

STATISTICAL-MECHANICAL CALCULATION OF THERMODYNAMIC PROPERTIES OF ALBITE USING A TWO-DIMENSIONAL MODEL

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Abstract

The thermodynamic properties of two-dimensional Ising-type models of albite predict that the low albite/high albite transition occurs continuously with temperature. First, a nearest-neighbor Ising model is used to calculate the thermodynamic properties accurately. The value of the excess entropy obtained is very close to values found by other approximate calculations (for the same model) at low temperatures but differs at high and especially at intermediate temperatures. Within various approximate calculations for the model, these differences are a few percent at low temperatures where the low albite is the stable phase. At high temperatures, where high albite is the stable phase, the entropy calculated by the approximate methods differs from the present result by as much as 10 percent. At intermediate temperatures (where the transition occurs) the calculated entropy of the present work differs from the previous results by 20 to 30 percent at the same temperature. Comparison of the calculated order parameter with experimental results suggests that the nearest-neighbor Ising-type model is not an appropriate model for albite. Second, we assumed that the site preference energy depends linearly on p (the fraction of T_{10} sites occupied by Al atoms), a fairly good agreement is found with experimental results. The excess thermodynamic properties are calculated and compared with those given by the Landau theory.

Introduction

Recently, a statistical-mechanical approach was used to calculate an accurate configurational entropy of the two-dimensional model of albite [1] introduced by Andersen and Mazo [2] which we shall refer to as I in this paper. This approach is called the "independent basic unit" or "IBU" [1]. In comparison with the exact values, IBU gives very accurate results for thermodynamic properties of the one-dimensional

model of albite [1]. In the IBU approach, the 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. A solid (nonsolid) site is a position which is occupied by a unit, and a unit is a square that includes one Al, three Si, and one Na atoms. The number of distributions of units among solid and nonsolid sites are calculated accurately under the usual constraints of Al-Al avoidance and local charge neutrality. The goal of this work is to use

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the results given in I to calculate the thermodynamic properties of the model.

In a classical Ising model, the lattice distortions (the site preference energy J in the case of albite) is effectively ignored and is replaced by one average number which is chosen to reproduce the experimental observations. We shall first use the model with nearest-neighbor interactions only to see what average value (if any) can be assigned for J . However, because albite shows a large elastic excess energy due to the Al, Si ordering process (Salje *et al.* [3]), we do not expect the nearest-neighbor Ising-type model to be appropriate for Na-feldspar. For this reason, we have then taken into consideration the long-range crystal interactions, by assuming that the site preference energy is a function of Al, Si ordering (Mazo [4], Senderov [5]).

Equilibrium State Considering the Nearest-Neighbor Interactions

In order to find the equilibrium state, the free energy, with respect to configuration, must be minimized. The reduced Helmholtz free energy is given by

$$A/NkT = E/NkT - S/Nk$$

where the reduced configurational energy, E/NkT , is given by $E = pJ/N$ where $J(J < 0)$ is the site preference energy and is defined for the energy of an Al atom on the T_{10} site, N is the total number of units, and p is a parameter related to the order parameter, Q_{od} , as (see I)

$$Q_{od} = \frac{4p - 1}{2p + 1}$$

By using the result given in I for the configurational entropy, we obtain the following expression for the free energy:

$$A/NkT = p(J/kT) - (1/N) \sum_i \sum_j [1n(g_{ij}) + 1n(g(S))] \quad (1)$$

where J/kT is the reduced site preference energy and g_{ij} is the number of ways to distribute the allowed units among specific types of nonsolid sites belonging to the basic units with Z_i configurations, and $g(S)$ is the number of ways for distribution of units among solid sites, given by

$$g(S) = \frac{(N/8)!}{\prod_i [(Q_i N/8)!]^{\lambda_i}} \quad (2)$$

where $\lambda_4 = 1$, $\lambda_3 = 12$, $\lambda_2 = 54$, $\lambda_1 = 106$, and $\lambda_0 = 81$. As shown in I, g_{ij} is given by

$$g_{ij} = \frac{(\lambda_{ij} Q_i N/2)!}{\prod_m (\lambda_{ij} Q_i m_{ij} N/2)!} \quad (3)$$

where each m represents one of the allowed units for the specific ij pair and m_{ij} is the probability that such nonsolid sites are occupied by this specific allowed unit. λ_{ij} is the multiplicity for the ij pair.

In order to obtain the equilibrium state, the function A/NkT is minimized in such a way that the following constraints are satisfied. The constraints can be categorized into two groups: the first group is concerned with the occupation of nonsolid sites by the allowed units given in Tables I through V (in I). The second group is concerned with the occupation of the solid sites.

The sum of the probabilities that each specific type of nonsolid site (with more than one allowed unit) is occupied by its allowed units has to be equal to one, the first group of constraints is then given by the general formula,

$$\sum_m m_{ij} = 1 \quad (4)$$

where each m represents one of the allowed units for each ij pair. Such a constraint must hold for each row (j) of Tables I-V (in I), in which their nonsolid sites are available for more than one unit. Therefore, Eq. 4 represents 11, 11, 9, 5, and 1 constraints for the basic unit with Z_0, Z_1, Z_2, Z_3 and Z_4 configurations, respectively. Hence there are 37 constraints in the first group. The constraint which belongs to the second group may be obtained by using the fact that the total number of basic units with any configuration must add up to $N/2$. This constraint is given by,

$$Q_4 + 12Q_3 + 54Q_2 + 106Q_1 + 81Q_0 = 1 \quad (5)$$

The parameter p can be obtained in terms of the Q s and A_{ij} s. The number of A units on solid sites, $N_A(S)$, is given by,

Table I. The values of m_{ij} in terms of $x = \exp(J/kT)$ at the equilibrium state, considering the nearest-neighbor interactions only.

j	A_{ij}	B_{ij}	C_{ij}	D_{ij}
1	$(1 + 3x)^{-1}$	$x(1 + 3x)^{-1}$	$x(1 + 3x)^{-1}$	$x(1 + 3x)^{-1}$
2	$(1 + 2x)^{-1}$	$x(1 + 2x)^{-1}$	$x(1 + 2x)^{-1}$	0
3	$(1 + 2x)^{-1}$	$x(1 + 2x)^{-1}$	0	$x(1 + 2x)^{-1}$
4	$(1 + 2x)^{-1}$	0	$x(1 + 2x)^{-1}$	$x(1 + 2x)^{-1}$
5	0	1/3	1/3	1/3
6	$(1 + x)^{-1}$	$x(1 + x)^{-1}$	0	0
7	$(1 + x)^{-1}$	0	$x(1 + x)^{-1}$	0
8	$(1 + x)^{-1}$	0	0	$x(1 + x)^{-1}$
9	0	1/2	1/2	0
10	0	1/2	0	1/2
11	0	0	1/2	1/2

$$N_A(S) = (1/4) \sum_i \lambda_i Q_i N/2$$

$$= (N/2) [Q_4 + 9Q_3 + 27Q_2 + (53/2)Q_1] \quad (6)$$

The number of A units on the nonsolid sites, $N_A(N)$, is given by,

$$N_A(N) = \sum_i \sum_j \lambda_{ij} A_{ij} Q_i N/2$$

$$= (N/2) [Q_0(4A_{01} + 4A_{02} + 5A_{03} + 4A_{04} + 5A_{06} + 4A_{07} + 5A_{08} + 5) + Q_1(8A_{11} + 8A_{12} + 10A_{13} + 8A_{14} + 7A_{16} + 8A_{17} + 7A_{18} + 4) + Q_2(4A_{21} + 6A_{22} + 5A_{23} + 6A_{24} + 3A_{26} + 8A_{27} + 3A_{28} + 2) + Q_3(2A_{32} + 2A_{34} + A_{36} + 4A_{37} + A_{38}) + Q_4 A_{47}] \quad (7)$$

On the one hand, the total number of A units in the lattice is equal to $N_A(S) + N_A(N)$, and on the other hand it is equal to pN . Therefore, the parameter p is given by

$$p = (1/N) [N_A(S) + N_A(N)] \quad (8)$$

This means that there is a total of 38 constraints, given by Eqs. 4 and 5, that have to be taken into account when the free energy is minimized. The minimization is done by using Lagrange multipliers as follows: Let us define the function ϕ' as,

$$\phi' = p(J/kT) + (1/2) \sum_i \sum_j \sum_m \lambda_{ij} Q_i m_{ij} \ln(m_{ij})$$

$$+ (1/8) (Q_4 \ln(Q_4) + 12Q_3 \ln(Q_3) + 54Q_2 \ln(Q_2) + 106Q_1 \ln(Q_1) + 81Q_0 \ln(Q_0)) - \sum_i \sum_j \alpha_{ij} (\sum_m m_{ij} - 1) \quad (9)$$

where the α_{ij} s are the undetermined multipliers. The prime on ϕ' simply shows that constraint 5 is not included. The last term is an abbreviation for 37 constraints given by Eq. 4. In order to find the equilibrium state, the partial derivative of ϕ' will first be taken with respect to the m_{ij} s, and then set equal to zero. Therefore, at this stage, where we are calculating $\partial\phi'/\partial m_{ij}$, the inclusion of the constraint 5 makes no difference and for this reason it is now dropped. The partial derivative of the function ϕ' with respect to m'_{ij} is given by

Table II. Calculated thermodynamic properties for the two-dimensional model of albite and values of different parameters appearing in Eq. 20 for the free energy, for some given values of the site preference energy, considering the nearest-neighbor interactions only.

(J/kT)	-A/NkT	S/Nk	p	Q ₄	Q ₃	Q ₂	Q ₁	Q ₀	x
0.0	1.065	1.065	.250	.003	.003	.004	.004	.004	1
.10	1.091	1.064	.264	.003	.004	.004	.004	.003	.905
.20	1.119	1.061	.289	.007	.006	.005	.004	.003	.819
.25	1.133	1.059	.296	.007	.006	.005	.004	.003	.779
.33	1.159	1.053	.318	.012	.007	.005	.004	.002	.717
.40	1.181	1.048	.333	.014	.009	.005	.004	.002	.670
.50	1.215	1.038	.353	.014	.012	.005	.004	.002	.607
.67	1.279	1.008	.406	.040	.014	.006	.003	.001	.513
.75	1.314	.992	.429	.047	.017	.006	.003	.001	.472
1.0	1.432	.916	.516	.110	.024	.006	.002	.001	.368
1.5	1.735	.687	.699	.336	.032	.004	.001	0	.223
2.0	2.122	.447	.837	.622	.024	.001	0	0	.135
2.6	2.654	.249	.925	.840	.012	0	0	0	.074
3.0	3.029	.176	.951	.909	.006	0	0	0	.050
3.6	3.609	.108	.972	.956	.002	0	0	0	.027
4.0	4.004	.075	.982	.974	.001	0	0	0	.018
4.6	4.581	.059	.983	.977	0	0	0	0	.010

$$\partial\phi/\partial m'_{ij} = (1/2)\lambda_{ij}Q_i(1 + 1/n m'_{ij}) - \alpha_{ij} \quad (10)$$

where $m' = B, C,$ and D (not A). If we set $\partial\phi/\partial m'_{ij} = 0$, we get

$$1/n m'_{ij} = -1 + \beta_{ij} \quad (11)$$

where

$$\beta_{ij} = \alpha_{ij}/(\lambda_{ij}Q_i/2)$$

At the equilibrium state, Eq. 11 holds for each of the allowed units m (except A) for each pair of ij given in Tables I-V (in I), in which their nonsolid sites are available for more than one unit. Since β_{ij} does not

depend on m'_{ij} , it follows from Eq. 11 that

$$B_{ij} = C_{ij} = D_{ij} \quad (12)$$

Now we take the derivative of ϕ' with respect to A_{ij} (note that p is a function of the A_{ij} s, see Equation 14 in I).

$$\begin{aligned} \partial\phi'/\partial A_{ij} &= (1/2)\lambda_{ij}Q_i(J/kT) + (1/2)\lambda_{ij}Q_i[1n(A_{ij}) + 1] - \alpha_{ij} \\ &= (1/2)\lambda_{ij}Q_i[(J/kT) + 1n(A_{ij}) + 1 - \beta_{ij}] \end{aligned} \quad (13)$$

If we substitute $\beta_{ij} = 1 + 1/n(m'_{ij})$ (from Eq. 11) into Eq. 13, we find the following result for the equilibrium state as well:

Table III. Same as the previous table for given values of J_0/kT , when the long-range interactions are included.

$-J_0/kT$	$-A/NkT$	S/Nk	ρ	Q_4	Q_3	Q_2	Q_1	Q_0	x
0	1.065	1.065	.250	.003	.003	.004	.004	.004	1
.10	1.065	1.065	.256	.004	.004	.004	.004	.003	.966
.20	1.065	1.064	.263	.004	.004	.004	.004	.003	.929
.30	1.066	1.064	.272	.005	.005	.004	.004	.003	.889
.40	1.067	1.062	.282	.006	.005	.004	.004	.003	.846
.50	1.068	1.060	.294	.008	.006	.005	.004	.003	.799
.60	1.070	1.056	.309	.010	.007	.005	.004	.002	.745
.70	1.073	1.049	.329	.014	.008	.005	.004	.002	.683
.80	1.078	1.036	.359	.022	.011	.006	.004	.002	.607
.90	1.084	1.003	.413	.043	.015	.006	.003	.001	.501
.95	1.090	.949	.481	.083	.021	.006	.002	.001	.406
1.00	1.106	.587	.762	.457	.029	.003	0	0	.183
1.05	1.136	.441	.841	.626	.024	.001	0	0	.135
1.10	1.171	.356	.881	.723	.019	.001	0	0	.109
1.20	1.251	.250	.926	.836	.012	0	0	0	.077
1.30	1.337	.185	.950	.898	.008	0	0	0	.057
1.32	1.355	.174	.953	.907	.007	0	0	0	.054

$$J/kT - \ln(m'_{ij}/A_{ij}) = 0 \tag{14}$$

or

$$m'_{ij} = xA_{ij} \tag{15}$$

where

$$x = \exp(J/kT) \tag{16}$$

By means of Eqs. 12 and 15, the probabilities for the allowed units of each ij pair given in Tables I-V (in I) can be expressed in terms of A_{ij} and x . Owing to the fact that there is a (normalization) relationship among A_{ij} , B_{ij} , C_{ij} and D_{ij} , all of these probabilities

can be expressed in terms of x only. For example, consider the case of $j = 1$ in Tables I-III ($i = 0, 1, 2$ of I), in which A , B , C , and D are allowed units. We have,

$$B_{i1} = C_{i1} = D_{i1} = xA_{i1} \tag{17}$$

and

$$A_{i1} + B_{i1} + C_{i1} + D_{i1} = 1 \tag{18}$$

From the combination of Eqs. 17 and 18 the probabilities A_{i1} , B_{i1} , C_{i1} , and D_{i1} may be expressed in terms of x as

$$\begin{aligned}
 A_{ii} &= 1/(1 + 3x) \\
 B_{ii} &= x/(1 + 3x) \\
 C_{ii} &= x/(1 + 3x) \\
 D_{ii} &= x/(1 + 3x)
 \end{aligned}
 \tag{19}$$

By using a similar argument, all values for m_{ij} can be expressed in terms of x only. The results are given in Table I.

The probabilities m_{ij} (Table I) are substituted in Eq. 3, and the resulting combinatorial factors g_{ij} are substituted in Eq. 1. The reduced free energy is then obtained in terms of Q_s and x . The following result is obtained:

$$\begin{aligned}
 A/NkT &= pJ/kT + (1/8) \{Q_4 1n(Q_4) + 12Q_3 1n(Q_3) \\
 &+ 54Q_2 1n(Q_2) + 106Q_1 1n(Q_1) + 81Q_0 1n(Q_0)\} \\
 &+ (1/2) \{(4Q_0 + 8Q_1 + 4Q_2) [3x 1n(x) / (1 + 3x) \\
 &- 1n(1+3x)] + (13Q_0 + 26Q_1 + 17Q_2 + 4Q_3) [2x 1n(x) / (1+2x) \\
 &- 1n(1 + 2x)] + (12Q_0 + 8Q_1) (-1n3) + (14Q_0 + 22Q_1 \\
 &+ 14Q_2 + 6Q_3 + Q_4) [x 1n(x) / (1 + x) - 1n(1 + x)] \\
 &+ (23Q_0 + 26Q_1 + 8Q_2) (-1n2)\}
 \end{aligned}
 \tag{20}$$

The probabilities A_{ij} are substituted in Eq. 7, and the resulting equation along with Eq. 6 is substituted in Eq. 8. The parameter p is then obtained in terms of the Q_s and x . The result is given by

$$\begin{aligned}
 2p &= Q_4 + 9Q_3 + 27Q_2 + (53/2) Q_1 + \\
 &Q_0 [4/(1 + 3x) + 13/(1 + 2x) + 14/(1 + x) + 5] + \\
 &Q_1 [8/(1 + 3x) + 26/(1 + 2x) + 22/(1 + x) + 4] + \\
 &Q_2 [4/(1 + 3x) + 17/(1 + 2x) + 14/(1 + x) + 2] + \\
 &Q_3 [4/(1 + 2x) + 6/(1 + x)] + Q_4 / (1 + x)
 \end{aligned}
 \tag{21}$$

In order to find the equilibrium state of the lattice, the free energy given in Eq. 20 has to be minimized in such a way that the constraints given by Eq. 5 (which has not been taken into account) and Eq. 21 are satisfied. The calculated results are given in Table II. The calculated values (from IBU) for the configurational entropy are given in Figure 1. The

resulting entropy is compared with those obtained by using the independent pairs and sites or IPS [6] and the modified sequential construction method or MSCM [7] for the same model as shown in this figure.

Equilibrium State Considering the Long-Range Interactions

In the previous section, an Ising-type model with the nearest-neighbor interactions only was used to calculate the thermodynamic properties of the lattice. Such a model is appropriate if an average value can be assigned for the site preference energy so that the experimental observations can be reproduced. We may compare our calculated parameter $p(J/kT)$ with the experimental value (given as a function of temperature) of Stewart *et al.* [8]. Therefore, we have $p(T)$ from experiment and $p(J/kT)$ from our calculation. For the same value of p , we have

$$p(T') = p(J/kT') \tag{22}$$

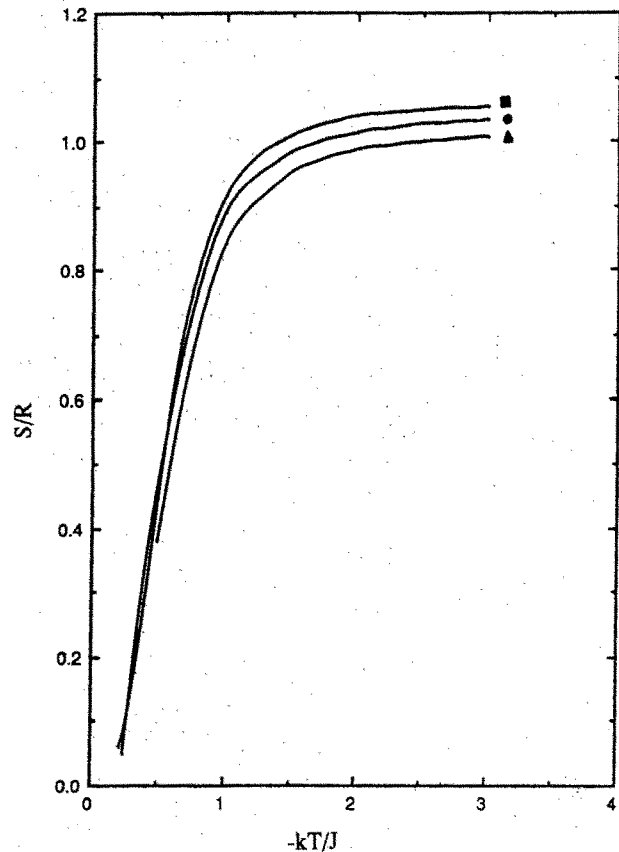


Figure 1. The reduced molar configurational entropy S/R versus the reduced temperature $-kT/J$ obtained by IBU (■), IPS (▲), and MSCM (●) approaches for the model with the nearest-neighbor interactions only.

where T' is any given T at which the equation is satisfied. The value of J at T' can be obtained by using Eq. 22. The result is plotted in Figure 2. As shown in this figure, the site preference energy strongly depends on temperature, especially around 770 K, where most of the ordering process takes place. Therefore, the change of the site preference energy with respect to temperature is so large that it makes it impossible to attribute a reasonably constant value to J . In fact, such a result is to be expected, because Na-feldspar shows a large elastic excess energy due to the Al, Si ordering process (Salje [9] and Salje, *et al.* [3]).

To include the lattice distortion in the model, the long-range crystal interactions (governed by Coulomb forces) have to be taken into account. Such interactions may be taken into account by considering the site preference energy to be dependent on p . For $J(p)$ no exact function is known, but a linear function has been used by Mazo [4] and Senderov [5]. We use $J(p) = 4J_0(p - 0.25)/3$ which was introduced and used by Mazo [4], where J_0 is a constant whose value is chosen to obtain good agreement with experiment. The configurational energy then is given by

$$E = [4J_0p(p - 0.25)/3]N \quad (23)$$

The expressions for the entropy and constraints given in the previous section remain unchanged.

To obtain the equilibrium state we have to minimize the new expression for the free energy, which differs from the previous one in the energy term only, with respect to configuration such that the constraints given by Eqs. 4 and 5 are satisfied. The result, which is given by Eq. 12 for the equilibrium state, will be obtained again because of the fact that the energy term of free energy does not depend on m'_{ij} (see Eqs. 6, 7, 8, and 23). However, $\partial\phi'/\partial A_{ij}$ becomes

$$\begin{aligned} \partial\phi'/\partial A_{ij} = & (1/2) \lambda_{ij} Q_i [(4/3) (J_0/kT) (2p - 0.25)] \\ & + (1/2) \lambda_{ij} Q_i [1n(A_{ij}) + 1] - \alpha_{ij} \end{aligned} \quad (24)$$

Combination of Eq. 24 with Eq. 11 leads to the following result for the equilibrium state

$$m'_{ij} / A_{ij} = \exp [4/3 (J_0 / kT) (2p - 0.25)] \quad (25)$$

where $m' = B = C = D$ (not A) is the same as before. We should redefine $x = m'_{ij} / A_{ij}$ (Eq. 15) as

$$x = \exp [(4/3) (J_0 / kT) (2p - 0.25)] \quad (26)$$

Such redefinition leads to the same functions for A_{ij} ,

B_{ij} , C_{ij} , and D_{ij} in terms of x as those given in Table I. Therefore, to obtain the equilibrium state, Eq. 20 has to be minimized subject to constraints given by Eqs. 5 and 21, except that the energy term has to be replaced by that given by Eq. 23. However, we need to include one more constraint, which is the new definition for x in terms of the site preference energy given by Eq. 26. The calculated equilibrium-state properties are given in Table III, also the calculated p parameter is compared in Figure 3 with the case when the site preference energy is assumed to be independent of the parameter p .

In order to present the calculated properties in terms of temperature, the value of J_0 must be known. We may obtain the value of this quantity by assuming that the equilibrium state of the model corresponds to that of the lattice when $p(J_0 / kT)$ from our calculation is equal to $p(T)$ given by experiment (Stewart *et al.* [8]). Since the calculated p against kT/J_0 has a steep slope at the point ($p \approx 0.75, kT/J_0 = -1$) (see Figure 3),

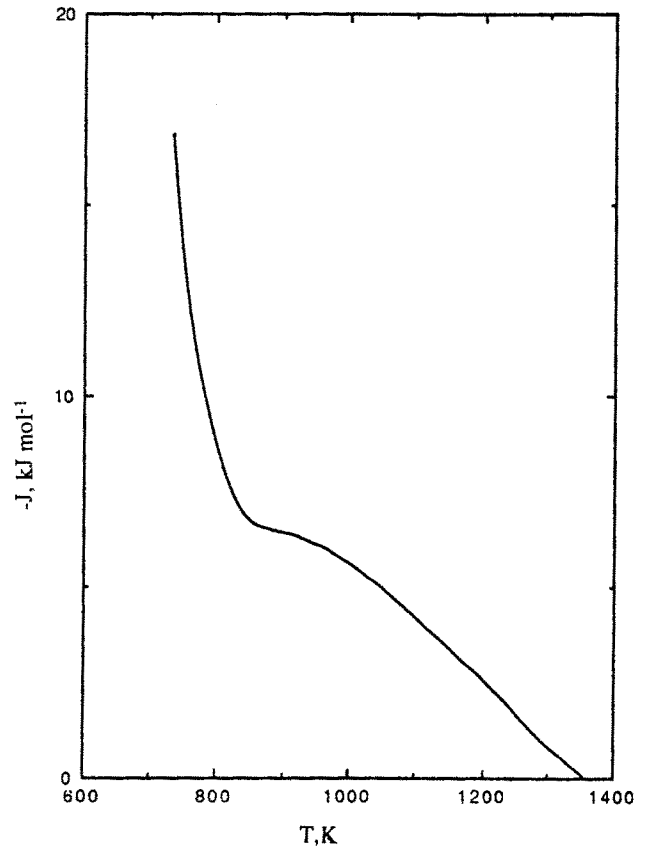


Figure 2. Site preference energy as a function of temperature by comparing the calculated and experimental values of the parameter p (an attempt to find an average constant number for J according to the nearest-neighbor classical Ising model).

and a similar behavior can be seen from the experimental data at the point ($p \approx 0.75$, $T \approx 773$ K) (see Figure 6 of Stewart *et al.* [8]), we consider these points to correspond to the same equilibrium state. Therefore, we may conclude that at 773 K, $kT/J_0 = -1$, or $J_0/k = -773$ K, and therefore the temperature (in Kelvin) for any equilibrium state of the model is simply given by $T = 773 (-kT/J_0)$.

We can now present the calculated parameter p in terms of T and compare it with the experimental values (Stewart *et al.* [8]). Such a presentation is given in Figure 4, in which the result obtained by using a Landau-type theory is also included (Salje [9] and Salje *et al.* [3]). Our result shows fairly good agreement with the experimental data. The excess entropy and energy obtained by the IBU and the Landau theory (Salje *et al.* [3]) are given in Figures 5 and 6, respectively. An excess quantity at a given temperature is defined as the difference between that quantity at such temperature with that of the high-temperature limit ($T \rightarrow \infty$).

Conclusion and Discussion

The result in I, obtained by applying the independent basic unit approach to the two-dimensional model of Andersen and Mazo [2], has been used in this work to calculate the thermodynamic properties of albite. First, the nearest-neighbor interactions are taken into consideration. The resulting entropy is compared with values obtained by the independent pairs and sites (IPS, [6]) and the modified sequential construction method (MSCM, [7]) for the same model. At very low temperatures, at which low albite is the stable phase, the configurational entropy calculated by IBU is almost the same as those obtained by IPS and MSCM. At high temperatures, at which high albite is the stable phase, the results are different but the differences are less than 10%. Such differences are due to the aluminum avoidance rule. At intermediate temperatures (especially around $kT/J = -0.6$) at which the transition takes place, the differences are between 20 to 30 percent (see Figure 1). This is due to the fact that both the phase transition

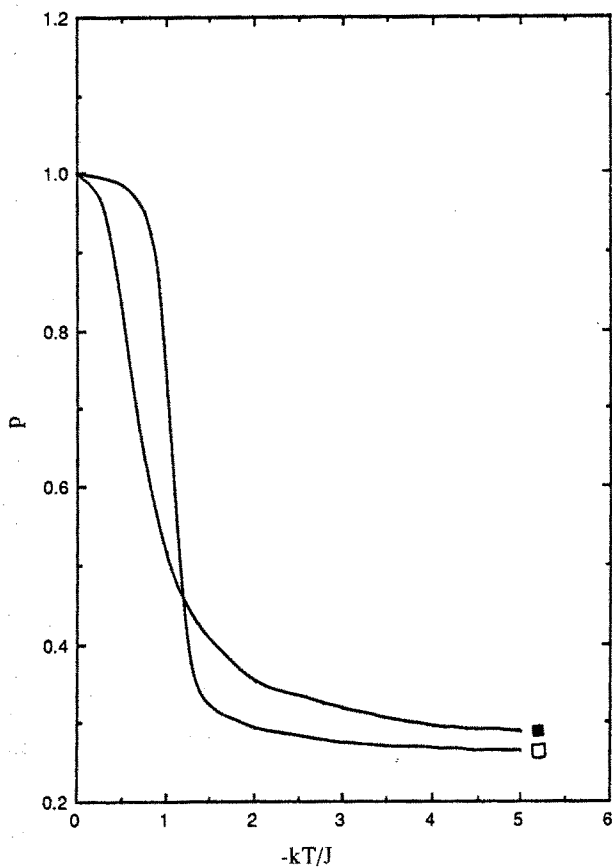


Figure 3. The parameter p versus $-kT/J$ for the case that J is independent of p (■) and versus $-kT/J_0$ when J varies linearly with respect to p (□).

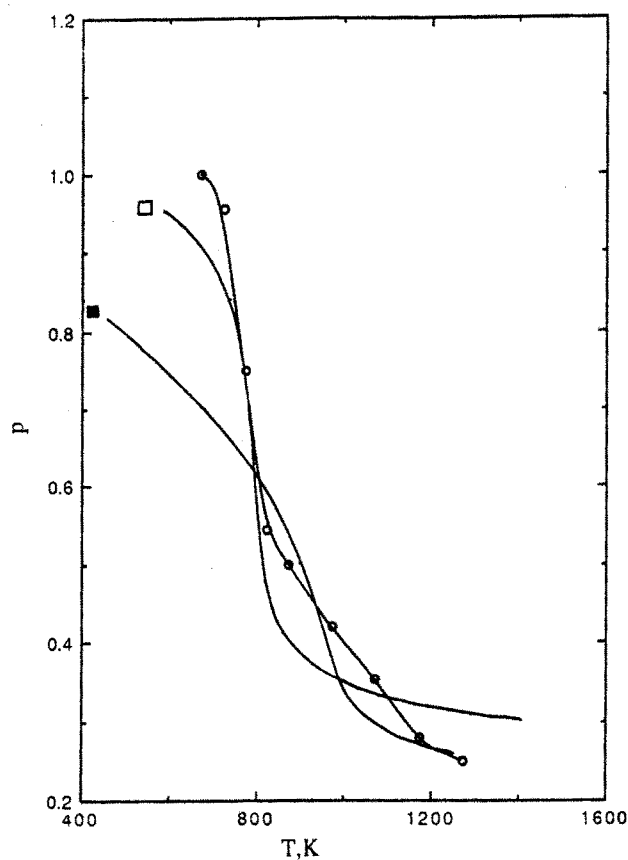


Figure 4. The parameter p versus temperature given by experiment (○), independent basic unit (□), and Landau theory (■).

and the aluminum avoidance have profound effects on the system, and the ability of earlier approaches to handle such a complicated system is limited. Therefore, we may conclude that some factors, such as the phase transition and the aluminum avoidance limitation have important effects on the thermodynamic properties of the system, and that using approximate methods may lead to significant errors.

Our next concern has been to see how appropriate the nearest-neighbor Ising model is for albite. This model would be justified if a constant value of the site preference energy could reproduce the experimental observations. Figure 2 shows that the site preference energy is so temperature dependent that it is impossible to assign a single constant value to J . Therefore, we may conclude that such a model is not appropriate for Na-feldspar. Such a conclusion is expected due to the fact that lattice distortions in albite are significant (Salje *et al.* [3]).

We have included the lattice distortions in the

model by considering the site preference energy as a function of the parameter p . For this function, we used the linear expression suggested by Mazo [4]. On including this function, the ordering process of the system, with respect to temperature, shows a remarkable change, so that (in comparison, with the case that only the nearest-neighbor interactions are considered) the disordering of low albite by raising the temperature begins at a higher T , and once it starts, the disordering is very much faster, i. e. dp/dT is much greater in absolute value when transition occurs (see Figure 3).

By including the site preference energy as a function of p , we found a fairly good agreement with experiment (see Figure 4). The calculated excess entropy and energy are compared with those obtained by Salje *et al.* [3] in Figures 5 and 6, respectively. The temperature dependence of the excess functions given, by both approaches (IBU and Landau theory) are very similar. The main differences are related to the T-axes, and such differences are due to the fact that the result

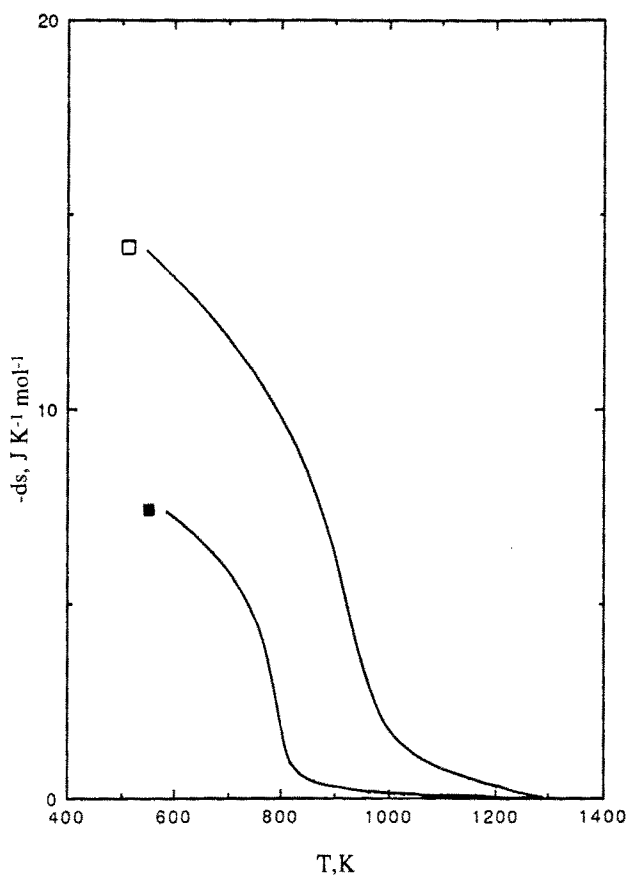


Figure 5. Excess entropy dS versus temperature given by IBU (■) and Landau theory (□)

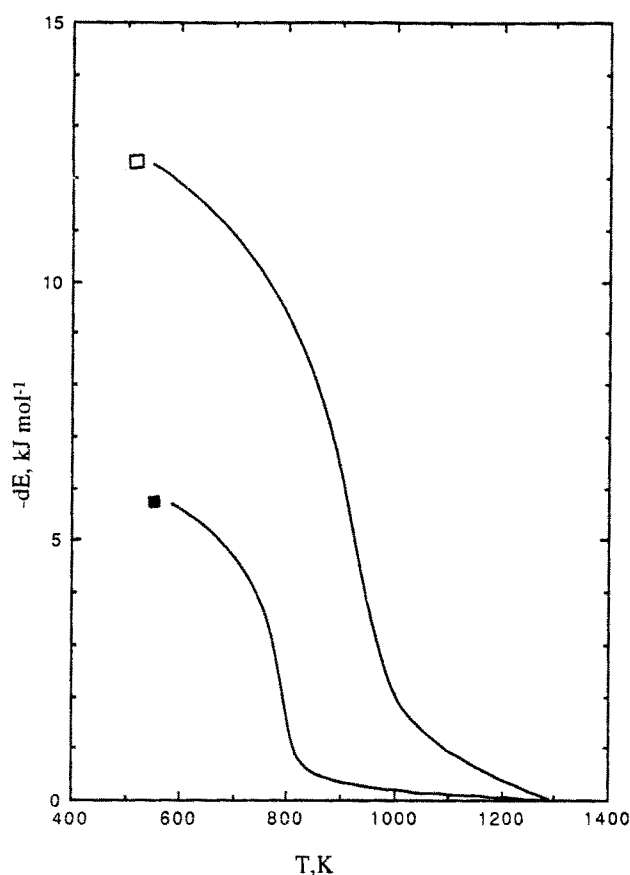


Figure 6. Excess energy dE versus temperature given by IBU (■) and Landau theory (□)

given by the Landau theory predicts that the most significant ordering process (the largest slope in Figure 4) occurs at a higher temperature (by 150K) than those given by IBU and experiment (see Figure 4).

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