American Mineralogist, Volume 74, pages 482–483, 1989

Ordering behavior in albite using the modified sequential construction method: Discussion

CHARLES R. ROSS II
Bayerisches Geoinstitut, Postfach 10 12 51, 8580 Bayreuth, Federal Republic of Germany

Rajabali (1988) recently presented a discussion of the behavior of a statistical-mechanical model of Al-Si ordering in albite. Rajabali (1988) concluded that the size of the unit within which charge balance is maintained is crucial to the determination of the character of the phase transition in the model. That one must be careful in choosing an appropriate subunit of the (semi-)infinite crystalline lattice when modeling its behavior is a point well taken (see, for example, Barker, 1952). In this case, however, the conclusion is based upon erroneous results.

The model, which follows upon work of Anderson and Mazo (1979), is based upon a square planar lattice. In the work of Anderson and Mazo and the first approximation of Rajabali (1988), charge balance was assumed to be maintained within each unit cell (a square of lattice sites). One lattice site in each unit cell was assigned a (negative) site-preference energy ϵ for Al, so that the ordering of Al and Si in the albite tetrahedral sites might be modeled. Higher-order approximations of Rajabali (1988) involved the stacking of two or three of these basic lattices and constraining charge balance within a set of two or three unit cells, one from each parallel plane. For further details, the reader is directed to Anderson and Mazo (1979) and Rajabali (1988).

The approximation method used to solve the statistical-mechanical models so constructed is the so-called modified sequential construction method (MSCM). The MSCM involves the construction of a closed-form approximation to the configurational entropy that in this case takes into account both Al-avoidance and long-range order. The discussion of this approximation in Rajabali (1988) is not easy to follow, but the method appears valid. The current difficulty lies with Rajabali's (1988) Figure 3 (reproduced in Fig. 1), a plot of $dS/dNkT$ vs. $-kT/\epsilon$ (note that the axes were incorrectly labeled). The diagram shows that there is only a small qualitative change in the behavior of the model when passing from one unit cell as the charge-balanced unit (to be referred to as the 1UCM) to two unit cells as the charge-balanced unit (the 2UCM). When increasing the size of the charge-balanced unit to three unit cells (the 3UCM), however, the change in the character of the transition is dramatic; the peak of the curve shifts to higher temperatures, and the transition becomes much more abrupt, as evidenced by the sharper peak in $dS/dNkT$.

Although this behavior is not impossible a priori, it is peculiar. Large changes in transition character generally occur when the dimensionality, connectivity, or interaction characteristics of the model change (Domb, 1974; Stanley, 1971; Green and Hurst, 1964). As none of these criteria apply to this series of models, the observation of Rajabali (1988) is provocative of further inquiry.

The equations describing the entropy S and the reduced free energy $\phi \equiv A/NkT$ were rederived and in all cases are in agreement with Rajabali (1988), although a few typographical errors were detected. These equations were used to determine the degree of order, entropy, and reduced free energy at equilibrium. Calculations were made at sufficiently close intervals that the approximation

$$(dS)/(dNkT) \approx (\Delta S)/(\Delta NkT)$$

is reasonable. A plot of the present results is to be seen in Figure 2, which may be compared with Rajabali's (1988) results in Figure 1; note that the vertical scales of the two figures differ.

The results of the 1UCM and the 2UCM are in agreement with those of Rajabali (1988); however, the increased number of data in the present work reveals much more quantitative detail, in particular the shift of the maximum of $dS/dNkT$ to lower temperatures and higher values in the 2UCM. The present work on the 1UCM and 2UCM also reproduced the values quoted by Rajabali relating $\epsilon/kT \equiv U$, S/Nk, and the order parameter p.

For the 3UCM, the present results differ greatly from those of Rajabali (1988). In Figure 2, the addition of a third unit cell to the charge-balanced unit has essentially the same qualitative effect as did the addition of the sec-

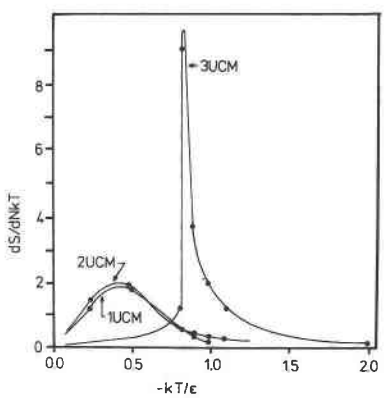

Fig. 1. $dS/dNkT$ vs. $-kT/\epsilon$ for the three different models (after Rajabali, 1988). Note that curve for the 3UCM is in error.

0003–004X/89/0304–0482$02.00

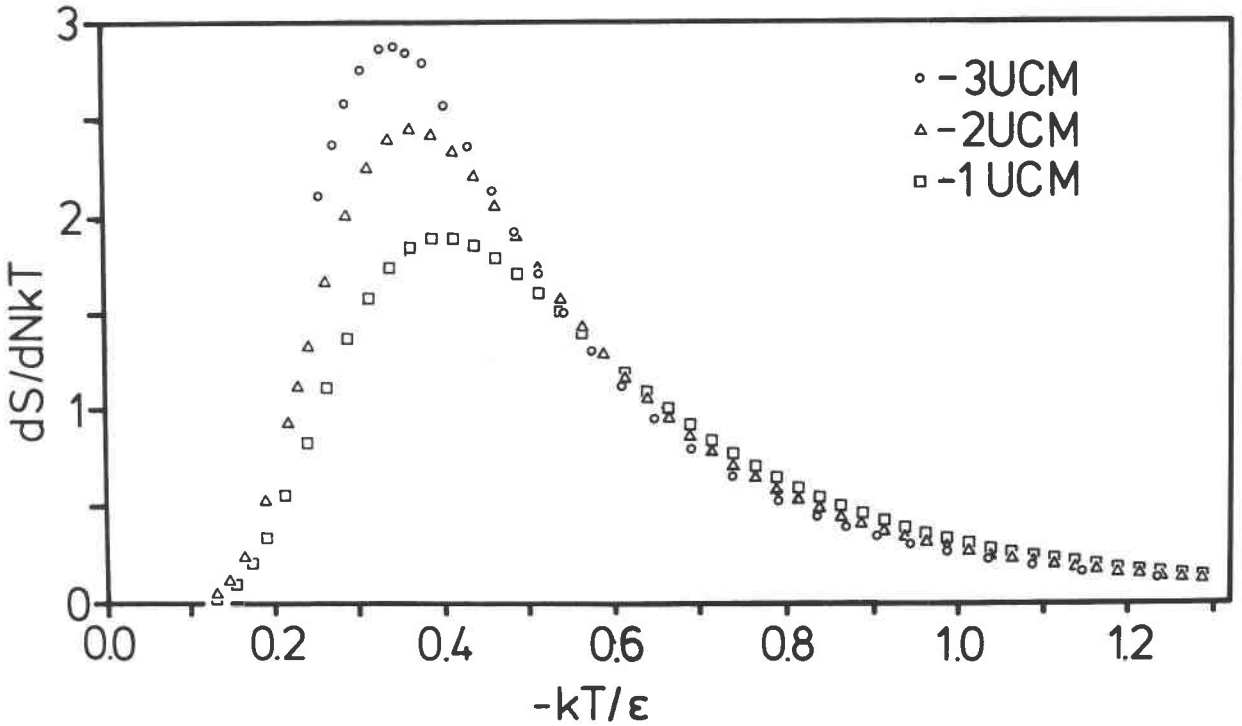

Fig. 2. Corrected values for $dS/dNkT$ vs. $-kT/\epsilon$ for the three different models. Note that the axis scales differ between Figs. 1 and 2.

ond. That is, the peak in $dS/dNkT$ is shifted to lower (rather than higher) temperatures and somewhat higher values; the great change in transition character described by Rajabali (1988) is not seen.

As the results of Rajabali (1988) regarding the 3UCM have been shown to be in error, the conclusions drawn in that paper must also be reconsidered. The first conclusion was that in the 3UCM model, the transition occurs at higher temperatures than in the 2UCM and 1UCM.

As may be seen from Figure 2, the transition (as marked by the maximum in $dS/dNkT$) shifts steadily to *lower* temperatures as the size of the charge-balanced unit increases. The second conclusion was that the plot of $dS/dNkT$ becomes sharper as the size of the charge-balanced unit increases, particularly for $n = 3$. As is seen in Figure 2, this conclusion is qualitatively correct, but is exaggerated in scale in Rajabali (1988). Considering the progression shown in Figure 2, it appears unlikely that any extension of this model to four or more charge-balanced unit cells would result in a close approach to a first-order transition.

As a further comment, Rajabali (1988) has claimed a degree of accuracy attained (1% or better) in a Monte Carlo solution of the 1UCM, citing Fosdick (1959). This attribution is without worth, as the accuracy to which a Monte Carlo model estimates thermodynamic parameters depends upon (among other things) the number of sites in the model, the boundary conditions, the number of Monte Carlo steps averaged to get a value for each run, and the number of Monte Carlo runs averaged together to get a final value (Binder, 1976); Fosdick suggested the accuracy which *may* be obtained, not that which *is* obtained.

References cited

Anderson, G.R., and Mazo, R.M. (1979) Electroneutrality effects on aluminum order in sodium feldspar: A two-dimensional model. Journal of Chemical Physics, 71, 1062–1065.

Barker, J.A. (1952) Methods of approximation in the theory of regular mixtures. Royal Society of London Proceedings, A216, 45–56.

Binder, K. (1976) Monte Carlo investigations of phase transitions and critical phenomena. In C. Domb and M. Green, Eds., Phase transitions and critical phenomena, vol. 5b, p. 1–105. Academic Press, New York.

Domb, C. (1974) Ising model. In C. Domb and M. Green, Eds., Phase transitions and critical phenomena, vol. 3, p. 357–484. Academic Press, New York.

Fosdick, L.D. (1959) Calculation of order parameters in a binary alloy by the Monte Carlo method. Physical Review, 116, 565–573.

Green, H.S., and Hurst, C.A. (1964) Order-disorder phenomena, 363 p. Wiley, New York.

Rajabali, G. (1988) Ordering behavior in albite using the modified sequential construction method. American Mineralogist, 73, 91–96.

Stanley, H.E. (1971) Introduction to phase transitions and critical phenomena, 308 p., Clarendon Press, Oxford.

Manuscript received May 23, 1988
Manuscript accepted October 31, 1988