Revista Brasileira de Física, Vol. 7, Nº 2, 1977

High-Ternperature Entropy of an Ionic Model for the Phase Transition in $SnCl_2 . 2H_2O$

L. C. DE FREITAS and S. R. SALINAS
Instituto de Física, Universidade de São Paulo, São Paulo SP*

Recebido em 21 de Março de 1977

We modify the basic model of the phase transition inthe hydrogen-bonded layered crystal $SnCl_2.2H_2O$ to account for the presence of ionic defects. It is easy to obtain a series expansion for the high-temperature entropy of the ionic model in terms of closed subgraphs, with vertices of degree two, of the original three-coordinated 4-8 lattice. We also show that the high-temperature entropy of the ionic model is identical to the residual entropy of a simple antiferromagnetic Ising model in a 3-4-8 lattice. This latter model can be solved exactly by a set of transformations which lead to a well studied Ising model in a Union Jack lattice.

Modificamos o modelo básico para a transição de fase no cristal $SnCl_2.2H_2O$, que apresenta ligações de hidrogênio dispostas em camadas, a fim de levar em conta a presença de defeitos iônicos. É fácil obter uma expansão em série para a entropia de transição deste modelo iônico em termos de subgráficos fechados, com vértices de grau dois, definidos na rede 4-8 original, de coordenação três. Também mostramos que a entropia de transição do modelo iônico é idêntica à entropia residual de um modelo antiferromagnético de Ising definido numa rede 3-4-8. Este modelo pode ser resolvido exatamente por um conjunto de transformações que o reduzem a um modelo de Ising bastante estudado, numa rede do tipo "Union-Jack".

* Postal address: C.P. 20516, 01000-São Paulo SP

1. INTRODUCTION

Stannous chloride dihydrate (SCD) is a layered hydrogen-bonded crystal which exhibits an order-disorder transition at T_c = 218K, Ref.1. Figure 1 depicts the schematic topology of a layer of hydrogen bonds, according to X-ray[2] and neutron diffraction results [3]. The water molecules are of two types. An oxygen of type I has both its proximal protons on hydrogen bonds joining this oxygen to other oxygens. An oxygen of type II has only one of its proximal protons on one of the three hydrogen bonds joining it to other oxygens; the remaining proton proximal to a type II oxygen points toward a chlorine atom. The phase transition has been definitely shown to be associated with the ordering of the protons on the hydrogen bonds [3].

The two-dimensional character of the hydrogen bonds in SCD is particularly attractive because it has been possible to obtain exact solutions for several two-dimensional statistical mechanical models. Salinas and Nagle[4] have solved basic protonic model of the phase transition in SCD, which had been previously proposed by Matsuo et *al*.[5]. This basic model assumes the socalled "ice-rules" in the context of SCD:

(i) each hydrogen bond has precisely one proton located in one of two off-center positions on the bond;

(i i) there are no ionic defects. That is, each oxygen of type I has precisely two proximal protons and one distal proton on its three hydrogen bonds. Each oxygen of type II has precisely one proximal and two distal protons on its three hydrogen bonds.

Rules (i) and (i i) determine all allowable protonic configurations on the hydrogen bonds. In order to calculate a partition function, and the thermodynamic properties as a functions of temperature, Salinas and Nagle have chosen a set of phenomenological vertex energies, just as Slater had done for KH_2PO_4, Ref.6. The total entropy of transition of the basic model, which had been previously obtained by Nagle[7], could be easily calculated as a by-product, making all vertex energies equal in the expression of the partition function. This theoretical value, ho-

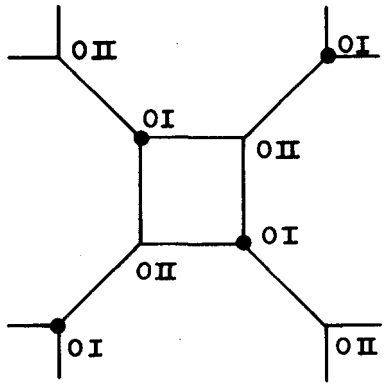

Fig. 1 — Topology of the hydrogen-bonded network with the two different types of oxigens. Oxygens of type II have one hydrogen fixed, pointing toward a Cℓ atorn. There are three inequivalent bon types, horizontal, vertical, and diagonal.

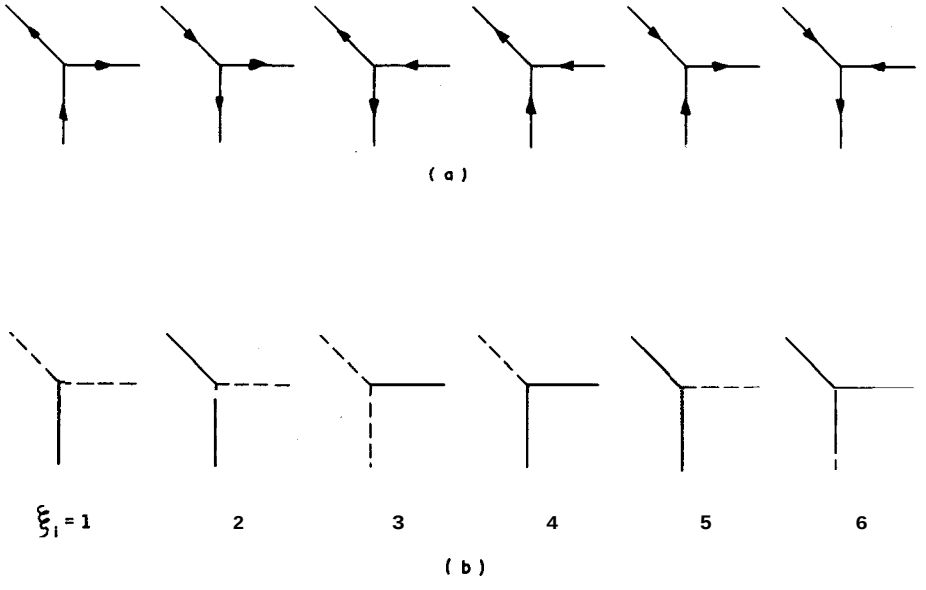

Fig. 2 — (a) Hydrogen configurations around an oxygen vertex. The direction of the arrow designates which of the two off-center positions on each hydroqen-bond is occupied by a proton. (b) The six allowable vertex configurations, in terms of half-edges, which occur in the weak-graph series expansion for the ionic model.

wever, is a bit small compared to experiments, so it is worth considering some refinements of the basic model.

Our aim in this work is to propose an ionic model for SCD, and to perforn an exact calculation of its high-temperature entropy. Ionic models allow violations of electrical neutrality, rule (ii), but do not allow the presence of Bjerrum faults, that is, of violations of rule (i). Thus, the existence of no protons per bond or of two protons per bond is supposed to be very rare and not to influence the equilibrium properties of SCD, as it is the case for ice. On the other hand, we suppose that ionic defects are quite nunerous, as in KH_2PO_4, despite being rare in ice. This is suggested by the lack of symmetry between oxygens of type I and oxygens of type II, and seems to be compatible with recent neutron diffraction results[3].

The particular ionic model we consider allows the three "free" hydrogens to be shared by both oxygens. Thus, oxygens OI and OII have either two or one hydrogen near by, which gives the six hydrogen configurations around each oxygen vertex shown in figure 2. The thermal behavior of this six-vertex model in a three-coordinated lattice has some theoretical interest on its own. However, in what follows we assume that all vertex configurations are equally probable, and evaluate the infinite temperature entropy only.

In Section 2, we obtain an exact series expansion for the high-temperature entropy in terms of weak-graphs on the 4-8 lattice. Several terms of the series, which involves closed graphs with vertices of degree 2 only, can be easily calculated to give an approximate value for the entropy of transition. The zeroth order term of the series turns out to be the same as Pauling's approximation in the context of this model. In Section 3, which is completely independent of Section 2, we show that the high-ternperature entropy of our ionic model is ident'ical to the zero temperature entropy of an antiferromagnetic Ising model in a 3-4-8 lattice. This Ising model can be solved by an application of the star-triangle, and the decoration transformation to another Ising model in the original 4-8 lattice. The approximate series result is very close to the exact value for the entropy of transition.

2. SERIES EXPANSION

The six hydrogen configurations around each oxygen vertex are characterized as shown in figure (2a); the direction of the arrow designates which of the two off-center positions on each hydrogen-bond is occupied by a proton. Each configuration of arrows in the 4-8 lattice defines an allowable state of the ionic model. If W_N is the total nurnber of states, the high-temperature entropy is given by

$$S = k \ln W_N \quad , \tag{2.1}$$

where k is the Boltzrnann constant, and N the nurnber of vertices.

As the 4-8 lattices can be divided into two sublattices, there is a one-to-one correspondence between hydrogen configurations of the ionic model and the subgraphs of certain type on the lattice. These subgraphs are obtained if we associated an edge to each arrow directed toward an oxygen of type I, for example. The total nurnber of subgraphs is W_N.

Let us now formulate the weak-graph expansion[8] for W_N. The vertex configurations (ξ_i; where i labels a lattice site, and $\xi_i = 1, \ldots, 6$) are shown in figure (2b). Each of the solid lines incident to a vertex may be throught of as a half-edge in one of the W_N subgraphs. Each of the dashed lines incident to a vertex may be thought of as a half-edge of the latticewhich is not included in the subgraph. Along the lines of weak-graph rnethod developed by Nagle[8,9] we can write

$$W_N = \sum_{\text{C edges}} \prod \frac{1}{3} \left[a + C_{ij}(\xi_i) C_{ji}(\xi_j)\right] \quad , \tag{2.2}$$

where the sum is over configurations, and the product is over all bonds ij. Tha variables $C_{ij}(\xi_i)$ are given by

$$C_{ij}(\xi_i) = a \quad \text{, if } \xi_i \text{ has a half-edge on edge } ij,$$

$$= -a^{1/2}, \text{ if } \xi_i \text{ does not have a half-edge on edge } ij.$$

Of course, the purpose of this choice is to provide for the matching and the mismatching of half-edges. We can now write:

$$W_N = \sum_G w(G), \tag{2.3}$$

where the weight of a graph G is given by

$$w(G) = \left(\frac{1}{a}\right)^{qN/2} \prod_{i=1}^{N} \sum_{\xi_i} \left(\frac{1}{a}\right)^{S_i/2} \prod_{\substack{k \\ ik \text{ in } G}} C_{ik}(\xi_i) \ . \tag{2.4}$$

We are using the standard notation of Nagle[8], where q=3 for the 4-8 lattice, and S_i is the degree of the i^{th} vertex in graph G. Now it ia easy to write expression (2.4) as

$$w(G) \equiv w(\vec{p}) = \left(\frac{1}{2}\right)^{3N/2} (6)^{p_0} (-2)^{p_2} \ , \tag{2.5}$$

where p_0 and p_2 are the number of vertices of degrees 0 and 2 respectively, and the graph G has no vertices of degree 1 or 3. So, we have

$$W_N = \left(\frac{6}{2^{3/2}}\right)^N \sum_{\vec{p}}{}' \ g(\vec{p}) \ v^{p_2} \ , \tag{2.6}$$

where $v = -1/3$, and $g(\vec{p})$ is the number of subgraphs of the 4-8 lattice defined by the vector $\vec{p} = (\vec{p}_1, \vec{p}_2, \vec{p}_3)$, that is, with p_i vertices of degree S_i for $i = 1,2,3$. The line in the sum indicates that we are restricted to subgraphs of vertices of degree two only, that is, $p_1 = p_3 = 0$.

In zeroth order, expansion (2.6) gives Pauling's approximation

$$W_N \simeq \left(\frac{6}{2^{3/2}}\right)^N \ , \tag{2.7}$$

which yields the following value for the entropy per vertex:

$$\frac{S}{kN} \simeq \ln \frac{6}{2^{3/2}} = 0.7520387\ldots \quad . \tag{2.8}$$

Without too much effort, we were able to calculate $\ln W_N$ up to terms of order v^{16}, which amounts to one of the longest available series for ice-type models[9]. So we have

$$\frac{1}{N} \ln W_N - \ln \frac{6}{2^{3/2}} = \frac{1}{4} v^4 + \frac{1}{8} v^8 +$$

$$+ v^{10} + \frac{7}{12} v^{12} - v^{14} + \frac{73}{16} v^{16} \quad . \tag{2.9}$$

This series in v is identical to the usual high-temperature $\tanh K$ series expansion for the Ising model in the 4-8 lattice. The connection between the ionic model and an Ising model in the 4-8 lattice will be fully explored in the next Section. A simple analysis of the series (2.9) yields an impressive result for high-temperature entropy, which is accurate up to at least six digits,

$$\frac{S}{kN} = 0.755162 \quad . \tag{2.10}$$

In Section 3, we compare the approximate value (2.10) with the exact result. This will be another example of the potentialities of the series method.

3. THE EXACT RESULT

The exact solution is obtained by observing that the high-temperature entropy of the ionic model is identical to the zero-temperature entropy of an antiferromagnetic Ising model (with spin 1/2 and nearest-neighbor interactions), in a 3-4-8 lattice. This 3-4-8 lattice is obtained from the basic 4-8 (or bathroom tile) lattice (Figure 3a) by the combination of a decoration[10,11] and a star-triangle transformation (Figure 3c) Ref. 11. We justify these assertions in the following way: (i) suppose that there is a spin at the middle of each bond of the basic 4-8 lattice

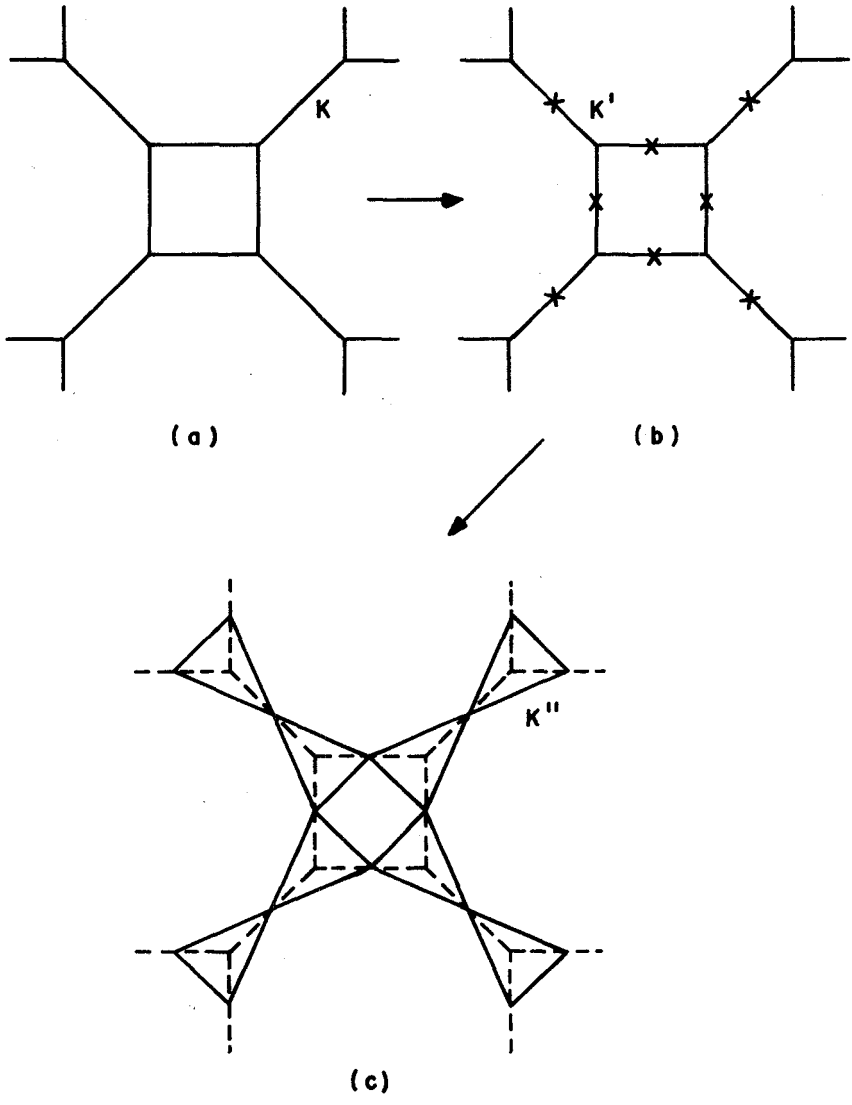

FIG.3 - (a) basic 4-8 lattice; (b) decorated 4-8 lattice;, (c) 3-4-8 lattice. The decoration transformation applied to the Ising model inthe 4-8 lattice **(a)** gives the Ising model in the decorated lattice (b). The star-triangle transformation applied to the Ising rnodel in the decorated 4-8 lattice (b) gives the Ising model in the 3-4-8 lattice (c).

(this leads to the decorated lattice of Figure 3b); (ii) suppose that the spin is pointing up (plus) if the arrow along the bond is directed from an oxygen of type I towards an oxygen of type II, and is pointing down (minus) otherwise; (iii) define an antiferromagnetic Ising model in "3-4-8" lattice of figure 3c. It is easy to see that each allowable configuration of arrows in the basic bathroom tile lattice corresponds to a certain configuration of spins in the antiferromagnetic transforrned lattice of Figure 3c; moreover, only spin configurations such that the three spins around any triangle do not have the same sign are going to occur. But these can be recognized as the configurations of the highly degenerate ground state of the antiferromagnetic spin -1/2 Ising model defined in the "3-4-8" lattice (this degeneracy of the ground state is a well-known fact for the Ising lattices that do not admit the subdivision into two sublattices; for example, the zero-temperature entropies of the antiferromagnetic triangular and the "kagomé" lattices are established results[11].

Our task then is to evaluate the partition function for an antiferromagnetic Ising model in the "3-4-8" lattice. This will be achieved by writing it, through the star-triangle and the decoration transformations (as indicated in Figure 3), in terms of the partition function for an Ising model in the 4-8 lattice.

(a) The star-triangle transformation[11] gives

$$Z_S(K') = g^{N_S} Z_T(K'') , \tag{3.1}$$

$$\exp(4K'') = \frac{\cosh 3K'}{\cosh K'} , \tag{3.2}$$

$$g = 2(\cosh 3K' . \cosh^3 K')^{1/4} , \tag{3.3}$$

where Z_S and Z_T are the partition functions for the star (Figure 3b) and the triangle lattices (Figure 3c); K' and K'' are the interaction parameters of the lattices divided by kT; in this particular case, N_S, the number of star vertices, is the same as N, the total number of spins in the basic 4-8 lattice.

(b) The decoration transformation[11] gives

$$Z_D(K') = f^{N_D} Z_B(K), \tag{3.4}$$

$$\exp(2K) = \cosh 2K' , \tag{3.5}$$

$$f^2 = 4 \cosh 2K' . \tag{3.6}$$

The decorated lattice is our old star lattice, that is, $Z_D = Z_S$, and the basic lattice is in Figure 3a. For this particular case, the following holds:

$$N_D = \frac{3N}{2} , \tag{3.7}$$

where N_D is the number of spins in the decorated lattice (that is, the number of bonds in the basic 4-8 lattice).

After some straighforward algebraic manipulations, we have:

$$Z_T(K'') = \frac{2^{3N/2} \left[\frac{1}{2} \left(e^{4K''} + 1 \right) \right]^{3N/4}}{e^{NK''} \left[e^{4K''} + 3 \right]^{N/2}} Z_B(K), \tag{3.8}$$

where

$$K = \frac{1}{2} \ln \left[\frac{1}{2} \left(e^{4K''} + 1 \right) \right] . \tag{3.9}$$

In the limit $T \to 0$, or $K'' = -\frac{|J|}{kT} \to -\infty$, we obtain

$$k \ln Z_T(K'' \to -\infty) = \frac{kN}{2} \ln \frac{2^{3/2}}{3} + \frac{N|J|}{T} + k \ln Z_B\left(K = -\frac{\ln 2}{2}\right). \tag{3.10}$$

From this expression, we have the ground state energy

$$U = - N|J| \ , \tag{3.11}$$

and the zero-temperature entropy of the antiferromagnetic Ising model in the "3-4-8" lattice,

$$S = \frac{kN}{2} \ln \frac{2^{3/2}}{3} + k \ln Z_B(K = - \frac{\ln 2}{2}), \tag{3.12}$$

where Z_B, N and K refer to the basic 4-8 or bathroom-tile lattice.

As far as we know, the Ising model in the 4-8 lattice has been solved only in the book by Hurst and Green[12].

However, the notation of these authors is not always very transparent, and they do not write down the prefactors of the partition function. So we decided to use a dual transformation[11] which relates the bathroom tile lattice to its dual, a sort of "Union Jack" lattice (see Figure 4) worked out in detail by Vaks et al.[13]. Before proceeding with this transformation, let us note that

$$Z_B(K=-\frac{\ln 2}{2}) = Z_B(K=+\frac{\ln 2}{2}) \tag{3.13}$$

(that is, the basic lattice is loose packed, its antiferromagnetic ground state being non-degenerate), and that

$$\tanh K = \frac{1}{3} \ , \text{ for } \ K = \frac{\ln 2}{2} \ . \tag{3.14}$$

Now we can use the formula"

$$\frac{Z_B(K)}{2^{N/2}(\sinh 2K)^{N/2}} = \frac{Z^*(K^*)}{2^{N^*/2}(\sinh 2K^*)^{N^*/2}} \ , \tag{3.15}$$

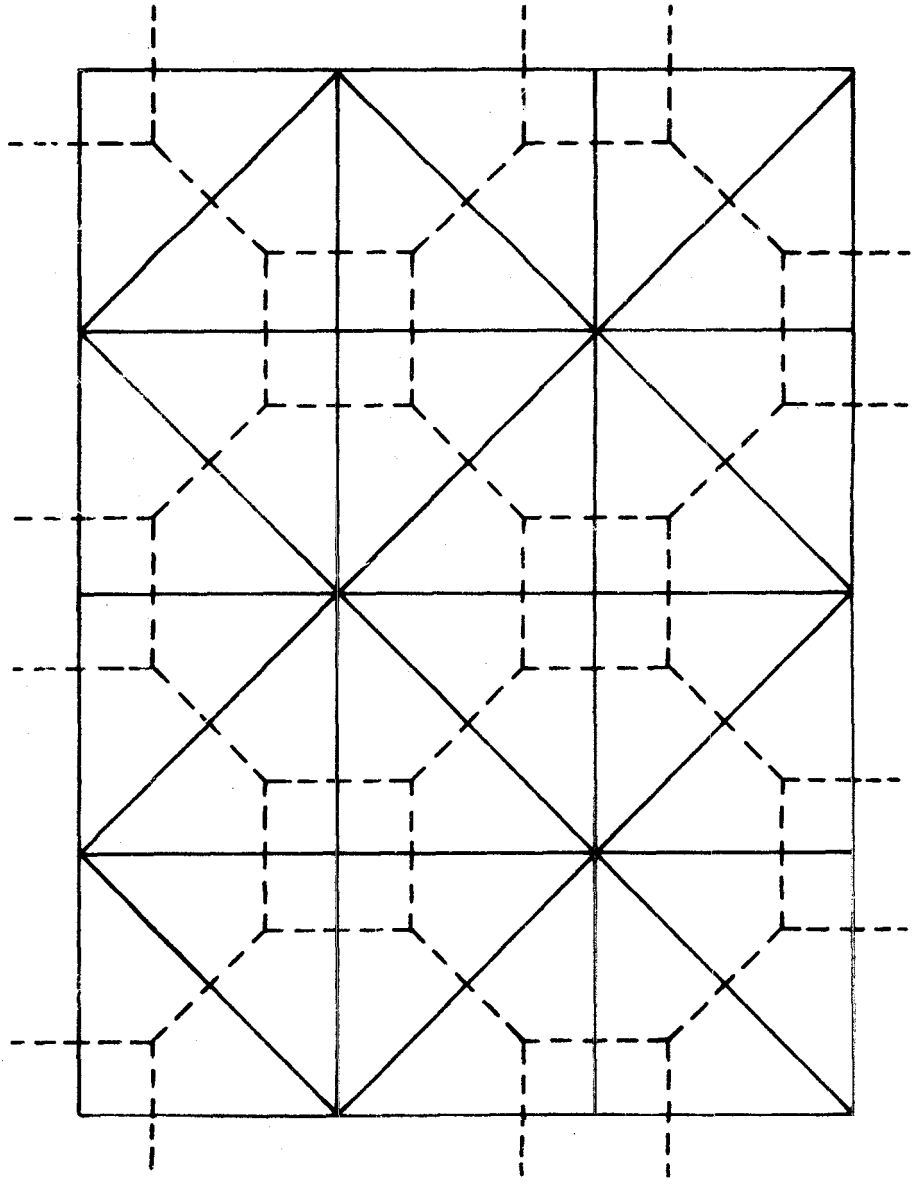

FIG.4 - The 4-8 lattice (dashed lines) and its dual, the "Union Jack" lattice.

where

$$\exp(2K^*) = \text{cotanh } K \ , \tag{3.16}$$

or

$$(\sinh 2K^*)(\sinh 2K) = 1 \ , \tag{3.17}$$

and the superscript star (*) refers to the dual lattice. The entropy (equation 3.12) can then be written as:

$$\frac{S}{Nk} = \ln \frac{3^{1/4}}{2^{1/2}} + \frac{1}{2}\left[\frac{1}{N^*} \ln Z^*(\tanh K^* = \frac{1}{2})\right] . \tag{3.18}$$

Using the results of Vaks *et al.*,[13] and evaluating one of their integrals, we have:

$$\frac{1}{N^*} \ln Z^*(x) = -\frac{1}{2} \ln \frac{(1-x^2)^3}{4} + \frac{1}{4} \ln \frac{A}{2} + \frac{1}{8\pi} \int_0^{2\pi} d\theta \ln \{(1 - \frac{B}{A}\cos\theta) +$$

$$+ \left[1 - \frac{B^2}{A^2} - 2\frac{B}{A}(1 + \frac{C}{A})\cos\theta + (\frac{B^2}{A^2} - \frac{C^2}{A^2})\cos^2\theta\right]^{1/2}\} \ . \tag{3.19}$$

where

$$x = \tanh K^* = \frac{1}{2} \ , \tag{3.20}$$

and

$$A = (x^2 + 1)^2 \left[x^8 + 14x^4 + 1 + 16x^3(x^2 + x + 1\right] \ ,$$

$$B = 2x(1 - x^2)^3(x^2 + 1)(x + 1)^2 \ , \tag{3.21}$$

$$C = 4x^2(x^2 - 1)^4 \ .$$

The integral of expression (3.19) was evaluated numerically, and the final result for the entropy per vertex, with six digits, is

$$\frac{S}{kN} = 0.755162 \ . \qquad (3.22)$$

This value shows how accurate is the series result (2.10). Indeed, Pauling's approximation, despite being a lower bound for the exact value, already gives a very good result. The entropy of transition of the basic model[4], which is of the order of the experimental values, is about four times smaller than the value for the ionic model. A too large entropy of transition does not rule out the ionic model. However, in order to fully assess its physical significance, we have to go beyond this high temperature calculation and define vertex energies for computing the thermodynamic properties as a function of temperatura. This is a more difficult task, which will be the subject of furthei- study.

We thank John F. Nagle for many discussions.

REFERENCES

1. H. Kiriyama, J. Phys. Soc. Jap. Suppl. 28, 114 (1970); T. Matsuo, M. Oguni, H. Suga and S. Seki, Proc. Jap. Acad. 48, 237 (1972).
2. H. Kiriyama, K. Kitahama, O. Nakamura and R. Kiriyama, Bull. Chem. Soc. Jap. 46, 1389 (1973).
3. R. Kiriyama, H. Kiriyama, K. Kitahama and O. Nakamura, Chem. Lett. (Chem.Soc.Jap.), 1105 (1973).
4. S.R. Salinas and J.F. Nagle, Phys.Rev. *B9*, 4920 (1974).
5. T. Matsuo, M.Oguni, H.Suga and S.Seki, in *Physics and Chemistry of Ice,* ed. by E. Whalley, S.J. Jones and L W. Gold (Royal Society of Canada, Ottawa, 1973), page 272.
6. J.C. Slater, J.Chem.Phys. 9, 16 (1941).
7. J.F. Nagle in *Physics and Chemistry of Ice,* ed. By E. Whalley, S.J. Jones and L.W. Gold (Royal Society of Canada, Ottawa, 1973), page 175.

8. J.F. Nagle, J.Math.Phys. 9, 1007 (1968).
9. J.F. Nagle, in *Phase Transitions and Critical Phenomena,* ed. by C. Domb and M.S. Green (Academic Press, London, 1974), vol. 3, page 653.
10. I. Syozi, Prog. Theor. Phys. 6, 306 (1951).
11. I. Syozi, in *Phase Transitions and Critical Phenomena,* ed. by C. Domb and M. S. Green (Academic Press, London, 1972), vol. 1 page 270.
12. H.S. Green and C.A. Hurst, *Order-Disorder Phenomena,* Interscience Publishers, N. York, 1964.
13. V.G. Vaks, A.I. Larkin and Yu. N. Ovchinnikov, Sov. Phys., JETP, *22,* 820 (1966).