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BRIEF REPORTS

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One-dimensional ferroelectric model with dipole-dipole interactions

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A one-dimensional ferroelectric six-vertex model with dipole-dipole interactions between nearest neighboring vertices has been calculated exactly by the transfer matrix method. The phase transition is first order, the low temperature phase is completely ordered ferroelectrically, and the correlation functions in the high temperature phase exhibit new periodic behavior with the periodicity depending upon detailed competition among the interaction parameters. [S1063-651X(98)10810-3]

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I. INTRODUCTION

Crystals with hydrogen bonds undergo phase transition induced by proton ordering specified by the ice rule [1], which forbids charged configurations (with very high energies $\xi \to \infty$) of protons. The thermodynamics of these systems is usually investigated by six-vertex models that take into account differences in energies of the allowed vertices and their compatibility with neighboring vertices [2]. Such lattice models have been solved exactly in one [3] or two dimensions [2]. In the one-dimensional model with finite ξ, no phase transition occurs. However, it was shown by Nagle [3] that the one-dimensional ferroelectric model with infinite ξ undergoes a first-order phase transition at the same temperature $T_c = \varepsilon / k_B \ln 2$ as the two-dimensional six vertex model and the thermodynamic function has a large and sharp anomaly in the vicinity of T_c, causing a finite entropy jump. It was also shown [3] that for physically realistic finite values of ξ, while the thermodynamic properties are analytic, a very sharp specific heat anomaly remains. These results suggest that the thermal behavior of such proton ordering systems can be fruitfully investigated using the ice rule in one dimension.

For the hydrogen bonded ferroelectrics, such as KH_2PO_4, dipole-dipole interactions are present. Therefore, investigation of the influence of dipole-dipole interactions on the thermodynamics of the phase transition should be of interest. In this paper, we discuss the influence of the dipole-dipole interaction taking into account the ice rule on the phase transition. This modified six-vertex model is solved using a transfer matrix method.

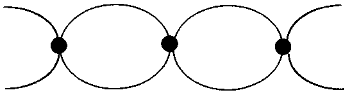

FIG. 1. One-dimensional H-bonded chain that consists of N vertices.

II. MODEL

The one-dimensional, four-fold coordinated chain with N vertices bonded by double hydrogen bonds is shown in Fig. 1. It is assumed that a proton on each of the hydrogen bonds is on either one of two possible sites. Then there are 2^4 types of vertices depending on the different arrangements of the protons on the four adjoining hydrogen bonds. Only six vertices shown in Fig. 2 obey the ice rule. The configuration states of those six vertices are denoted by the six unit vectors $\boldsymbol{\sigma}(k)$ $(k=1,2,\ldots,6)$. As shown in Fig. 2, they are divided into three classes with the energies ω_1 $(=-\omega)$ for $k=1,2$, ω_2 $(=-\omega+\varepsilon_1)$ for $k=3,4$ and ω_3 $(=-\omega+\varepsilon_2)$ for $k=5,6$. Furthermore, the dipole-dipole interactions, satisfying the ice rule between nearest neighboring vertices, can be divided into three classes of interaction by considering the pair vertex symmetry, as shown in Fig. 3. We define the interaction energies between the neighboring parallel dipole

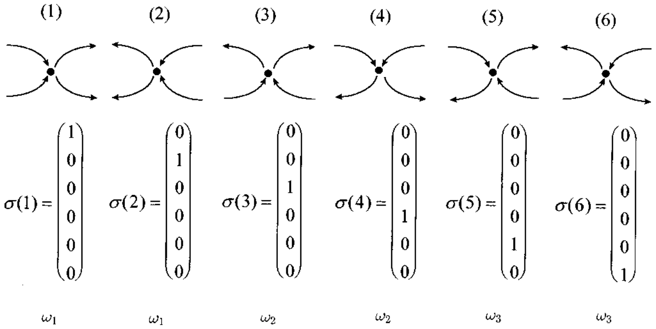

FIG. 2. Six-vertix model. Configuration states $\boldsymbol{\sigma}(k)$ $(k=1,2,\ldots,6)$ are divided into three classes with the energies ω_1 $(=-\omega)$ for $k=1,2$, ω_2 $(=-\omega+\varepsilon_1)$ for $k=3,4$ and ω_3 $(=-\omega+\varepsilon_2)$ for $k=5,6$ from the viewpoint of symmetry.

moments by v_1 $(=-v)$, the neighboring antiparallel ones by v_2 $(=-v+\delta_1)$, and the neighboring ones being at right angles to each other by v_3 $(=-v+\delta_2)$. We note that the parameters ε_i and δ_i will vary with the specific crystal structure of hydrogen bonded crystals in ways that are difficult to quantify.

The energy of each microstate of the model consists of the sum of the vertex energies ω_i shown in Fig. 2 and the nearest neighbor dipolar pair energies v_i shown in Fig. 3. Further neighbor dipolar pair energies are small and will be ignored. No other nearest neighbor pairs are allowed than those shown in Fig. 3 because for other pairs the arrows on at least one of the bonds joining the two vertices run in opposite directions; this corresponds to zero or two protons on a bond, which costs much higher energy which is taken to be infinity in ice-rule and six-vertex models.

Then, the partition function Z_N for one-dimensional chain with N vertices is obtained using the transfer matrix

$$\boldsymbol{M}=\begin{pmatrix}\boldsymbol{M}_1 & \boldsymbol{O}\\ \boldsymbol{O} & \boldsymbol{M}_2\end{pmatrix}e^{\beta(\omega+v)} \tag{1}$$

with

$$\boldsymbol{M}_1=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix},\quad \boldsymbol{M}_2=\begin{pmatrix}0 & e^{-\beta(\varepsilon_1+\delta_1)} & e^{-\beta(\varepsilon_1+\delta_2)} & 0\\ e^{-\beta(\varepsilon_1+\delta_1)} & 0 & 0 & e^{-\beta(\varepsilon_1+\delta_2)}\\ 0 & e^{-\beta(\varepsilon_2+\delta_2)} & e^{-\beta\varepsilon_2} & 0\\ e^{-\beta(\varepsilon_2+\delta_2)} & 0 & 0 & e^{-\beta\varepsilon_2}\end{pmatrix}. \tag{2}$$

It is noted that the transfer matrix $\boldsymbol{M}$ breaks up into two diagonal blocks: 2×2 unit matrix $\boldsymbol{M}_1$ and 4×4 matrix $\boldsymbol{M}_2$, namely, $\boldsymbol{M}=\boldsymbol{M}_1\oplus\boldsymbol{M}_2$, where $\oplus$ means direct sum. Finally, Z_N can be calculated analytically as

$$Z_N=\sum_{k_1=1}^{6}\boldsymbol{\sigma}^T(k_1)\boldsymbol{M}^N\boldsymbol{\sigma}(k_1)=\mathrm{Tr}\{(\boldsymbol{M})^N\}=e^{N\beta(\omega+v)}\sum_{n=1}^{6}\lambda_n^N, \tag{3}$$

where λ_1 and λ_2 come from $\boldsymbol{M}_1$ and $\lambda_3\sim\lambda_6$ come from $\boldsymbol{M}_2$. The eigenvalues can be written as follows:

$$\lambda_1=\lambda_2=1, \tag{4}$$

$$\lambda_3=\frac{e^{-\beta\varepsilon_2}}{2}\{1+e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)}+\sqrt{(1-e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)})^2+4e^{-\beta(\varepsilon_1-\varepsilon_2+2\delta_2)}}\}, \tag{5}$$

$$\lambda_4=\frac{e^{-\beta\varepsilon_2}}{2}\{1+e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)}-\sqrt{(1-e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)})^2+4e^{-\beta(\varepsilon_1-\varepsilon_2+2\delta_2)}}\}, \tag{6}$$

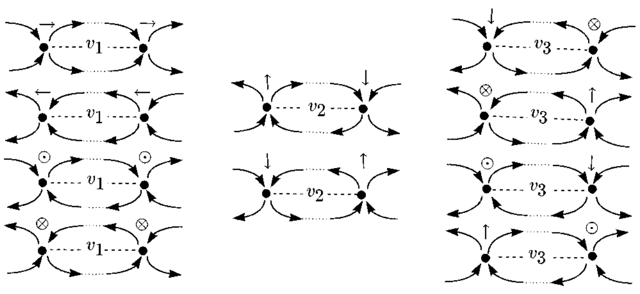

FIG. 3. Ten types of the dipole-dipole interactions, which are divided into three classes with the energies v_1 $(=-v)$, v_2 $(=-v+\delta_1)$, and v_3 $(=-v+\delta_1)$. The arrow marked above each vertex denotes the dipole moment.

$$\lambda_5=\frac{e^{-\beta\varepsilon_2}}{2}\Big\{1-e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)}+\sqrt{(1+e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)})^2-4e^{-\beta(\varepsilon_1-\varepsilon_2+2\delta_2)}}\Big\}, \tag{7}$$

and

$$\lambda_6=\frac{e^{-\beta\varepsilon_2}}{2}\Big\{1-e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)}-\sqrt{(1+e^{-\beta(\varepsilon_1-\varepsilon_2+\delta_1)})^2-4e^{-\beta(\varepsilon_1-\varepsilon_2+2\delta_2)}}\Big\}, \tag{8}$$

where λ_3, which is the largest eigenvalue of the matrix $\boldsymbol{M}_2$, is unique as shown by Frobenius's theorem and a positive analytic function that increases monotonically with temperature T. Now we consider the case of $N\to\infty$. If λ_3 is smaller than $\lambda_1=\lambda_2=1$, then $Z_N=2\exp\{N\beta(\omega+v)\}$, while if $\lambda_3>1$ then $Z_N=\exp\{N\beta(\omega+v)\}\lambda_3^N$. Consequently, the free energy F_N $(=-k_BT\ln Z_N)$ is given as

$$F_N/N=\begin{cases}-(\omega+v) & \text{for }\ \lambda_3<1\\ -(\omega+v)-k_BT\ln\lambda_3 & \text{for }\ \lambda_3>1\end{cases}. \tag{9}$$

III. FIRST-ORDER TRANSITION

If ε_2 is negative, then λ_3 is always larger than unity for any temperature and the free energy is analytic for all T. Consequently no phase transition occurs for $\varepsilon_2<0$.

In contrast to this, for $\varepsilon_2>0$, the possibility exists that λ_3 increases continuously from $\lambda_3<1$ to $\lambda_3>1$ as the temperature increases from $T=0$. That is, if the following relations hold:

$$\varepsilon_2>0,\quad \delta_1+\varepsilon_1>0,$$

and (10)

$$\varepsilon_1+\varepsilon_2+2\delta_2>0,$$

then λ_3 increases from 0 at $T=0$ to 2 at $T=\infty$. Consequently, the system undergoes a first-order transition at a

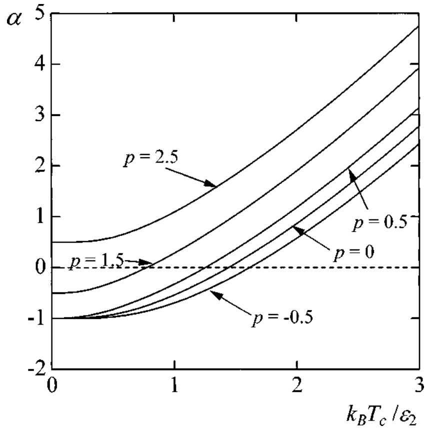

FIG. 4. The α dependences of T_c for various values of p. The ordered phase (the low temperature phase) lies above α-T_c curve and the disordered phase (the high temperature phase) lies below.

transition temperature T_c with a jump in entropy ΔS, where the T_c is determined by the substitution of $\lambda_3=1$ into Eq. (5) and is obtained as

$$\exp(-\hat{\beta}_c\alpha)=\frac{\exp(\hat{\beta}_c)\{\exp(\hat{\beta}_c)-1\}}{\exp(\hat{\beta}_c)+\exp(\hat{\beta}_c p)-1}, \tag{11}$$

where

$$\hat{\beta}_c=\frac{\varepsilon_2}{k_BT_c}, \quad \alpha=\frac{\delta_1+\varepsilon_1}{\varepsilon_2}-1, \quad \text{and } p=\frac{\delta_1-2\delta_2}{\varepsilon_2}. \tag{12}$$

If we put $\delta_1=\delta_2=0$ $(p=0)$ into Eq. (11), which corresponds to the case for the consideration of the ice rule only without the dipole-dipole interaction, then we obtain

$$\exp\left(-\frac{\varepsilon_2}{k_BT_c}\right)=1-\exp\left(-\frac{\varepsilon_1}{k_BT_c}\right). \tag{13}$$

If one replaces ε_1 with $\varepsilon_1'-\varepsilon_2'$ and ε_2 with $-\varepsilon_2'$, corresponding to Zubkus's definitions [4] of the configuration energies, then the formulas (13) agrees with the result of Zubkus's model:

$$\exp\left(-\frac{\varepsilon_2'}{k_BT_c}\right)=1+\exp\left(-\frac{\varepsilon_1'}{k_BT_c}\right) \quad (\varepsilon_2'<0). \tag{14}$$

Especially, in the case $\varepsilon_1=\varepsilon_2$ in Eq. (13) [or $\varepsilon_1'=0$ in Eq. (14)], then Nagle's result [3] $T_c=\varepsilon/k_B\ln 2$ is obtained, where $\varepsilon=\varepsilon_2$ (or $\varepsilon=-\varepsilon_2'$).

In Fig. 4, the α dependences of T_c for various values of p are illustrated. The transition temperature T_c increases as p decreases or α increases. When T_c approaches zero, α approaches α_0, where $\alpha_0=-1$ for $p<1$ and $\alpha_0=p-2$ for $p>1$. Therefore, the first-order transition occurs in the region satisfying both inequalities of $\alpha>-1$ and $\alpha>p-2$, which agree with the relations (10). The curves α versus T_c for various values of p, shown in Fig. 4, represent a coexisting surface on (T_c,α,p).

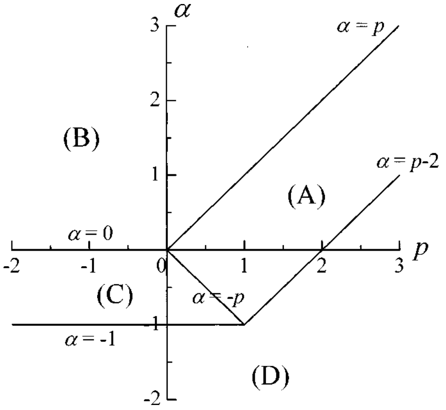

FIG. 5. Region of different ground states of the H phase in the α-p plane. The structure in region (A) is [5,4,6,3,5, . . .], in region (B) is [5,5,5, . . .] (or [6,6,6, . . .]), and in region (C) is [4,3,4,3, . . .]. In region (D), no phase transition occurs.

IV. CORRELATION FUNCTIONS OF PHASES

In this section, for the case of $\varepsilon_2>0$ for which a first-order transition occurs, we discuss the dominant structure. Let us define a structure in which the configuration states of vertices align in order with $\boldsymbol{\sigma}(k_1),\boldsymbol{\sigma}(k_2),\boldsymbol{\sigma}(k_3),\ldots$ $(k_i=1-6)$, as $[k_1,k_2,k_3,\ldots]$.

For $T<T_c$ the low-temperature phase (L phase) with free energy per vertex $F_N/N=-(\omega+v)$ is stable. The L phase is a ferroelectric one whose structure is composed of only one configuration state $\boldsymbol{\sigma}(1)$ [or $\boldsymbol{\sigma}(2)$] (refer to Fig. 2) with configuration energy ω_1 $(=-\omega)$ and the dipole-dipole interaction energy v_1 $(=-v)$. Then the structure of the L phase is represented as [1,1,1, . . .] (or [2,2,2, . . .]).

For $T>T_c$, the high-temperature phase (H phase) with the free energy per vertex $F_N/N=-(\omega+v)-k_BT\ln\lambda_3$ $(\lambda_3>1)$ becomes stable. On the coexisting surface, two phases (L and H phase) coexist. We are interested in how the structure of the H phase varies in the phase diagram in Fig. 5. Since the H phase is disordered, only short range order exists. To describe this short range order it is convenient to describe the long range order that would exist in the H phase if the transition into the L phase did not take place. This is the ground state $(T=0)$ of the H phase whose energy per vertex is higher by $\Delta\varepsilon$ than that of L phase, where

$$\Delta\varepsilon=-\lim_{T\to 0}k_BT\ln\lambda_3. \tag{15}$$

For $\alpha>0$, $\Delta\varepsilon$ is

$$\Delta\varepsilon=\begin{cases}(\varepsilon_1+\varepsilon_2)/2+\delta_2 & \text{for } p>\alpha\\ \varepsilon_2 & \text{for } p<\alpha\end{cases} \tag{16}$$

and for $\alpha<0$

$$\Delta\varepsilon=\begin{cases}(\varepsilon_1+\varepsilon_2)/2+\delta_2 & \text{for } p>-\alpha\\ \varepsilon_1+\delta_1 & \text{for } p<-\alpha .\end{cases} \tag{17}$$

In Fig. 5 in the region (A) the H phase at the ground state is a periodic structure [5,4,6,3,5, . . .] whose energy is higher by $\Delta\varepsilon=(\varepsilon_1+\varepsilon_2)/2+\delta_2$ than that of L phase, in the region (B) a ferroelectric phase [5,5,5, . . .] (or [6,6,6, . . .]) being higher by $\Delta\varepsilon=\varepsilon_2$ than that of L phase, and in the region (C) a periodic structure $[4,3,4,3,\ldots]$ being higher by $\Delta\varepsilon=\delta_1+\varepsilon_1$ than that of L phase. In the region (D), no phase transition occurs.

Consequently, in the case of $\varepsilon_2>0$, it is clear that the first order transition occurs by competition between the L phase and the H phase and the correlation functions in the H-phase exhibit the periodic behavior with the periodicity depending upon detailed competition among the interaction parameters. On the other hand, in the case of $\varepsilon_2<0$ where no phase transition occurs, the H phase is stable for any temperature and the structure is the same as the case of $\varepsilon_2>0$ and $T>T_c$.

Since the interaction parameters depend delicately upon the detailed geometry of H-bonding groups in actual crystals, this work shows that a variety of short range ordering may be expected. Experimental observation of such short range ordering could then be used, together with this kind of theory, to estimate the basic ε_i and δ_i interactions energies in hydrogen bonded crystals.

[1] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1938).

[2] E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, New York, 1971), Vol. 1, p. 332.

[3] J. F. Nagle, Am. J. Phys. **36**, 1114 (1968); C. Mjkenezes and S. R. Salinas, Nuovo Cimento B **39**, 105 (1977).

[4] V. E. Zubkus, V. A. Onischuk, E. E. Tornau, and A. Rosengren, Phys. Rev. B **49**, 3774 (1994).