

Importance of the size of the unit in models of ordering behavior for albite

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ABSTRACT

The method of independent pairs and sites (IPS) is used to study the ordering behavior of the feldspar mineral albite. Unlike recent models, in which local charge neutrality was not introduced, here it is imposed by using Andersen's two-dimensional model of albite. Even though the same approximation (IPS method) has been used in both Andersen's model and the present treatment, the final results for the ordering behavior are quite different, in the sense that a metastable (solid) phase is predicted at some temperatures in the former, and no such behavior is predicted in the latter. One should therefore expect that the size of the local structural unit used to impose electroneutrality can be very important in model calculations on albite.

INTRODUCTION

Feldspar minerals display some interesting ordering phenomena and have been extensively studied. Their structure is a framework of TO_4 units linked together at their vertices to make double-crankshaft chains in a three-dimensional network. Each oxygen is located at the corner of a tetrahedron, and the T atoms (Al or Si) are at the center of tetrahedra. The double crankshaft consists of 4-membered rings, which are alternately parallel to each other; the rings make an angle of about 70° to the chain. The structure can, alternatively, be described as a series of sheets composed of 4- and 8-membered rings, in which each site is shared by two 8-membered and one 4-membered ring.

The occupation of T sites by Al and Si atoms appears to follow rigorously the empirical Al avoidance principle at all temperatures below the melting point. This principle states that certain distributions of Al and Si on T sites are not acceptable. Specifically, no two tetrahedra sharing a corner oxygen can both contain Al. In addition, the T sites are not all energetically equivalent. There are four sites that are crystallographically distinct and that usually are referred to as $T_1(\text{O})$, $T_2(\text{O})$, $T_1(\text{m})$, $T_2(\text{m})$. Experimentally it is found that at low temperatures, Al atoms preferentially occupy $T_1(\text{O})$ sites. As temperature increases, Al atoms migrate to other sites, and the distribution of Al atoms on all sites becomes more uniform. Unlike most other order-disorder phenomena, which are governed by the interaction of atoms on various sites, present models indicate that in feldspar the site energy is more important than interaction energies (Mazo, 1977). The site $T_1(\text{O})$ is a special site, which we call an *a* site. Since the other three types are rather similar to each other with regard to their occupancy by Al, we shall call them *b* sites. Each *a* site has four *b* neighboring sites. Each *b* site has, on the average, $(4/3)a$ and $(8/3)b$ neighbors.

For more details regarding the structure of feldspar minerals, the reader is referred to Smith (1974) and Mackenzie and Zussman (1974).

CALCULATION OF THE ENTROPY AND ORDER PARAMETER

As pointed out by Andersen and Mazo (1979), in order to avoid charge segregation in the lattice of feldspar minerals, local charge neutrality has to be taken into account. It is not clear how big the smallest part of the lattice that is neutral should be, however. One might even conjecture that the size of the appropriate unit changes with temperature, becoming larger as temperature increases.

A simple two-dimensional model of albite exhibiting local charge neutrality (temperature independent) has been introduced by Andersen and Mazo (1979). This is shown in Figure 1, where crosses are secondary sites, showing the positions of alkali metal atoms, and the corners of squares are T sites representing the position of Al or Si. The T sites are referred to as primary sites. Mazo and Andersen (1979) suggested that, in order to impose the local charge neutrality condition onto this model, each square with Na at its center must have three Si and one Al on its corners. From now on these squares will be referred to as "units" of the model.

We want to calculate the probability of occupation of *a* sites by *A* (Al) atoms as a function of temperature and site-preference energy, this probability of occupation being an order parameter. In the IPS method, the lattice is considered to be composed of (independent) pairs and "sites," in such a way that each independent site is surrounded only by pairs and vice versa (see Fig. 2). Independent sites are considered those sites that have no interaction with each other, and independent pairs are composed of the remaining sites that interact only with their adjacent independent sites. The sites, however, need not be just lat-

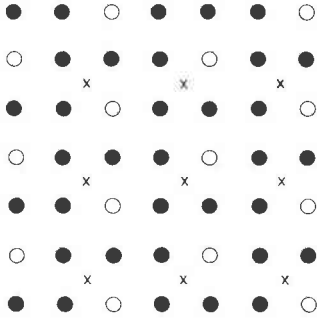


Fig. 1. Andersen and Mazo's (1979) two-dimensional model of albite, where empty and solid circles are a and b sites, respectively, and X's are Na atoms.

tice points. We are free to choose the sites as large as necessary. Since we are interested in this paper in applying the local charge neutrality condition in our calculation, it is an appropriate choice to take a unit as an independent site. So, if N is the number of Na atoms, there are $N/2$ independent sites and $N/4$ independent pairs.

Now, let p be the probability of an a site being occupied by an Al atom in albite. Since one quarter of the atoms are A , the probability of a b site being occupied by an A atom, P_A^b , is given by,

$$P_A^b = \frac{1-p}{3}.$$

The site-preference energy (energy of A atom on a site with all other site energies taken as zero) is E_A^a , and all interaction energies are taken to be zero, except for A - A nearest-neighbor pairs (which are not allowed in the model and whose energies are therefore infinite). The primary sites of an independent pair are numbered in clockwise sequence, as shown in Figure 3.

If P_{ij} denotes the probability that site i of the square on the left and site j of the square on the right of an independent pair are occupied both by A atoms, we have the following equations:

$$P_{11} = P_1 \quad (1)$$

$$P_{12} = P_{13} = P_{14} = P_{21} = P_{31} = P_{41} = P_2 \quad (2)$$

$$P_{22} = P_{23} = P_{24} = P_{32} = P_{33} \quad (3)$$

$$= P_{34} = P_{42} = P_{43} = P_{44} = P_3.$$

For simplicity the terminology is reduced to P_1 , P_2 , and P_3 as defined by these equations. The equalities are from the equal probability of distributions with the same number of A atoms on a sites of an independent pair.

On the one hand, $2(N/4) = N/2$ units are involved in the independent pairs, and the a site of each unit is occupied by an A atom with probability p . Thus the number of A atoms on a sites of independent pairs is $(N/2)p$. On the other hand, there are $P_1(N/4)$ independent pairs with two A atoms on their two a sites, and $6P_2(N/4)$ independent pairs with one A atom on one of their a sites. That gives $[2 \times P_1(N/4) + 1 \times 6P_2(N/4)]$ A atoms on all a sites

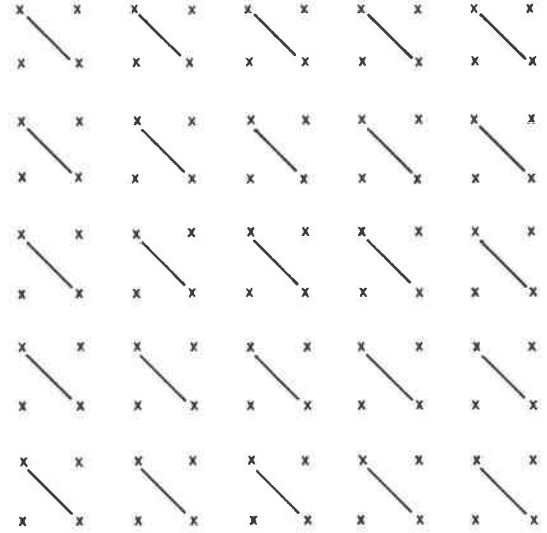


Fig. 2. The representation of two-dimensional model of albite by independent pairs and sites. An X represents a unit. Independent sites are shown by X's and independent pairs by lines.

of the independent pairs. Therefore, we have the following consistency equation:

$$(N/2)p = (P_1 + 3P_2)(N/2)$$

or

$$p = P_1 + 3P_2. \quad (4)$$

Also, the normalization condition gives

$$\sum_i \sum_j P_{ij} = 1$$

or

$$P_1 + 6P_2 + 9P_3 = 1. \quad (5)$$

For simplicity, let us write $P_1 = x$ and solve the above equations for P_2 and P_3 . This gives rise to

$$P_1 = x$$

$$P_2 = (1/3)(p - x)$$

$$P_3 = (1/9)(1 + x - 2p).$$

The number of ways of distributing atoms among independent pairs are

$g(\text{pair})$

$$= \frac{\left(\frac{N}{4}\right)!}{\left[x\left(\frac{N}{4}\right)!\left\{\left[\left(\frac{p-x}{3}\right)\left(\frac{N}{4}\right)!\right]^6\left\{\left[\left(\frac{1+x-2p}{9}\right)\left(\frac{N}{4}\right)!\right]^9\right\}\right]} \quad (6)$$

Now, it is necessary to find the number of ways of distributing the atoms on the independent sites. To do so,

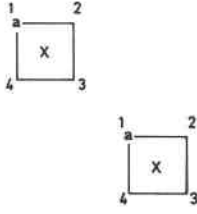


Fig. 3. The representation of an independent pair; each site is specified by a number.

we notice that in order to impose the AI avoidance principle, some primary sites of the independent sites are not available for A occupation. For example, consider the sublattice with five units in Figure 4. The middle unit is considered to be an independent site, and others belong to four different independent pairs (half of each pair is not shown). Let us first consider the distribution of $(N/2)p$ A atoms on the available a sites of the independent sites. Since the a site of each independent site is next to two b sites of pairs, each of which is occupied by an A atom with probability $(1-p)/3$, the probability of availability of an a site of each independent site for A occupation is

$$1 - 2[(1-p)/3] = [(1+2p)/3].$$

Therefore, $[(1+2p)/3](N/2)$ a sites of the independent sites are available for A occupation. Then, we have $(N/2)p$ A atoms that have to be distributed among $[(1+2p)/3](N/2)$ available a sites of independent sites. There are $g(a)$ ways for such distributions,

$$g(a) = \frac{\left[\left(\frac{1+2p}{3}\right)\left(\frac{N}{2}\right)\right]!}{\left[\left(\frac{N}{2}\right)^p\right]! \left[\left(\frac{1-p}{3}\right)\left(\frac{N}{2}\right)\right]!}. \quad (7)$$

Now, $(N/2)(1-p)$ independent sites are left with no A atoms on their a sites. We have to set only one A atom on one b site of each of them. The probability of availability of each b site of independent pairs (for A occupation) is (see Fig. 4) $1 - [p + (1-p)/3]$ (for site 3), $1 - [(1-p)/3 + (1-p)/3]$ (for site 2), $1 - [p + (1-p)/3]$ (for site 4), and $(5-2p)/3$ (for sites 2, 3, and 4). So,

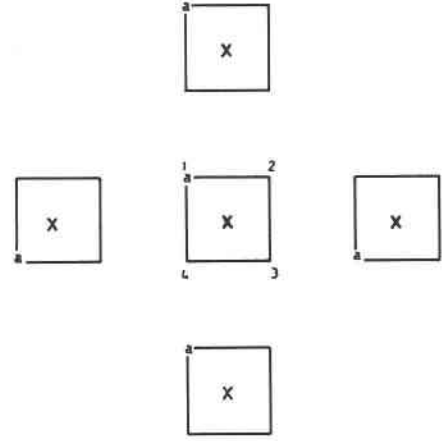


Fig. 4. A sublattice with five units.

on the average, each remaining independent site has $(5-2p)/3$ b sites for occupation by one A atom. Therefore, the number of ways for distribution of A atoms on the b sites of independent pairs (with restrictions of local charge neutrality and the AI avoidance principle) is

$$g(b) = [(5-2p)/3]^{(N/2)(1-p)}. \quad (8)$$

The total combinatorial factor, g , is given by

$$g = g(\text{pairs})g(a)g(b)$$

or

$$g = \frac{\left(\frac{N}{4}\right)!}{\left(x\frac{N}{4}\right)! \left[\left(\frac{p-x}{3}\right)\frac{N}{4}\right]! \left[\left(\frac{1+x-2p}{9}\right)\left(\frac{N}{4}\right)\right]!} \times \frac{\left[\left(\frac{1+2p}{3}\right)\left(\frac{N}{2}\right)\right]!}{\left(\frac{N}{2}\right)^p \left[\left(\frac{1-p}{3}\right)\left(\frac{N}{2}\right)\right]!} \times [(5-2p)/3]^{(N/2)(1-p)}.$$

For the entropy, S , we have

$$S = k \ln g$$

Table 1. The calculated configurational entropy and order parameter of model albite

U	$4/U$	$S_{MC/R}$	P_{MC}	$S_{IPS/R}$	P_{IPS}
4	1	0.098	0.98	—	—
2	2	0.510	0.824	0.378	0.86
1	4	0.923	0.543	0.842	0.54
2/3	6	1.014	0.435	0.951	0.41
1/2	8	1.048	0.385	0.986	0.35
0.4	10	1.057	0.355	0.999	0.32
1/3	12	1.065	0.334	1.007	0.30

Note: Values calculated by Monte-Carlo ($S_{MC/R}$, P_{MC}) and IPS ($S_{IPS/R}$, P_{IPS}) methods. The Monte Carlo results are from Rajabali (1981).

Table 2. The exact configurational entropy of a one-dimensional model of albite (S_E/R) compared to that of the IPS approximation

U	S_E/R	$S_{IPS/R}$
0.00	1.23	1.24
1.00	1.09	1.10
2.00	0.72	0.72
3.00	0.38	0.35
4.00	0.18	0.15
5.00	0.08	0.06

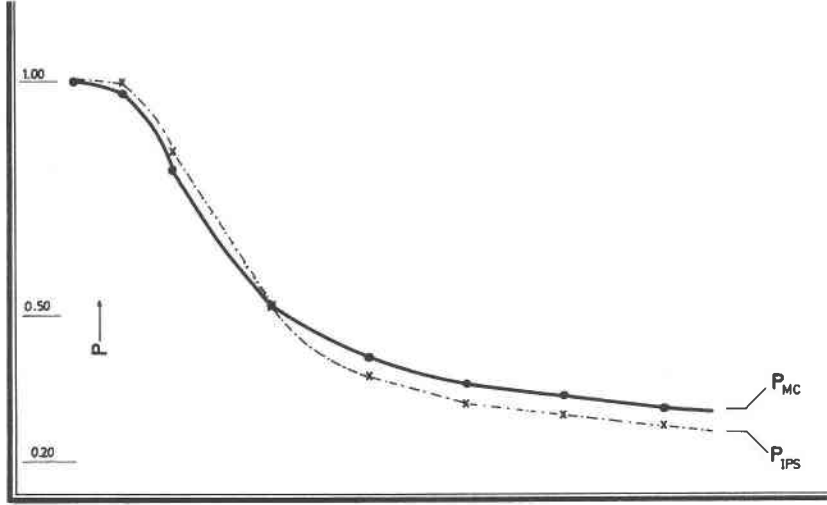


Fig. 5. The order parameter of the two-dimensional model of albite versus $(4/U)$ (or T), by using the IPS method and a Monte-Carlo calculation.

or

$$-\frac{S}{Nk} = \frac{1}{4} \left[x \ln x + 6 \left(\frac{p-x}{3} \right) \ln \left(\frac{p-x}{3} \right) + 9 \left(\frac{1+x-2p}{9} \right) \ln \left(\frac{1+x-2p}{9} \right) \right] + \frac{1}{2} \left[- \left(\frac{1+2p}{3} \right) \ln \left(\frac{1+2p}{3} \right) + p \ln p + \left(\frac{1-p}{3} \right) \ln \left(\frac{1-p}{3} \right) \right] - \frac{1}{2} (1-p) \ln \left(\frac{5-2p}{3} \right) + \left(\frac{1-p}{3} \right) \ln \left(\frac{1-p}{3} \right) - \frac{1}{2} (1-p) \times \ln \left(\frac{5-2p}{3} \right).$$

To find the equilibrium state, we must minimize $A/(NkT)$ with respect to p and x .

$$\left[\frac{\partial [A/(NkT)]}{\partial x} \right]_p = \frac{1}{4} \ln \left[\frac{x(1+x-2p)}{(p-x)^2} \right] = 0 \text{ (equilibrium state)}$$

or

$$\frac{x(1+x-2p)}{(p-x)^2} = 1. \quad (9)$$

The energy of the lattice is

$$E = NpE_A^a,$$

where $E_A^a < 0$ is the site-preference energy. Let us define $-E_A^a/kT = U$. For the Helmholtz free energy, we have

$$A = E - TS$$

and

$$\frac{A}{NkT} = -Up - \frac{S}{Nk}$$

or

$$\frac{A}{NkT} = -Up + \frac{1}{4} \left[x \ln x + 6 \left(\frac{p-x}{3} \right) \ln \left(\frac{p-x}{3} \right) + 9 \left(\frac{1+x-2p}{9} \right) \ln \left(\frac{1+x-2p}{9} \right) \right] + \frac{1}{2} \left[- \left(\frac{1+2p}{3} \right) \ln \left(\frac{1+2p}{3} \right) + p \ln p \right]$$

The solution of Equation 9 gives

$$x = p^2. \quad (10)$$

Since the two sites of an independent pair are noninteracting, this result might be expected in advance.

The other condition for the equilibrium state is,

$$\left[\frac{\partial [A/(NkT)]}{\partial p} \right]_x = 0$$

or

$$-U + \frac{1}{2} \ln \left[\frac{p^2(5-2p)}{3 \left(\frac{1+2p}{3} \right)^{2/3} \left(\frac{1-p}{3} \right)^{4/3}} \right] + \frac{1-p}{5-2p} = 0. \quad (11)$$

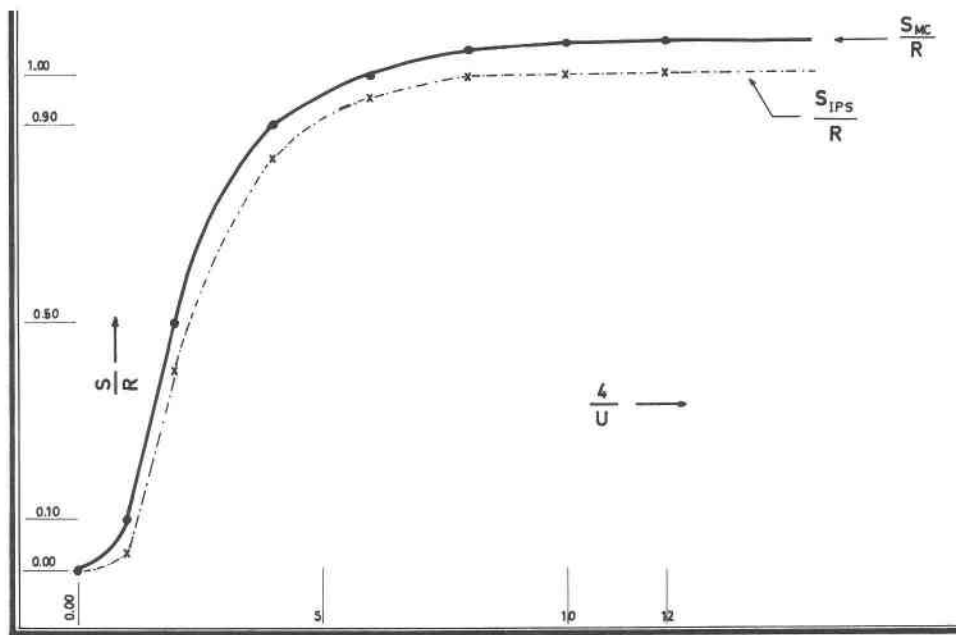


Fig. 6. The configurational entropy of the two-dimensional model of albite versus $(4/U)$ (or T), by using the IPS method and a Monte-Carlo calculation.

If one substitutes Equation 10 into 11 and then solves for U , one gets,

$$U = \frac{1}{2} \ln \left[\frac{3p^2(5-2p)}{(1+2p)^{2/3}(1-p)^{4/3}} \right] + \frac{1-p}{5-2p}. \quad (12)$$

The results are given in Table 1 and also are plotted in Figures 5 and 6.

DISCUSSION

Statistical mechanics plays an important role in the study of the ordering behavior in lattices. It was applied to albite by Mazo (1977) (quasi-chemical approximation). Also recently, the ordering behavior of albite was studied by others, e.g., Salje (1985), Salje et al. (1985), and Rajabali and Mazo (1982) (Kikuchi method). Mazo and Andersen (1979) suggested that lattice configurations should be restricted to those that obey local charge neutrality, in order to be energetically favorable. For albite, they suggested that around any Na atom there must be three Si and one Al. Their idea of local charge neutrality has been used to study the ordering behavior of feldspar minerals. In this paper, the IPS method has been used with Andersen's two-dimensional model of albite, and the results show a sharper curve for the ordering phenomena of model albite with respect to temperature than obtained in other calculations (see Fig. 5). A step on the ordering-behavior curve would represent a phase transition; no such phase transition is predicted by the model.

A significant point relates to the importance of the size of the local unit. To test the effect of this size, the IPS

method was recently used to study the ordering behavior of albite without taking local charge neutrality into account. The results obtained predict that albite should have a metastable phase at some intermediate temperatures (Rajabali, in prep.); in minimizing the free energy (at intermediate temperatures), the stable phase is the one with the lowest free energy and the other, with the highest free energy, is considered to be the metastable state. This behavior has not been predicted by other approximations (except by Salje and his group). The IPS method was tested by applying it to Andersen's one-dimensional model (one row of squares). The one-dimensional case can be solved exactly by the method of Kramers and Wannier (1941), and this has been carried out by Andersen (unpub.). The results are given in Table 2. As shown, the results of the IPS model are satisfactory for the one-dimensional case.

In the present paper the IPS method has been applied with the restriction of local charge neutrality. In the previous calculation (Rajabali, in prep.), the whole lattice was effectively chosen as the unit; here the smallest possible size for the unit has been considered. Since the method of calculation in the two cases is the same, one may expect that the difference in the resulting predicted ordering behavior is due to the size of the unit. It is, of course, difficult to propose a generally acceptable unit, and one might even expect that the size of unit changes with temperature. It is probably true that the unit is neither as small as that of Andersen, nor so big that the whole lattice can be treated as a unit. These are just the smallest and the largest possible units, respectively, and are chosen primarily to simplify the mathematics of the

problem. Since it is likely that neither of these models perfectly represents feldspar minerals, it seems that the size of the neutral unit may play an important role in the ordering behavior. In the framework of feldspar minerals, it seems that each secondary site (alkali metal) is surrounded by 12 primary sites. One might conjecture that the smallest realistic unit is three times as big as that used by Andersen and Mazo (1979). In order to have such a unit, we may consider a model with three non-interacting parallel squares with Na at their centers. To take local charge neutrality into account, each unit must have three Al and nine Si atoms, but this model has not been carried any further.

Finally, let us consider the IPS approximation more closely. Since it is not possible to find the exact number of distributions of Al and Si atoms on sites, we divided units into two groups, independent pairs and sites, such that each independent site interacts only with its adjacent independent pairs. Such a division is, of course, artificial. In order to enforce self consistency between the units, we required that the global order parameter of units be the same for the independent pairs and sites. In order to study how one can calculate the number of distributions by the IPS method, consider the distributions of N_A A atoms and N_B B atoms on N sites of a two-dimensional lattice with unit of squares, such that

$$N_A = N_B = N/2$$

and all site and interaction energies are zero. We have

$$g(\text{pair}) = \frac{(N/4)!}{(N/16)!(N/16)!(N/16)!(N/16)!},$$

where $N/4$ is the number of independent pairs and

$$N_{AA} = N_{AB} = N_{BA} = N_{BB} = 1/4(N/4).$$

The number of distributions of atoms on the independent sites is

$$g(\text{site}) = \frac{(N/2)!}{(N/4)!(N/4)!},$$

where $N/2$ is the number of independent sites.

Then, using the IPS approximation, the total number of distributions is given by,

$$g = \frac{(N/4)!}{[(N/16)!]^4} \times \frac{(N/2)!}{[(N/4)!]^2}.$$

By using Stirling's approximation, one gets

$$S = Nk \ln 2$$

for the configurational entropy of the lattice, which is equal to the exact value. Applying the method to a non-interacting system is not a very stringent test, but it does indicate a basic internal consistency.

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