

Cluster Approximations for Order-Disorder-Type Hydrogen-Bonded Ferroelectrics. I. Small Clusters

R. BLINC* AND S. SVETINA

*University of Washington, Seattle, Washington
and*

Nuclear Institute "J. Stefan," Ljubljana, Yugoslavia

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A high-temperature cluster series is derived for the partition function of an order-disorder-type hydrogen-bonded ferroelectric crystal, taking into account a simplified interaction between protons as well as the overlap of the protonic wave functions between the two sites in a hydrogen bond. The zero-order result is the Weiss molecular-field approximation, and the two-particle-cluster result reduces in the classical limit to the Bethe treatment of the Ising model. The specific properties of crystal lattices can be taken into account in higher order terms. The results of the above approximations as well as the results of an "Oguchi"-type treatment, valid at all temperatures, are compared with exact solutions in the case of a simple soluble model.

I. INTRODUCTION

WITHIN the past several years, a considerable effort has been made to understand the nature of second-order phase transitions.¹ In particular, a recent study of the far-infrared absorption spectra of KH_2PO_4 type ferroelectrics² has shown that the ferroelectric transitions in these crystals cannot be explained simply in terms of an instability of the lattice against a certain vibrational mode as in the case of perovskite-type ferroelectrics,³ and that the order-disorder nature of the transitions has to be taken into account. Contrary to the case of the Ising and Heisenberg⁴ models, however, relatively little attention has been devoted to the statistical mechanics of order-disorder-type hydrogen-bonded ferroelectric crystals.^{1,5}

The elementary excitations from the ferroelectric ground state of a simplified model of a KH_2PO_4 -type ferroelectric have recently been studied by de Gennes,⁶ but any really satisfactory treatment at intermediate temperatures is still lacking.

Though the breakdown of the classical molecular-field model near the critical point has been clearly shown,^{5,7} this model is still widely used because of its simplicity.⁸⁻¹¹ In particular, the quantization of the

protonic vibrational energy levels (which seems to be important for the ferroelectric behavior of such crystals in view of the rather large isotope effects on replacing hydrogen by deuterium,⁵ can be easily taken into account within the molecular field model.^{9,10} Quantum effects have so far not been incorporated in the Slater-type theories¹²⁻¹⁵ of the ferroelectric phase transitions. These theories, which have shown relatively good results, though they were not able to give a really satisfactory explanation for the observed isotope effects and predicted a consistently too large heat of the transition, are based on the specific properties of KH_2PO_4 -type crystal lattices. They take certain interactions into account exactly and others only on the average, but neglect the quantization of the protonic energy levels.

The purpose of the present work is to derive a cluster approximation for the partition function of an order-disorder-type hydrogen-bonded ferroelectric crystal, which should be capable of taking into account simultaneously all important interactions, i.e., short-range and long-range forces as well as the effects of the quantization of the protonic energy levels. The zero-order result is the Weiss molecular-field approximation, and the two particle cluster result is in the classical limit identical with the Bethe¹⁶ treatment of the Ising model. The specific properties of crystal lattices can be incorporated in higher order terms. As shown in a subsequent paper, the four-particle-cluster result for KH_2PO_4 reduces in the classical limit to the Slater-Takagi-Senko-Uehling model of the order-disorder transition in this crystal.

We would like to stress that our purpose is to derive a high-temperature-cluster expansion, where successive approximations are made by taking progressively larger linked clusters. We do not claim that the leading terms of this series represent a satisfactory approximation,

* On leave of absence from Nuclear Institute "J. Stefan," Ljubljana, Yugoslavia. Present address: Nuclear Institute "J. Stefan," Ljubljana.

¹ Proceedings of the International Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 1965 (to be published).

² A. S. Barker, Jr., and M. Tinkham, *J. Chem. Phys.* **38**, 2257 (1963).

³ W. Cochran, *Advan. Phys.* **9**, 387 (1960); P. W. Anderson, paper presented at the Conference on Dielectrics, Moscow, 1958 (unpublished).

⁴ See for example: (a) G. A. Baker, *Phys. Rev.* **129**, 99 (1963); (b) B. Strieb, H. B. Callen, and G. Horwitz, *Phys. Rev.* **130**, 1798 (1963).

⁵ F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

⁶ P. G. De Gennes, *Solid State Commun.* **1**, 132 (1964).

⁷ S. Hoshino, T. Mitsui, F. Jona, and R. Pepinsky, *Phys. Rev.* **107**, 1255 (1957).

⁸ T. Mitsui, *Phys. Rev.* **111**, 1259 (1958).

⁹ J. Pirrenne, *Physica* **15**, 1019 (1949).

¹⁰ R. Blinc, *J. Phys. Chem. Solids* **13**, 204 (1960).

¹¹ A. F. Devonshire, *Advan. Phys.* **3**, 85 (1954).

¹² J. C. Slater, *J. Chem. Phys.* **9**, 16 (1961).

¹³ Y. Takagi, *J. Phys. Soc. Jap.* **3**, 271 (1948).

¹⁴ M. Senko, *Phys. Rev.* **121**, 1599 (1961).

¹⁵ H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, *Phys. Rev.* **133**, A165 (1964).

¹⁶ H. Bethe, *Proc. Roy. Soc. (London)* **A150**, 552 (1935).

though small clusters might be suitable for a description of certain properties of ferroelectric crystals in a restricted temperature range.

II. HAMILTONIAN

The basic aspects of our problem can be studied on the following simplified model: each of the N protons of our system occupies one of the two states $k = \uparrow$ or \downarrow inside a given hydrogen bond and interacts with q nearest neighbors. In the representation of localized particles, the given problem is described by the following Hamiltonian (Appendix A):

$$H = H_i + H_I = \sum_{i=1}^N [-\Gamma(S_i^+ + S_i^-) - \frac{1}{4}J \sum_{j=1}^q (n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow})], \quad (1)$$

where n_k is the proton "number" operator

$$n_{ik} = b_{ik}^\dagger b_{ik}, \quad k = \uparrow, \downarrow \quad (2)$$

and $(S_i^+ + S_i^-)$ is the proton "jump" operator

$$\begin{aligned} S_i^+ &= b_{i\uparrow}^\dagger b_{i\downarrow}, \\ S_i^- &= b_{i\downarrow}^\dagger b_{i\uparrow}, \end{aligned} \quad (3)$$

with b_{ik}^\dagger and b_{ik} being the creation and annihilation operators for the proton at the site i and the state k : $\Psi_{ik} = b_{ik}^\dagger |0\rangle$.

The vacuum state $|0\rangle$ is defined as a state with no proton present. Γ stands for the proton tunneling integral

$$-\Gamma_i = \langle \Psi_{i\uparrow} | H_i | \Psi_{i\downarrow} \rangle, \quad (4)$$

and J for the nearest neighbor's interaction parameter. In this paper we shall consider only the case $J > 0$. The assumption of the model that there is one and only one proton in each hydrogen bond can be expressed by

$$n_{i\uparrow} + n_{i\downarrow} = 1. \quad (5)$$

The above model represents an extreme simplification since the protons are assumed to move in a rigid lattice potential, thus neglecting proton-lattice interactions.¹⁷ However, as shown in the subsequent paper, a major part of this interaction as well as long range forces and specific properties of crystal lattices (which have also been neglected) can be readily incorporated in our model without changing the basic procedure, so that their omission at this point seems to be justified. The same is the situation with the effects of one proton on the tunneling integral of another, which are as well taken into account in the subsequent paper. The neglect of higher vibrational states of the proton is not serious since they are in the 2000 cm^{-1} range, while kT_e is of the order of 200 cm^{-1} . It should be noted that for the

classical limit ($\Gamma = 0$) the above Hamiltonian reduces to the Hamiltonian of the Ising model.

As ferroelectricity represents an example of the so called "broken symmetry" [see, for example, R. H. Brout, *Phase Transitions* (W. A. Benjamin Inc., 1965)] the variational ground state of the above Hamiltonian can be easily derived with the help of a trial function,

$$\Psi = \prod_{i=1}^N [(\cos\theta)b_{i\uparrow}^\dagger + (\sin\theta)b_{i\downarrow}^\dagger] |0\rangle, \quad (6)$$

which has a lower symmetry than the original Hamiltonian. Minimizing the expectation value,

$$E(\theta) = \langle \Psi | H | \Psi \rangle = N[-(\sin 2\theta)\Gamma - (\cos^2 2\theta)(qJ/4)], \quad (7)$$

with respect to the variational parameter θ , we find that a partially polarized ground state with an energy

$$E_0 = -N(\Gamma^2/qJ + qJ/4) \quad (8)$$

is stable as long as $(2\Gamma/qJ) < 1$. If we define a reduced hydrogen-bond-dipole-moment operator as the difference between the proton occupation numbers of the two possible states \uparrow and \downarrow within a hydrogen bond,

$$p_i = n_{i\uparrow} - n_{i\downarrow}, \quad (9)$$

then the expectation value of this operator in the ground state,

$$p_0 = [1 - (2\Gamma/qJ)^2]^{1/2}, \quad (10)$$

depends on the ratio of the proton tunneling integral to the effective strength of the interproton interactions. The above model thus predicts a small mass dependence of the saturation polarization of an H-bonded ferroelectric crystal. Such effects have indeed been observed in a number of H-bonded ferroelectrics as KH_2PO_4 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, Rochelle salt, etc.

III. CLUSTER EXPANSION

In order to make a cluster expansion feasible, let us divide the Hamiltonian in an unperturbed part, which will be treated exactly, and a perturbed part, which will be taken into account only approximately. In the unperturbed Hamiltonian, which is linear in the hydrogen-bond-dipole-moment operators, we describe each proton as moving in the effective average field (Δ) of its neighbors, whereas the perturbation stands for the difference between the instantaneous and the average value of the interproton interactions, i.e., for the difference between the total and the unperturbed Hamiltonian:

$$H = H_0 + H', \quad (11)$$

with

$$H_0 = \sum_{i=1}^N H_{0,i} = \sum_{i=1}^N [-\Gamma(S_i^+ + S_i^-) - \Delta(n_{i\uparrow} - n_{i\downarrow}) + \Delta^2/qJ], \quad (12)$$

¹⁷ R. Blinc and M. Ribarič, *Phys. Rev.* **130**, 1816 (1963).

and

$$H' = H - H_0 = \sum_{i=1}^N [\Delta(n_{i\uparrow} - n_{i\downarrow}) - \frac{1}{4}J \sum_{j=1}^q (n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow}) - \Delta^2/qJ]. \quad (13)$$

The above division is equivalent to an expansion in terms of hydrogen-bond-dipole-moment-deviation operators. It is analogous to the expansion of the Heisenberg and Ising models in terms of spin-deviation operators by Horwitz, Callen and Strieb.⁴ Here, as well as in the work of the above-mentioned authors, the "best" value of the expansion parameter Δ is determined in each stage by a minimization of the approximately determined free energy. This procedure is based on the Peierls theorem¹⁸ on the minimum property of the exact free energy (which is an extension of the well-known variational principle for the lowest eigenvalue of the Hamiltonian) and the requirement that in each stage the approximate free energy should be stable with respect to small variations in the expansion parameters. For an approximate determination of the free energy, a high-temperature-cluster expansion is used. Following the usual procedure, we divide the total free energy in an unperturbed part F_0 and a correction term F' :

$$F = F_0 + F', \quad (14)$$

where

$$F_0 = -kT \ln \text{Tr} \exp(-\beta H_0) = NkT \ln \text{Tr} \exp(-\beta H_{0,i}), \quad (15)$$

and

$$F' = F - F_0 = kT [\ln \text{Tr} \exp(-\beta H) - \ln \text{Tr} \exp(-\beta H_0)] = -kT \ln [\text{Tr} \exp(-\beta H) / \text{Tr} \exp(-\beta H_0)], \quad (16)$$

with $\beta = 1/kT$. Defining an operator V by the equation

$$\exp[-\beta(H_0 + H')] = \exp(-\beta H_0) \exp(-\beta V), \quad (17)$$

we get F' as

$$F' = -kT \ln \text{Tr} \rho_0 \exp(-\beta V) = -kT \ln \langle \exp(-\beta V) \rangle, \quad (18)$$

where the average is defined through the unperturbed density matrix:

$$\rho_0 = \exp(-\beta H_0) / \text{Tr} \exp(-\beta H_0). \quad (19)$$

The cluster approximation consists in an approximate determination of the correction term F' and hence of $\langle \exp(-\beta V) \rangle$. To determine this average, we must first determine the operator V , which is not simply equal to H' since H_0 and H' do not commute. It should be noted that in the case of the Heisenberg ferromagnet^{4b} H_0 and H' commute.

As shown in Appendix B, the operator V can be written as:

$$V = H' + (\beta/2!) [H_0, H'] + (\beta^2/3!) [H_0, [H_0, H']] + \dots \quad (20)$$

In order to be able to expand $\langle \exp(-\beta V) \rangle$ in a cluster series, let us first rearrange the perturbation term H' and the operator V into a sum of links (particle pairs) after which it will be quite easy to regroup the terms of this series so that they refer to clusters of protons.

From Eq. (13) we note that H' can be written as

$$H' = \frac{1}{2} \sum_{i=1}^N \sum_{i=1}^q Q_{ij} = \sum_{\alpha} Q_{\alpha}, \quad (21)$$

where the index α numbers the pairs (ij) or links in the system:

$$Q_{\alpha} = (\Delta/q)(n_{i\uparrow} - n_{i\downarrow} + n_{j\uparrow} - n_{j\downarrow}) - (J/2)(n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow}).$$

Using Eq. (20) we see that V is given by

$$V = \frac{1}{2} \sum_{ij} Q_{ij}' = \sum_{\alpha} Q_{\alpha}', \quad (22)$$

with

$$Q_{ij}' = Q_{ij} + (\beta/2!) [H_0, Q_{ij}] + (\beta^2/3!) [H_0, [H_0, Q_{ij}]] + \dots \quad (23)$$

Using the cluster-expansion technique of Kubo,¹⁹ we regroup the above expression for $\langle \exp(-\beta V) \rangle$ into a cumulant series

$$\ln \langle \exp(-\beta V) \rangle = \ln \langle \exp(-\beta \sum_{\alpha} Q_{\alpha}') \rangle = \sum_m K_m, \quad (24)$$

where K_m is determined by the number (m) of links it comprises and hence by the magnitude of the cluster:

$$\begin{aligned} K_1 &= \sum_{\alpha} K_1(Q_{\alpha}'), \\ K_2 &= \sum_{\alpha, \beta} K_2(Q_{\alpha}', Q_{\beta}'), \\ &\vdots \\ K_n &= \sum_{\alpha, \beta, \dots, n} K_n(Q_{\alpha}', Q_{\beta}', \dots, Q_n'). \end{aligned} \quad (25)$$

Here $K_1(Q_{\alpha}')$ is the collection of all the terms in the cumulant series, which contain the variable Q_{α}' , $K_2(Q_{\alpha}', Q_{\beta}')$ the collection of all the terms that contain two variables Q_{α}' , Q_{β}' , etc. Following Kubo, we have

$$\begin{aligned} \exp K_1(Q_{\alpha}') &= M_1(Q_{\alpha}') = \langle \exp(-\beta Q_{\alpha}') \rangle, \\ \exp K_2(Q_{\alpha}', Q_{\beta}') &= M_2(Q_{\alpha}', Q_{\beta}') / M_1(Q_{\alpha}') M_1(Q_{\beta}'), \end{aligned} \quad (26)$$

with

$$M_2(Q_{\alpha}', Q_{\beta}') = \langle \exp[-\beta(Q_{\alpha}' + Q_{\beta}')] \rangle, \text{ etc.}$$

Every cumulant K_m can be evaluated in terms of functions $M_{m'}$, where $m' \leq m$. The basic advantage of

¹⁸ R. E. Peierls, Phys. Rev. 54, 918 (1938).

¹⁹ R. Kubo, J. Phys. Soc. Japan 17, 1100 (1962).

the above expansion consists in the fact that the logarithm of the average of a term of $\frac{1}{2}qN$ links has been written as a series of averages over one, two, and more links, so that the leading terms of this series can be easily evaluated. Successive approximations are made by taking progressively larger linked clusters; this procedure involves the diagonalization of progressively larger energy matrices. It is important to note that the above expansion is valid though the Q_{α}' do not commute.

IV. ZERO-ORDER APPROXIMATION THE MOLECULAR FIELD

Let us first evaluate the zero-order term represented by the unperturbed free energy F_0 . Here every proton moves in the average molecular field of its neighbors, Δ , and F_0 is easily obtained as

$$F_0 = -NkT \ln 2 \cosh \beta(\Gamma^2 + \Delta^2)^{1/2} + N\Delta^2/qJ. \quad (27)$$

The mean value of the molecular field Δ is determined by a minimization of F_0 with respect to Δ :

$$\partial F_0 / \partial \Delta = 0. \quad (28)$$

Equation (28) represents in fact a consistency relation for Δ and can be explicitly written as:

$$\left[\frac{2\Delta/qJ}{(2\Delta/qJ)^2 + (2\Gamma/qJ)^2} \right]^{1/2} = \tanh \left\{ \beta(qJ/2) \left[\frac{2\Delta/qJ}{(2\Delta/qJ)^2 + (2\Gamma/qJ)^2} \right]^{1/2} \right\}. \quad (29)$$

This equation, which determines the temperature dependence of Δ as well as of the spontaneous polarization—since $\langle p \rangle = 2\Delta/qJ$ as it follows from $\langle \partial H_0 / \partial \Delta \rangle = \partial F_0 / \partial \Delta = 0$ —is identical with the expression obtained in the usual molecular field treatment.¹⁰ The polarization at $T=0$ is the same as the one obtained by variational determination of the ground state [Eq. (10)]. The model shows a considerable isotope effect in the transition temperatures, which are determined as solutions of Eq. (29) for $\Delta=0$:

$$2\Gamma/qJ = \tanh(\beta\Gamma). \quad (30)$$

V. FIRST APPROXIMATION: TWO-PARTICLE CLUSTER

In the two-particle-cluster approximation, which corresponds to $m=1$ (one link per cluster), and already includes some short-range correlations, we have

$$\langle \exp(-\beta V) \rangle = e^{K_1} = \Pi_{\alpha} [\text{Tr} \rho_0 \exp(-\beta Q_{\alpha}')] = [\text{Tr} \rho_0 \exp(-\beta Q_{\alpha}')]^{qN/2}; \quad (31)$$

the correction term to the free energy is obtained after a straightforward manipulation as

$$F_{(2)}' = -kT \times \frac{1}{2} qN [\ln \text{Tr} \exp(-\beta H_{(2)}) - 2 \ln \text{Tr} \exp(-\beta H_{(1)})], \quad (32)$$

where $H_{(2)}$ and $H_{(1)}$ are the two- and single-particle-

cluster Hamiltonians:

$$H_{(2)} = -\Gamma(S_i^+ + S_i^- + S_j^+ + S_j^-) - \Delta(1-1/q)(n_{i\uparrow} - n_{i\downarrow} + n_{j\uparrow} - n_{j\downarrow}) - (J/2)(n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow}), \quad (33)$$

$$H_{(1)} = -\Gamma(S_i^+ + S_i^-) - \Delta(n_{i\uparrow} - n_{i\downarrow}).$$

The total free energy in this approximation equals

$$F_{(2)} = -kTN \left\{ (q/2) \ln \text{Tr} \exp(-\beta H_{(2)}) + (1-q) \ln \text{Tr} \exp(-\beta H_{(1)}) \right\}. \quad (34)$$

Minimizing $F_{(2)}$ with respect to Δ ,

$$\delta F_{(2)} / \delta \Delta = 0, \quad (35)$$

we find that the average field is determined by the solution of the following equation:

$$\text{Tr}(n_{i\uparrow} - n_{i\downarrow})\rho_{(1)} = \frac{1}{2} \text{Tr}(n_{i\uparrow} - n_{i\downarrow} + n_{j\uparrow} - n_{j\downarrow})\rho_{(2)} \quad (36)$$

where

$$\rho_{(1)} = \exp(-\beta H_{(1)}) / \text{Tr} \exp(-\beta H_{(1)}) \quad (37)$$

is the single-particle density matrix, and

$$\rho_{(2)} = \exp(-\beta H_{(2)}) / \text{Tr} \exp(-\beta H_{(2)}) \quad (38)$$

the two-particle density matrix. The physical meaning of Eq. (36) is that the value of the molecular field Δ which minimizes the free energy is such that the canonical average of the dipole-moment operator $p_i = n_{i\uparrow} - n_{i\downarrow}$ is the same when computed from either the one-particle or the two-particle density operator.

From Eq. (36) the temperature dependence of the ensemble average of the expectation value of the dipole moment, i.e., the temperature dependence of the spontaneous polarization can be computed (Appendix C). Some results are shown in Fig. 1. It can be seen that the transition temperatures (i.e. the temperatures at which the molecular field Δ and the associated long range order vanish) decrease with a decreasing number of nearest neighbors. In the limiting case, $q = \infty$, the two-particle cluster yields the same results as the molecular field approximation. In contrast to the molecular-field case, however, there is no transition for a linear chain, i.e., for $q=2$. The accuracy of the obtained results can be

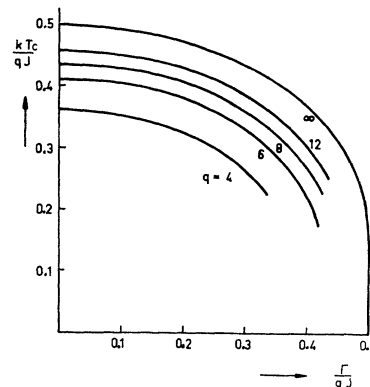


FIG. 1. Transition temperatures as a function of the tunneling integral in the two-particle-cluster approximation.

best judged by a comparison with the exact solutions of the Ising model ($\Gamma = 0$). For instance, for $q = 4$, the ratio of the transition temperature, derived from the above two-particle cluster, to the exact transition temperatures is $T_{c,2}/T_{c,\text{exact}} = 1.275$. Similar to the molecular-field case, the transition temperatures decrease with an increasing value of the proton tunneling integral.

The increase of the spontaneous polarization in the vicinity of the transition temperature (Fig. 2) is, for a finite q , significantly sharper than the one obtained in the molecular-field case, thus demonstrating the importance of short-range correlations in the neighborhood of T_c . The shape of the specific-heat anomaly

$$C = \delta W / \delta T, \quad (39)$$

with

$$W = \frac{1}{2} q N \text{Tr} H_{ij} \rho(2) \\ H_{ij} = -(\Gamma/q)(S_i^+ + S_i^- + S_j^+ + S_j^-) \\ - \frac{1}{2} J (n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow}), \quad (40)$$

and particularly its high-temperature tail (for $T > T_c$), are as well very sensitive to short-range order correlations (Fig. 3). Whereas there is no such high-temperature tail in the classical limit ($\Gamma = 0$) of the molecular-field approximation, there is one in the corresponding two-particle cluster case. In the quantum case ($\Gamma \neq 0$), however, a small high- T tail is found even in the molecular-field case (where above T_c each proton is assumed to move independently of its neighbors).

In this case we have

$$W = N[-2\Gamma^2/qJ - (qJ/4)\langle p \rangle^2], \quad T < T_c, \\ \text{and} \quad (41)$$

$$W = N\Gamma \tanh(\beta\Gamma), \quad T > T_c.$$

The anomalous-specific-heat tail in the two-particle cluster is thus a combined effect of short-range correlations, which in this approximation persist even above T_c , and quantum phenomena due to proton tunneling. A measurement of the specific-heat anomaly on a deuterated and an undeuterated sample of the same compound could determine the relative weights of these two contributions.

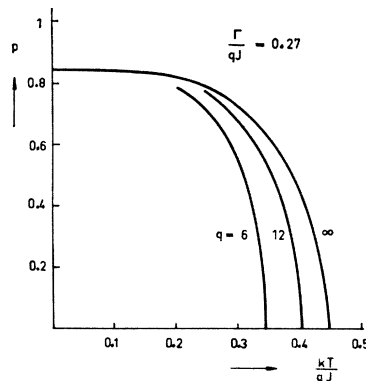


FIG. 2. Temperature dependence of the reduced dipole moment in the two-particle-cluster approximation.

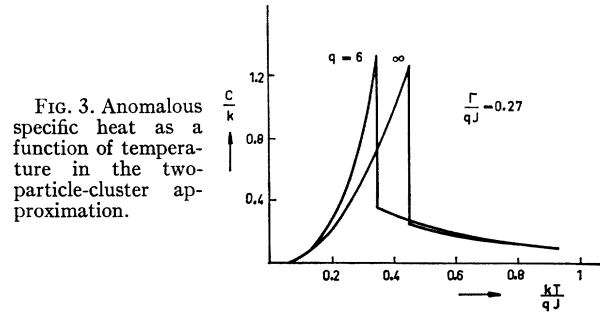


FIG. 3. Anomalous specific heat as a function of temperature in the two-particle-cluster approximation.

VI. HIGHER ORDER APPROXIMATIONS

Higher order approximations reflect the specific properties of crystal lattices and should be based on a knowledge of the crystal structure of the compound we are studying. In the three-particle cluster case, which represents the next approximation, we have, depending on the crystal structure, two different types of contributions to the correction term: the contribution of joined pairs of links (V -type linkages, $2Q'$ term) and the contribution of triangles (three Q' term), which occur if two nearest neighbors share a common nearest neighbor (fcc lattice, for instance). For the case of KH_2PO_4 , on the other hand, the smallest cluster which is compatible with the crystal structure is a four-particle one, which takes into account the correlations in the motion of the four protons surrounding a given PO_4 group.

Rather than to go into details of this specific case, which is treated in the following paper, we would like to stress that, whereas the above expansion is exact for $\Gamma = 0$, it is only a high-temperature expansion for $\Gamma \neq 0$. The two-particle cluster, in particular, breaks down at low temperatures, if $\Gamma \neq 0$, and shows an anti-Curie-point (similar to the one obtained in the Peierls-Weiss approximation of ferromagnetism), which however, vanishes for $\Gamma \equiv 0$.

VII. "OGUCHI"-TYPE SMALL-CLUSTER APPROXIMATION

In view of the occurrence of an "anti-Curie" point in the two-particle-cluster approximation for $\Gamma \neq 0$, it seems worth while to look for a small-cluster treatment, which, though perhaps less accurate than the above high T expansion, would not be limited to the neighborhood of T_c and would work for any value of Γ even at low temperatures. Such an approximation can be relatively easily constructed along the lines of Oguchi's²⁰ treatment of ferromagnetism.

Let us consider the case of a two-particle cluster, where the interactions between the two protons in the cluster are taken into account exactly, and all the other interactions only on the average, i.e., the instantaneous values of the dipole-moment operators p of the H bonds

²⁰ T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

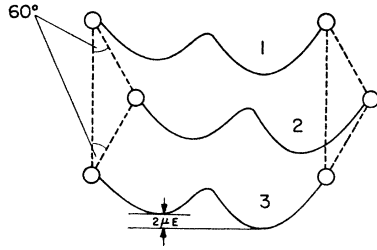


FIG. 4. Exactly soluble model, consisting of three linked H bonds in an external field.

outside the cluster are assumed to be equal to their mean value $\langle p \rangle$:

$$H_{1,2} = \sum_{i=1}^2 [-\Gamma(S_i^+ + S_i^-) - \frac{1}{2}qJ(1-1/q)\langle p \rangle \times (n_{i\uparrow} - n_{i\downarrow})] - \frac{1}{2}J(n_{1\uparrow} - n_{1\downarrow})(n_{2\uparrow} - n_{2\downarrow}). \quad (42)$$

The consistency relation is obtained from the requirement that the mean values of the dipole moments of the

H bonds within the cluster $p_1 = (n_{1\uparrow} - n_{1\downarrow})$ and $p_2 = (n_{2\uparrow} - n_{2\downarrow})$ should be the same as the mean dipole moments of the H bonds outside the cluster:

$$\langle p \rangle = \frac{1}{2}\langle p_1 + p_2 \rangle = \frac{1}{2} \text{Tr} \sum_{i=1}^2 (n_{i\uparrow} - n_{i\downarrow}) \times \exp(-\beta H_{1,2}) / \text{Tr} \exp(-\beta H_{1,2}). \quad (43)$$

In the representation of localized particles,

$$\begin{aligned} |1\rangle &= b_{1\uparrow}^\dagger b_{2\uparrow}^\dagger |0\rangle, \\ |2\rangle &= b_{1\uparrow}^\dagger b_{2\downarrow}^\dagger |0\rangle, \\ |3\rangle &= b_{1\downarrow}^\dagger b_{2\uparrow}^\dagger |0\rangle, \\ |4\rangle &= b_{1\downarrow}^\dagger b_{2\downarrow}^\dagger |0\rangle, \end{aligned} \quad (44)$$

we obtain the Hamiltonian of the two-particle cluster in matrix form as

$$H_{1,2} = qJ \begin{vmatrix} -(1-1/q)\langle p \rangle - 1/2q & -\Gamma/qJ & -\Gamma/qJ & 0 \\ -\Gamma/qJ & 1/2q & 0 & -\Gamma/qJ \\ -\Gamma/qJ & 0 & 1/2q & -\Gamma/qJ \\ 0 & -\Gamma/qJ & -\Gamma/qJ & (1-1/q)\langle p \rangle - 1/2q \end{vmatrix}. \quad (45)$$

The consistency relation, Eq. (43), can be now written in the form

$$\langle p \rangle = \sum_i (c_{i\uparrow}^2 - c_{i\downarrow}^2) \exp(-\beta\lambda_i) / \sum_i \exp(-\beta\lambda_i), \quad (46)$$

where the c_{ij} are the eigenvectors and λ_i the eigenvalues of the above matrix (45). Both λ_i and c_i are of course functions of $\langle p \rangle$. By solving Eq. (46) we can get the temperature dependence of the spontaneous polarization at all temperatures as there is no anti-Curie point even for $\Gamma \neq 0$. The transition temperatures are in general intermediate between those predicted by the molecular-field method and those obtained from Eq. (36). In particular, Eq. (46) predicts, in contrast to the two-particle-cluster-expansion case, a Curie point for a linear chain. Thus this treatment does not seem to be as good an approximation as the corresponding two-particle cluster-expansion term (34), but it has the advantage that it works at all temperatures.

VIII. COMPARISON WITH AN EXACTLY SOLUBLE MODEL

In order to get a better feeling for the relative merits of the molecular-field, two-particle cluster-expansion, and two-particle Oguchi-type approximations, let us compare their predictions with those of an exactly soluble model.

Let us consider a linked system of three hydrogen bonds in an external electric field (Fig. 4) and compare the temperature dependence of the field-induced dipole moment, obtained by an exact solution of this system with the one obtained on the basis of the above approximations.

The Hamiltonian of the above system can be written as

$$H_\Delta = \sum_{i=1}^3 [-\Gamma(S_i^+ + S_i^-) - \mu E(n_{i\uparrow} - n_{i\downarrow}) - \frac{1}{2}J[(n_{1\uparrow} - n_{1\downarrow})(n_{2\uparrow} - n_{2\downarrow}) + (n_{2\uparrow} - n_{2\downarrow})(n_{3\uparrow} - n_{3\downarrow}) + (n_{3\uparrow} - n_{3\downarrow})(n_{1\uparrow} - n_{1\downarrow})], \quad (47)$$

where E is the external electric field and

$$\mu_i = e_p \langle \Psi_{ik} | \zeta_i | \Psi_{ik} \rangle \quad (48)$$

is the expectation value of the dipole moment of the i th H bond with the proton (having an effective charge e_p) fixed in the k th site at a distance ζ_i from the center of the H bond.

The above Hamiltonian can be exactly diagonalized, and the free energy and the mean value of the field-induced dipole moment obtained as

$$F_\Delta = -kT \ln \text{Tr} \exp(-\beta H_\Delta), \quad (49)$$

$$3\mu \langle p \rangle = -\delta F_\Delta / \delta E = \mu \text{Tr} \sum_{i=1}^3 (n_{i\uparrow} - n_{i\downarrow}) \rho_\Delta,$$

respectively, where

$$\rho_\Delta = \exp(-\beta H_\Delta) / \text{Tr} \exp(-\beta H_\Delta). \quad (50)$$

In Fig. 5, the temperature dependence of the field-induced reduced dipole moment $\langle p \rangle$, obtained from Eq. (50), is compared with the predictions obtained from the corresponding molecular-field, two-cluster-expansion, and two-cluster Oguchi approximations for

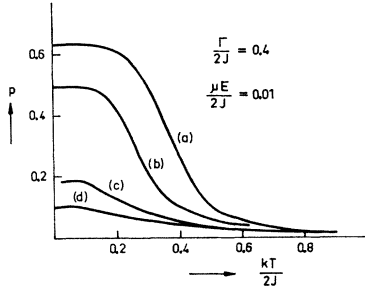


FIG. 5. Mean value of the field-induced dipole moment in the three-H-bond system as a function of temperature: (a) molecular-field approximation. (b) "Oguchi" two-particle approximation. (c) two-particle-cluster expansion approximation. (d) exact solution.

the Hamiltonian (47). As can be seen, the exact solution gives by far the smallest field-induced dipole moment, whereas the two-cluster-expansion result represents a remarkably good approximation at higher temperatures though it fails as $T \rightarrow 0$. The "Oguchi" two-cluster result is intermediate between the one predicted by the two-particle expansion and the molecular-field method, and shows no anomalies as $T \rightarrow 0$.

APPENDIX A

Let us indicate a short derivation of the interaction term in Hamiltonian (1).

The interaction $V(\mathbf{r}, \mathbf{r}')$ between two H-bonded protons i and i' , which move in double minimum potentials, can be written in the representation of localized particles as

$$I_0 n_{i\downarrow} n_{i'\uparrow} + I_1 n_{i\downarrow} n_{i'\downarrow} + I_{-1} n_{i\uparrow} n_{i'\uparrow} + I_2 n_{i\uparrow} n_{i'\downarrow}, \quad (\text{A1})$$

if overlap terms can be neglected. Here

$$\begin{aligned} I_0 &= \langle \Psi_{i\downarrow} \Psi_{i'\uparrow} | V(\mathbf{r}_i, \mathbf{r}_{i'}) | \Psi_{i\downarrow} \Psi_{i'\uparrow} \rangle, \\ I_1 &= \langle \Psi_{i\downarrow} \Psi_{i'\downarrow} | V(\mathbf{r}_i, \mathbf{r}_{i'}) | \Psi_{i\downarrow} \Psi_{i'\downarrow} \rangle, \\ I_{-1} &= \langle \Psi_{i\uparrow} \Psi_{i'\uparrow} | V(\mathbf{r}_i, \mathbf{r}_{i'}) | \Psi_{i\uparrow} \Psi_{i'\uparrow} \rangle, \\ I_2 &= \langle \Psi_{i\uparrow} \Psi_{i'\downarrow} | V(\mathbf{r}_i, \mathbf{r}_{i'}) | \Psi_{i\uparrow} \Psi_{i'\downarrow} \rangle. \end{aligned} \quad (\text{A2})$$

Using the constraint (5) that there is one and only one proton in each H bond, and summing over all proton pairs in the crystal, the interaction Hamiltonian can be written up to constant terms as

$$H_I = \frac{1}{4} \sum_{i, i'} (-J_{ii'}) (n_{i\uparrow} - n_{i\downarrow}) (n_{i'\uparrow} - n_{i'\downarrow}), \quad (\text{A3})$$

with

$$J_{ii'} = [(I_0 + I_2)/2 - (I_1 + I_{-1})/2]_{ii'} \quad (\text{A4})$$

APPENDIX B

In this Appendix, we shall indicate a short derivation of expression (20) for the operator V , which has been defined by the equation

$$\exp[-\beta(H_0 + H')] = \exp(-\beta H_0) \exp(-\beta V). \quad (\text{B1})$$

Let us introduce a function $u(s)$:

$$u(s) = \exp[-\beta(H_0 + H')s], \quad (\text{B2})$$

which is the solution of the following differential equation:

$$\delta u(s)/\delta s = -u(s)[\beta H_0 + \beta H'], \quad (\text{B3})$$

with $u(0) = 1$. If we now define a new function $v(s)$:

$$u(s) = \exp(-\beta H_0 s) v(s), \quad (\text{B4})$$

we may easily see that this function is a solution of

$$\frac{\delta v(s)}{\delta s} = -\exp[-\beta H_0 s] \beta H' \exp[\beta H_0 s] v(s), \quad (\text{B5})$$

with $v(0) = 1$. Using the identity

$$\exp(a)b \exp(-a) = b + [a, b] + (1/2!) [a, [a, b]] + \dots,$$

we can write Eq. (B5) as

$$\delta v(s)/\delta s = -\beta \{ H' + s\beta [H_0, H'] + (s^2/2!) \beta^2 \times [H_0, [H_0, H']] \dots \} v(s), \quad (\text{B6})$$

and obtain, after integration between 0 and 1,

$$\begin{aligned} \exp[-\beta(H_0 + H')] &= \exp(-\beta H_0) \\ &\times \exp(-\beta \{ H' + (\beta/2!) [H_0, H'] \\ &+ (\beta^2/3!) [H_0, [H_0, H']] + \dots \}), \end{aligned} \quad (\text{B7})$$

the desired expression for V .

APPENDIX C

Here we present explicitly the expressions from which the temperature dependence of the spontaneous polarization and the transition temperatures are calculated in the two-particle-cluster-expansion approximation.

The two-particle cluster Hamiltonian (33) can be transformed into a simpler form and written as

$$H_2 = \begin{vmatrix} -J/2 & -2\Gamma & 0 & -2\Delta(1-1/q) \\ -2\Gamma & J/2 & 0 & 0 \\ 0 & 0 & J/2 & 0 \\ -2\Delta(1-1/q) & 0 & 0 & -J/2 \end{vmatrix}, \quad (\text{C1})$$

whereas the consistency relation (36) amounts to

$$\begin{aligned} \Delta \tanh(\beta[\Delta^2 + \Gamma^2]^{1/2}) / [\Delta^2 + \Gamma^2]^{1/2} \\ = 2 \sum_{i=1}^4 c_{i1} c_{i4} \exp(-\beta \lambda_i) / \sum_{i=1}^4 \exp(-\beta \lambda_i), \end{aligned} \quad (\text{C2})$$

with the c_{ij} and the λ_i being the eigenvectors and eigenvalues of the matrix (C1). The transition temperatures are again obtained as the boundary of the region beyond which Eq. (C2) ceases to have nonzero solutions for Δ .