one way to do such a distribution:

$$g_{0\,12} = g_{0\,13} = g_{0\,15} = 1$$

The number of ways for the distribution of units among all nonsolid sites belonging to the basic units with Z_0 configuration, is given by g_0, where

$$g_0=\Pi_j g_{0j}=\Pi_j\frac{(\lambda_{0j}Q_0N/2)!}{\Pi_m(\lambda_{0j}m_{0j}Q_0N/2)!} \qquad (6)$$

Now we can calculate the number of ways for the distribution of units among the nonsolid sites belonging to Z_1. We have to classify these nonsolid sites into special groups, in such a way that each of the special nonsolid sites is allowed to be occupied by special units. This classification is shown in Table II, in exactly the same manner as that for Z_0 in the previous table. Note that each j (or row) in this table corresponds to the same j in the previous table, meaning that the same j represents the same allowed units in both tables. For instance, j = 7 represents the special configurations with their nonsolid sites

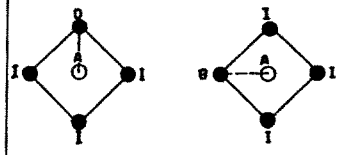
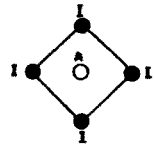
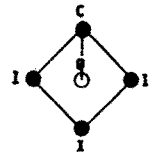
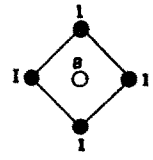
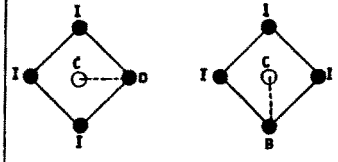
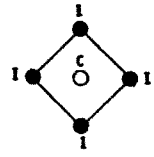
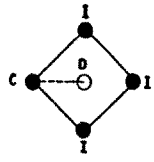
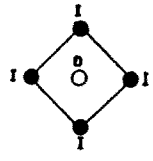
Nonallowed configurations	Multiplicity	Allowed configurations (remaining)	Multiplicity
	45		36
	27		54
	45		36
	27		54

Figure 7. Allowed and disallowed configurations and the multiplicities for the basic unit with Z_0 configuration

available for *A* and *C* units in both tables. This correspondence is followed for the other tables as well. Also note that there is one more row in this table, j = 16. This row represents two configurations whose nonsolid sites are not available for *A*, *B*, *C* or *D* units. It means that the number of basic units with Z_1 configuration is actually equal to $106Q_1N/2$. This is due to the fact that $2Q_1N/2$ of the nonsolid sites belonging to such basic units (specifically those with *DABC* and *CDAB* configurations) cannot be occupied by any unit, because of the aluminum avoidance rule.

The number of distributions on all nonsolid sites belonging to basic units with Z_i configuration, g_i, may be calculated following similar arguments that led to g_0. The result is:

$$g_i = \Pi_j \frac{(\lambda_{ij} Q_i N/2)!}{\Pi_m (\lambda_{ij} m_{ij} Q_i N/2)!} \qquad (7)$$

where i = 1,2,3, and 4. The classifications of nonsolid sites belonging to the basic units with Z_1, Z_2, Z_3, and Z_4 configurations are given in Tables II, III, IV, and V, respectively.

The total number of distributions among the nonsolid sites is then equal to $g(N)$, where

$$g(N) = g_0 g_1 g_2 g_3 g_4 \qquad (8)$$

and the total number of distributions in the model lattice is

$$g = (g_0 g_1 g_2 g_3 g_4)\, g(S)$$

or

$$g = \{\Pi_{i=0}^{4} \Pi_j \frac{(\lambda_{ij} Q_i N/2)!}{\Pi_m (\lambda_{ij} m_{ij} Q_i N/2)!}\} \frac{(N/8)!}{\Pi_i [(Q_i N/8)!]^{\lambda_i}} \qquad (9)$$

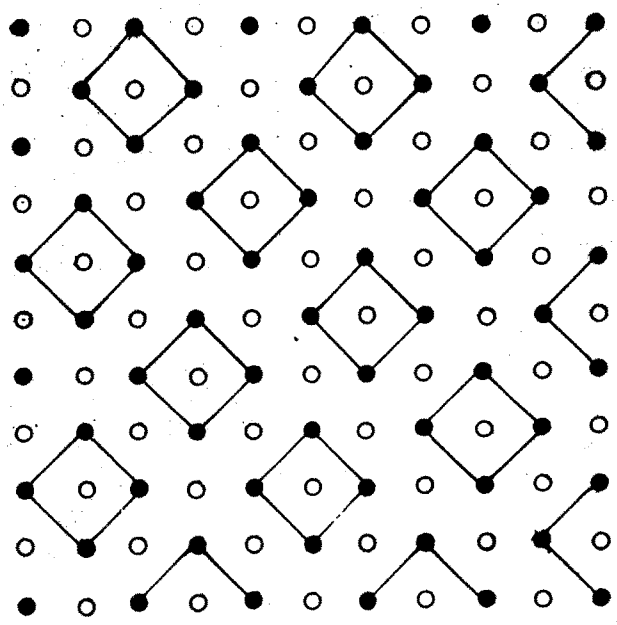


Figure 8. Illustration of the independent basic units of the model. Independent basic units are shown by connected lines. These basic units include all solid sites.

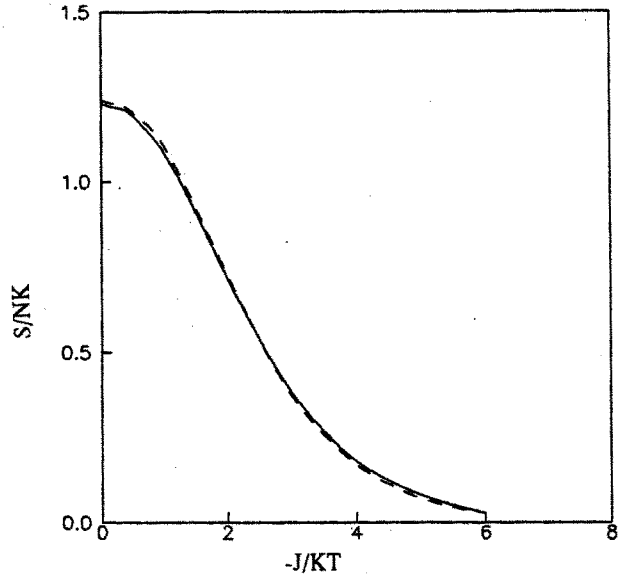


Figure 9. Reduced configurational entropy of the one-dimensional model of albite given by **IBU** (dash curve) and the transfer-matrix method (solid curve) versus the reduced site preference energy, *J/kT*

By knowing the combinatorial factor, g, the configurational entropy can be readily calculated, by using the Boltzman factor, $S = k \ln g$.

Order Parameter and Constraints

The order parameter of Al, Si ordering in Na-feldspar is defined as Q_{od} (Salje [10]). We express this order parameter in terms of the Q_s and the $m_{ij}s$. Suppose that the probability of having aluminum atoms on the "a" sites is equal to p. The number of A units on all solid and nonsolid sites must then be equal to p N. The number of A units located on solid sites, $N_A(S)$, can be calculated by referring to Figure 2. It is given by

$$N_A(S)=\frac{1}{4}\sum_{i=0}^{4} i\lambda_i Q_i \frac{N}{2} \qquad (10)$$

where the factor $\frac{1}{4}$ is to avoid overcounting (each solid site belongs to four basic units). Note that $\lambda_1 = 106$, not 108 as given in Figure 2. This is due to the fact that two states with Z_1 configuration are not allowed (see Table II).

The number of A units on nonsolid sites is calculated in terms of A_{ij}s and Q_i by referring to Tables I to V. Since $(\lambda_{ij}\, Q_i\, A_{ij})$ (N/2) is the number of A units on the nonsolid sites of basic units with Z_i configuration given in row j of the tables, the number of A units on the nonsolid sites, $N_A(N)$, is

$$N_A(N)=(N/2)\left(\sum_{i=0}^{4}\sum_{j}\lambda_{ij}Q_iA_{ij}\right) \qquad (11)$$

where the first summation is taken over all tables (i = 0, 1, 2, 3, 4), and the second summation is taken over those rows (j) of these tables, in which their nonsolid sites are available for A units.

The order parameter is given by:

$$Q_{od}=\frac{4\left(\frac{N_A(S)+N_A(N)}{N}\right)-1}{2\left(\frac{N_A(S)+N_A(N)}{N}\right)+1} \qquad (12)$$

or, by using Eqs. 10 and 11

$$Q_{od}=\frac{4p-1}{2p+1} \qquad (13)$$

where

$$p=\frac{1}{8}\sum_{i=0}^{4} i\lambda_i Q_i+\frac{1}{2}\sum_{i}\sum_{j}\lambda_{ij}Q_iA_{ij} \qquad (14)$$

Table I. Classification of basic units with Z_0 configuration, based on the allowed units on their nonsolid sites

j	Allowed configurations	λ_{0j}	Allowed units on nonsolid site
1	*BBCD, BBDD, BCCD, BCDD*	4	*A, B, C, D*
2	*BBCC, BBDC, BCCC, BCDC*	4	*A, B, C*
3	*BBBD, BCBD, BDBD, BDCD, BDDD*	5	*A, B, D*
4	*CBCD, CBDD, CCCD, CCDD*	4	*A, C, D*
5	*BBCB, BBDB, BCCB, BCDB, DBCB, DBCD, DBDB, DBDD DCCB, DCCD, DCDB, DCDD*	12	*B, C, D*
6	*BBBC, BCBC, BDBC, BDCC, BDDC*	5	*A, B*
7	*CBCC, CBDC, CCCC, CCDC*	4	*A, C*
8	*CBBD, CCBD, CDBD, CDCD, CDDD*	5	*A, D*
9	*DBCC, DBDC, DCCC, DCDC*	4	*B, C*
10	*BBBB, BCBB, BDBB, BDCB, BDDB DBBB, DBBD, DCBB, DCBD, DDBB DDBD, DDCB, DDCD, DDDB, DDDD*	15	*B, D*
11	*CBCB, CBDB, CCCB, CCDB*	4	*C, D*
12	*CBBC, CCBC, CDBC, CDCC, CDDC*	5	*A*
13	*DBBC, DCBC, DDBC, DDCC, DDDC*	5	*B*
14		0	*C*
15	*CBBB, CCBB, CDBB, CDCB, CDDB*	5	*D*

The first constraint can be obtained based on the fact that the total number of basic units in the lattice must be equal to N/2. Since there are Q_4 N/2, $12Q_3$ N/2, $54Q_2$ N/2, $106Q_1$ N/2 and $81Q_0$ N/2 basic units with Z_4, Z_3, Z_2, Z_1 and Z_0 configuration, respectively

$$Q_4+12Q_3+54Q_2+106Q_1+81Q_0=1 \qquad (15)$$

The remaining constraints are due to the fact that the probabilities of each type of nonsolid site being occupied by all allowed units must add up to one. For instance, for those nonsolid sites belonging to Z_0 which are available for *A*, *B*, *C* and *D* units (see j = 1 in Table I), we have

$$A_{01}+B_{01}+C_{01}+D_{01}=1 \qquad (16)$$

where A_{01}, B_{01}, C_{01} and D_{01} are the probabilities that these special nonsolid sites ($j = 1$) belonging to Z_0 ($i = 0$) are occupied by *A*, *B*, *C* and *D* units, respectively. In general, such normalization relationships may be written as

$$\sum_m m_{ij}=1 \qquad (17)$$

where each specific pair of i and j represents one specific row in Tables I to V. Therefore, this constraint must hold for each row in these tables, in

Table II. Classification of basic units with Z_1 configuration, based on the allowed units on their nonsolid sites

j	Allowed configurations	λ_{1j}	Allowed units on nonsolid site
1	*ABCD, ABDD, ACCD, ACDD, BBCA, BBDA, BCCA, BCDA*	8	*A, B, C, D*
2	*ABCC, ABDC, ACCC, ACDC, BBAC, BBAD, BCAC, BCAD*	8	*A, B, C*
3	*ABBD, ACBD, ADBD, ADCD, ADDD, BBBA, BCBA, BDBA, BDCA, BDDA*	10	*A, B, D*
4	*BACD, BADD, CACD, CADD, CBCA, CBDA, CCCA, CCDA*	8	*A, C, D*
5	*ABCB, ABDB, ACCB, ACDB DBCA, DBDA, DCCA, DCDA*	8	*B, C, D*
6	*ABBC, ACBC, ADBC, ADCC ADDC, BDAC, BDAD*	7	*A, B*
7	*BACC, BADC, CACC, CADC, CBAC, CBAD, CCAC, CCAD*	8	*A, C*
8	*BABD, CABD, CBBA, CCBA, CDBA, CDCA, CDDA*	7	*A, D*
9	*BBAB, BCAB, DBAB, DBAC, DBAD, DCAB, DCAC, DCAD*	8	*B, C*
10	*ABBB, ACBB, ADBB, ADCB, ADDB, DBBA, DCBA, DDBA, DDCA, DDDA*	10	*B, D*
11	*BACB, BADB, CACB, CADB, DACB, DACD, DADB, DADD*	8	*C, D*
12	*BABC, CABC, CDAC, CDAD*	4	*A*
13	*BDAB, DDAB, DDAC, DDAD*	4	*B*
14	*CBAB, CCAB, DACC, DADC*	4	*C*
15	*BABB, CABB, DABB, DABD*	4	*D*
16	*DABC, CDAB*	2	–

Table III. Classification of basic units with Z_2 configuration, based on the allowed units on their nonsolid sites

j	Allowed configurations	λ_{2j}	Allowed units on nonsolid site
1	*ABCA, ABDA, ACCA, ACDA*	4	*A, B, C, D*
2	*ABAC, ABAD, ACAC, ACAD, BBAA, BCAA*	6	*A, B, C*
3	*ABBA, ACBA, ADBA, ADCA, ADDA*	5	*A, B, D*
4	*AACD, AADD, BACA, BADA, CACA, CADA*	6	*A, C, D*
5		0	*B, C, D*
6	*ADAC, ADAD, BDAA*	3	*A, B*
7	*AACC, AADC, BAAC, BAAD, CAAC, CAAD, CBAA, CCAA*	8	*A, C*
8	*AABD, BABA, CABA*	3	*A, D*
9	*ABAB, ACAB, BDAA, DCAA*	4	*B, C*
10		0	*B, D*
11	*AACB, AADB, DACA, DADA*	4	*C, D*
12	*AABC, CDAA*	2	*A*
13	*ADAB, DDAA*	2	*B*
14	*BAAB, CAAB, DAAB, DAAC, DAAD*	5	*C*
15	*AABB, DABA*	2	*D*

which the nonsolid sites can be occupied by more than one unit. Specifically, there are 11, 11, 9, 5 and 1 of such normalization requirements for the nonsolid sites belonging to Z_0, Z_1, Z_2, Z_3 and Z_4 configuration, respectively.

Results and Discussion

In the **IBU** approach we have actually assumed that the distribution of N/8 independent basic units of type Z_0, Z_1, Z_2, Z_3, Z_4 on the solid sites gives 3N/8 dependent basic units with the same probability for each type of basic unit. In other words, we have assumed that Q_4 is the probability that any basic unit of the lattice will be in the state of Z_4, with similar assumptions for other states of basic units. In order to investigate the effect of these assumptions on the configurational entropy, we applied the **IBU** on the one-dimensional model of albite. The model is simply a row of squares, in which every other square has a sodium atom at its center. Subject to the aluminum avoidance rule and local charge neutrality, the model can be solved exactly by the transfer-matrix method [11]. For the one-dimensional model, the appropriate transfer-matrix is a 4×4 matrix, whose maximum eigenvalue λ_0 is given by

$$\lambda_0=\frac{x+3+\sqrt{x^2+2x+5}}{2}$$

Table IV. Classification of basic units with Z_3 configuration, based on the allowed units on their nonsolid sites. Each j represents the same j in all tables

j	Allowed configurations	λ_{3j}	Allowed units on nonsolid site
2	*ABAA, ACAA*	2	*A, B, C*
4	*AACA, AADA*	2	*A, C, D*
6	*ADAA*	1	*A, B*
7	*AAAC, AAAD, BAAA, CAAA*	4	*A, C*
8	*AABA*	1	*A, D*
14	*AAAB, DAAA*	2	*C*

Table V. Basic unit with Z_4 configuration which belongs to j = 7 (its nonsolid site is available for *A* and *C* units only)

j	Allowed configurations	λ_{4j}	Allowed units on nonsolid site
7	*AAAA*	1	*A, C*

where $x = exp\ (-J/kT)$ and J is the site preference energy. The partition function λ_0 can be used to calculate the thermodynamic properties of the model exactly. It is also a straightforward procedure to apply **IBU** to the one-dimensional model of albite, in order to obtain an expression for the free energy which has to be minimized subject to appropriate constraints to obtain the equilibrium properties. We found that the free energy given by **IBU** has a deviation of less than 0.8%. The calculated configurational entropy given by **IBU** is compared with the exact value in Figure 9. We may conclude from these results that the assumptions used in **IBU** have a minor effect on thermodynamic properties of the model lattice, and in fact **IBU** may be considered to be an accurate approach for the calculation of thermodynamic properties of the lattice models of albite.

The equilibrium configurational entropy in the high-temperature limit can now be calculated. At high temperatures, the sites are occupied by Al and Si atoms with equal probabilities ($Q_{od} = 0$). In this case, the equilibrium state is expected to be that in which all possible configurations have equal probabilities. Thus:

$$\mathbf{A}_{i1}=\mathbf{B}_{i1}=\mathbf{C}_{i1}=\mathbf{D}_{i1}=\frac{1}{4}(\mathrm{i}=0,1,2)$$

$$\mathbf{A}_{i2}=\mathbf{B}_{i2}=\mathbf{C}_{i2}=\frac{1}{3}(\mathrm{i}=0,1,2,3)$$

$$A_{i3}=B_{i3}=D_{i3}=\frac{1}{3}(\mathrm{i}=0,1,2)$$

$$A_{i4}=C_{i4}=D_{i4}=\frac{1}{3}(\mathrm{i}=0,1,2,3)$$

$$B_{i5}=C_{i5}=D_{i5}=\frac{1}{3}(\mathrm{i}=0,1)$$

$$A_{i6}=B_{i6}=\frac{1}{2}(\mathrm{i}=0,1,2,3)$$

$$A_{i7}=C_{i7}=\frac{1}{2}(\mathrm{i}=0,1,2,3,4)$$

$$A_{i8}=D_{i8}=\frac{1}{2}(\mathrm{i}=0,1,2,3)$$

$$B_{i9}=C_{i9}=\frac{1}{2}(\mathrm{i}=0,1,2)$$

$$B_{i10}=D_{i10}=\frac{1}{2}(\mathrm{i}=0,1)$$

$$C_{i11}=D_{i11}=\frac{1}{2}(\mathrm{i}=0,1,2)$$

If we minimize the free energy subject to constraint 15, and use the values given above for m_{ij}, for $T \to \infty$ we get,

$$\frac{S}{Nk} = 1.065$$

It is interesting to compare this result with the values of 1.12 from the quasi-chemical method given by Andersen and Mazo [2], 1.043 from the **SCM** approach [12], 1.007 from the **IPS** method [4], and 1.032 from the **MSCM** approach [5], which are calculated and reported for the reduced configurational entropy of a two-dimensional model of albite at high-temperature limit. Actually, the last three numbers are not for the high-temperature limit, that is $J/kT = 0$, but for $J/kT = -1/3$, so that the values of entropy given by these methods must be higher than these values (but insignificantly). The reason is that at such a high temperature the entropy almost does not change with J/kT; see the appropriate figures in the above-mentioned references. Therefore, even at the high-temperature limit the values given by different approximate calculations for the configurational entropy are different from the accurate value of 1.065 given by our approach. However, such differences are less than six percent. If there were no aluminum avoidance rule, these methods would all give $S/Nk = \ln(4) = 1.386$, because solid and nonsolid sites would be available for all units (A, B, C, D) with equal probabilities. The differences in entropy at the high-temperature limit are due to the aluminum avoidance rule only. However, at intermediate temperatures, where the order-disorder transition occurs, such differences are expected to be more significant.

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