Cluster approximation for q-dependent correlations in magnetic and ferroelectric systems

S. Havlin
Department of Physics, Bar-Ilan University, Ramat-Gan, Israel

H. Sompolinsky
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

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A self-consistent cluster approximation is developed for the wave-vector ($\vec{q}$)-dependent spin-spin correlation in Ising models describing magnetic and ferroelectric systems. The method is particularly suitable for describing systems with competing short-range interactions. The self-consistent approximation for the $\vec{q}$-dependent susceptibilities with clusters of size N is found to be $\chi_\nu^{-1}(\vec{q}) = C^{-1}T[M_\nu^{-1}(\vec{q}) - (1-C)]$, $\nu = 1, 2, \ldots, N$, where $M_\nu^{-1}(\vec{q})$ are the eigenvalues of the Fourier transform of $(M^{-1})_{ij}$ where M_{ij} is the pair-correlation matrix of spins within the cluster calculated by the exact Hamiltonian of the cluster. The constant C is the ratio of the number of nearest neighbors inside the cluster to the total number of nearest neighbors. The method is applied to calculate scattering intensities in potassium-dihydrogen-phosphate-type hydrogen-bonded ferroelectrics. We find a strong anisotropy in the $\vec{q}$ dependence of the intensity, exhibiting a strong suppression of fluctuations along the easy (z) axis. The results are found to be in good agreement with neutron scattering data in KD_2PO_4. We also investigate the ice-rule limit of our results. In that case a singularity of the type $\chi^{-1}(\vec{q}) \simeq \chi^{-1}(0) + B(T)q_z^2/(2q_\perp^2 + q_z^2)$ for $q \to 0$ is found, similar to that generated by long-range dipolar forces.

I. INTRODUCTION

In recent years, there has been great progress in understanding critical phenomena using scaling ideas and renormalization-group techniques.[1-3] However, simple analytical approximations are useful in understanding thermodynamic properties of specific systems, in particular, for temperatures and length scales outside the critical region. While the Curie-Weiss mean-field approximation usually provides a starting point for qualitative understanding of the phase transition, in many cases a significant improvement is achieved by using cluster approximation methods,[4-8] in which the effect of fluctuations is incorporated in a self-consistent way. This is particularly true for systems which possess *competing* short-range interactions, which give rise to strong fluctuations in the effective interactions which are not accounted for in the simple mean-field treatment.[9] Another example is hydrogen-bonded systems in which the strong correlations between the neighboring hydrogens are adequately taken into account by cluster methods.[7,8] In fact, in ice-rule systems where the number of hydrogens in each vertex is fixed, the results of the cluster method for the value of the transition temperature T_c and some of its critical properties agree with the known exact solutions.[10] It should be also noted that self-consistent cluster methods may be a useful starting point for renormalization schemes, especially in real-space renormalization-group methods.[11]

In the present work, we construct a self-consistent cluster approximation for $\vec{q}$-dependent correlations in spin systems. This is done by extending the $\vec{q} = 0$ cluster method of Strieb *et al.*[4] to nonuniform ($\vec{q} \neq 0$) cases. The main advantage of the present method is that it yields a simple general expression in closed form for any cluster size. Our results are expressed in terms of the inverse of the spin-spin correlation matrix within the cluster, thus revealing the basic physical content of the cluster approximation, i.e., the renormalization of the bare short-range interactions by the short-range correlations. We treat explicitly spin systems described by the Ising Hamiltonian although our results can be generalized in a straightforward way to other spin models.

The method is applied in detail to calculate the scattering intensity for potassium-dihydrogen-phosphate (KDP)-type hydrogen-bonded ferroelectrics. We show that the anisotropic correlations between the hydrogen bonds produce strong anisotropy in the $\vec{q}$ dependence scattering intensity quite similar to the anisotropy generated by long-range dipolar force. Qualitatively similar anisotropy has previously been found using a simple mean-field approximation.[12] However, the temperature dependence predicted by the mean-field results is known to be incorrect even for $q = 0$ and certainly cannot be used

for quantitative comparison with the scattering data.[8] The present results are found to be in good agreement with the available neutron scattering data for KD_2PO_4.[13,14] This agreement indicates that the origin of the observed anisotropy in this material is the short-range hydrogenic interactions, rather than long-range electrostatic forces that were previously suggested.[13] This view is supported by recent scattering results in another hydrogen-bonded system, viz., copper formate tetrahydrate.[15] We also investigate the $\vec{q}$-dependent scattering intensity in the ice-rule limit. In this case, our results predict a dipolartype singularity at $q=0$, in agreement with the recent calculations of Youngblood and Axe[15] as well as with the exact results in a particular 2D (two-dimensional) six-vertex model.[16]

The outline of the paper is as follows. In Sec. II, we derive the general equation for the wave-vector-dependent susceptibility in an N-cluster approximation for an Ising system. In Sec. III, the results for KDP-type ferroelectrics are derived and compared with experiment. In Sec. IV, the ice-rule limit is discussed.

II. CLUSTER APPROXIMATION FOR SUSCEPTIBILITIES IN ISING MODEL

We consider a d-dimensional Ising Hamiltonian

$$H=-\sum_{\langle ij\rangle}J_{ij}S_i^zS_j^z-\sum_i H_iS_i^z \ , \tag{1}$$

where the J_{ij} are short-range interaction constants and H_i are inhomogeneous external fields. Similar to previous treatments of the homogeneous case,[7,8,17] we construct a self-consistent N-cluster approximation of the spin-spin correlation functions of the model (1) by writing the following self-consistent Hamiltonian H_N associated with a cluster of N spins, $(S_i^z,\ i=1,\ \ldots,N)$,

$$H_N=-\sum_{i,j<N}J_{ij}S_i^zS_j^z-\sum_{i=1}^{N}[H_i+(z-z_i)\Delta_i]S_i^z \ . \tag{2}$$

The first term represents the exact interaction energies of the spins within the cluster. The second term represents the interaction of the spins with their local fields. These fields contain an internal contribution $(z-z_i)\Delta_i$ resulting from the interactions with the neighboring spins outside the cluster. The contribution of each neighboring spin outside the cluster to the effective field at site i is denoted by Δ_i. The quantities z and z_i are, respectively, the number of neighbors and the number of neighbors inside the cluster of the ith spin. The fields Δ_i are eliminated through the self-consistency requirement that the thermal average of each spin $\langle S_i\rangle_N$, calculated via H_N, be equal to the local magnetization generated by the total mean field, $H_{\rm MF}=H_i+z\Delta_i$, at site i,

$$\langle S_i^z\rangle_N=\tanh(\beta H_i+\beta z\Delta_i) \ . \tag{3}$$

Using this form for $H_{\rm MF}$ implies that the average internal field per spin generated by the spins inside the cluster is equal to that of the spins outside it. This ansatz is trivial in the uniform case ($\langle S_i^z\rangle=\langle S^z\rangle$). However, in the nonuniform case ($\vec{q}\neq 0$), one has to take into account the different location of these spins. In order to get a symmetric contribution from the spins inside and outside the cluster, we use an extended cluster which contains the reflection ($\vec{R}\rightarrow -\vec{R}$) of the original cluster about one of the N original sites. An example of this construction for two cluster in a 1D lattice and four cluster in a square lattice is shown in Fig. 1.

Restricting ourselves to $T>T_c$ and small fields H_i and Δ_i, $\langle S_i^z\rangle_N$ are given by

$$\langle S_i^z\rangle_N\equiv \mathrm{Tr}(S_i^z e^{-\beta H_N})/\mathrm{Tr}(e^{-\beta H_N}) \simeq \beta\sum_j^N M_{ij}X_j, \quad i=1,\ \ldots,N \ , \tag{4}$$

where

$$X_i=H_i+(z-z_i)\Delta_i \ , \tag{5}$$

$$M_{ij}=\langle S_i^zS_j^z\rangle_N^0=\mathrm{Tr}(S_i^zS_j^z e^{-\beta H_N^0})/Z_N^0 \ , \tag{6}$$

and

$$H_N^0=-\sum_{i,j<N}J_{ij}S_i^zS_j^z, \quad Z_N^0=\mathrm{Tr}e^{-\beta H_N^0} \ . \tag{7}$$

Substitution of (4) in (3) yields the following N equations

$$\langle S_i^z\rangle=\beta\sum_j^N M_{ij}H_jz_j/z+\sum_j^N M_{ij}\langle S_j\rangle(1-z_j/z) \ , \tag{8}$$

where the subscript N has been dropped from $\langle S_i^z\rangle$. Note that the summation over j in (8) stands for the summation over the extended cluster defined above. Depending on the structure of the lattice and the cluster, z_i may in general depend on i. We will deal

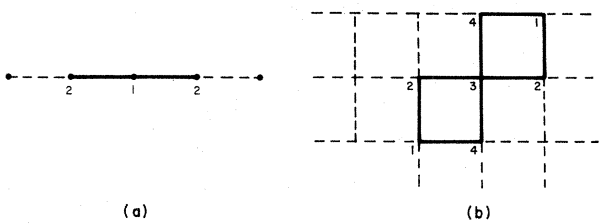

FIG. 1. Extended cluster which contains the reflection $\vec{R}\rightarrow -\vec{R}$ for (a) two cluster in one-dimensional lattice, (b) four cluster in two-dimensional lattice.

here only with the case

$$\frac{z_i}{z} = c$$

independent of i. Equation (8) now yields

$$(1-c)\langle S_i^z\rangle = \sum_j (M^{-1})_{ij}\langle S_j^z\rangle - \beta H_i c \ , \tag{9}$$

where M^{-1} is the inverse of the matrix M. In order to solve (9), we have to specify the fields H_i. We write

$$\begin{aligned} H_i &= H_q^\nu \exp(i\vec{q}\cdot\vec{R}_i)a_\nu^i(\vec{q}) \ , \\ \langle S_i^z\rangle &= \langle S_q^\nu\rangle \exp(i\vec{q}\cdot\vec{R}_i)a_\nu^i(\vec{q}) \ , \end{aligned} \tag{10}$$

where $a_\nu^i(\vec{q})$ $(\nu = 1, \ldots, N)$, which will be determined later, are associated with the phases of the N normal modes of the cluster. Substituting (10) in (9) yields

$$(1-c)\langle S_q^\nu\rangle a_\nu^i(\vec{q}) = \langle S_q^\nu\rangle \sum_j^N (M^{-1})_{ij}\cos[\vec{q}\cdot(\vec{R}_j - \vec{R}_i)]a_\nu^j(\vec{q}) - \beta c H_{\vec{q}}^\nu a_\nu^i(\vec{q}) \ . \tag{11}$$

The factor $\cos[\vec{q}\cdot(\vec{R}_j - \vec{R}_i)]$ results from the sum of the two contributions (in the extended cluster) $\exp[\pm i\vec{q}\cdot(\vec{R}_j - \vec{R}_i)]$ of each bond $\langle ij\rangle$. Thus, choosing $a_\nu^i(\vec{q})$ to be the eigenvector of the matrix

$$M^{-1}(\vec{q}) \equiv (M^{-1})_{ij}\cos[\vec{q}\cdot(\vec{R}_i - \vec{R}_j)] \tag{12}$$

with eigenvalue $\lambda_\nu(\vec{q})$,

$$(M^{-1})_{ij}(\vec{q})a_\nu^j(\vec{q}) = \lambda_\nu(\vec{q})a_\nu^i(\vec{q}), \quad \nu = 1, \ldots, N \ , \tag{13}$$

we obtain from (11) the following result

$$\chi_\nu(\vec{q}) \equiv \langle S_q^\nu\rangle / H_q^\nu = c\beta/[\lambda_\nu(\vec{q}) - (1-c)] \ , \quad \nu = 1, \ldots, N \tag{14}$$

for the N $\vec{q}$-dependent staggered susceptibilities. If the interactions J_{ij} are identical to each other, then the existence of N susceptibilities is a spurious consequence of the enlargement of the unit cell by the cluster treatment. In such a case, all the susceptibilities are related to each other by appropriate shifting of the wave vector. However, when not all the J_{ij} are equal, there will be n-independent modes, where n is the number of nonequivalent spins in the cluster. Finally, it is instructive to compare the result (14) with the corresponding mean-field result[18] $\chi_\nu(\vec{q}) = \beta/[1-\beta J_\nu(\vec{q})]$, where $J_\nu(\vec{q})$ is the eigenvalue of the original interaction matrix $J_{ij}\cos\vec{q}\cdot(\vec{R}_i - \vec{R}_j)$. Hence, the essence of the cluster approximation is to replace the original bare interaction J_{ij} by the self-consistent renormalized value given by the correlations $M_{ij} = \langle S_i S_j\rangle_N$. We now present two examples of the method.

A. One-dimensional Ising model

We apply a two-cluster approximation for the 1D Hamiltonian (1) with only nearest-neighbors interactions $J_{ij} = J$. For that case, the matrix M reduces to

$$M = \begin{pmatrix} 0 & \tanh\beta J \\ \tanh\beta J & 0 \end{pmatrix} \ , \tag{15}$$

leading to

$$M^{-1}(q) = \frac{1}{\mathrm{sech}^2\beta J}\begin{pmatrix} 1 & -\tanh\beta J\cos qa \\ -\tanh\beta J\cos qa & 1 \end{pmatrix} \ , \tag{16}$$

where a is the lattice constant. Thus,

$$\lambda_{1,2}(q) = \frac{1}{\mathrm{sech}^2\beta J}(1 \mp \tanh\beta J\cos qa) \ , \tag{17}$$

and

$$\chi_1(q) = \beta/(\cosh 2\beta J - \sinh 2\beta J\cos qa) \ . \tag{18}$$

It is readily shown that (18) holds for any size cluster, and therefore is also the *exact* value of the q-dependent magnetic susceptibility for the 1D Ising model.[19] In this case, $\chi_2(q)$ is simply $\chi_1(q + \pi/a)$.

B. Two-dimensional Ising model on a square lattice

We calculate the magnetic susceptibility of a 2D Ising Hamiltonian (1) with only nearest-neighbor interactions $J_{ij} = J$ in a four-cluster approximation with the cluster shown in Fig. 1(b). Consider for simplicity the case $\vec{q} = (q,q)$. Then,

$$M^{-1}(q) = A\begin{pmatrix} \frac{2}{1-a} & \frac{-1}{1+a}\cos\pi q & 0 & \frac{-1}{1+a}\cos\pi q \\ \frac{-1}{1+a}\cos\pi q & \frac{2}{1-a} & \frac{-1}{1+a}\cos\pi q & 0 \\ 0 & \frac{1}{1+a}\cos\pi q & \frac{2}{1-a} & \frac{-1}{1+a}\cos\pi q \\ \frac{-1}{1+a}\cos\pi q & 0 & \frac{-1}{1+a}\cos\pi q & \frac{2}{1-a} \end{pmatrix} \tag{19}$$

with

$$A=(1+6a+a^2)(1-a)/16a$$

and $a\equiv\exp(-\beta J)$. Thus, using the eigenvector (1,1,1,1), we obtain

$$\chi^{-1}(q)=T\left\{\frac{1+6a+a^2}{2a(1+a)}\left[a+(1-a)\sin^2\left[\frac{q\pi}{2}\right]\right]-1\right\} . \tag{20}$$

Equation (20) at $q=0$ gives the condition $a_c^2+4a_c-1=0$, where $a_c=\exp(-\beta_c J)$ for T_c.[4] It should be noted that $\chi(q)$ of (20) has a maximum as a function of T above T_c for a fixed q greater than q_0, where q_0 is given by

$$\sin^2\frac{q_0\pi}{2}=\frac{5+2a_c+a_c^2}{10+a_c^{-2}+2a_c+a_c^2+2a_c^{-1}}\simeq 0.15 . \tag{21}$$

It is of interest to compare this result with a two-cluster approximation consisting of two nearest-neighbor spins in the x direction for the 2D case. The result is similar to the 1D case except for the value of c which is now $\frac{1}{4}$, yielding

$$\chi^{-1}(q)=2T(\cosh 2\beta J-\sinh 2\beta J\cos qa-\tfrac{1}{2}) , \tag{22}$$

which gives for T_c, $\cosh 2\beta_c J-\sinh 2\beta_c J=\frac{1}{2}$ and for q_0

$$\sin^2\frac{q_0 a}{2}=\tfrac{1}{2}(1-\tanh\beta_c J)=0.25 . \tag{23}$$

Comparing (23) and (21) shows that the value of q_0 decreases as the size of the cluster increases. Indeed, it was found by using series expansion methods[20] and by renormalization-group theory[21] that $\chi(q)$ has a maximum value as a function of T for any fixed value of $q\neq 0$. It should be noted that in contrast to the present theory, a simple mean-field theory does not predict any maximum for $\chi(q)$.

III. WAVE-VECTOR-DEPENDENT SUSCEPTIBILITIES FOR KDP-TYPE FERROELECTRICS

The static and dynamic properties of KDP-type ferroelectrics are reasonably well described by a pseudospin Ising Hamiltonian of the form (1) (Refs. 7,8,17) in which the exchange interactions J_{ij} represent the short-range interactions between neighboring hydrogen bonds, and $S_i^z=\pm 1$ stands for the position of the proton in the double-well potential along its bond. The smallest cluster which is compatible with the structure of KDP-type crystals is a cluster of four pseudospins representing the four bonds surrounding a single PO_4 group (see Fig. 2). Indeed,

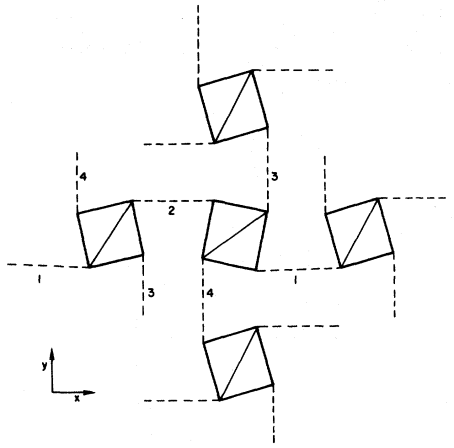

FIG. 2. z-axis projection of the hydrogen bonds connecting K-PO_4 groups showing the different labels of the four pseudospins.

the $q=0$ four-cluster method has been shown to lead to a good approximation for the uniform static and dynamic response of these systems.[7,8,17] This is particularly true for systems which are near the ice-rule limit (see Sec. IV), such as KD_2PO_4, since in that limit the cluster treatment gives the exact value of T_c as well as the critical behavior of the susceptibility and polarization. This indicates the dominant role of the strong short-range correlations among the four neighboring hydrogens. Here, we extend this approximation to the $q\neq 0$ case.

The four pseudospin Hamiltonian H_4^0, given in (7), for KDP-type crystals has the form

$$H_4^0=-V(S_1^zS_3^z+S_2^zS_3^z+S_2^zS_4^z+S_4^zS_1^z)-U(S_1^zS_2^z+S_3^zS_4^z) , \tag{24}$$

as illustrated in Fig. 2. The energies U and V are related to the Slater energy levels ϵ_0, ϵ_1 of the PO_4 groups through

$$\begin{aligned} 4U&=-2\epsilon_1+2\epsilon_0 ,\\ 4V&=2\epsilon_1-\epsilon_0 . \end{aligned} \tag{25}$$

Note that since $\epsilon_1 >> \epsilon_0$ in KDP, U and V are strongly competing interactions with $U<0$, $V>0$, $U+V<<V$.

The matrix $M_{ij}=\langle S_i^zS_j^z\rangle_4^0$ given in (6) is readily found to be

$$M=\frac{2}{Z_4}\begin{pmatrix} Z_4/2 & 1-2a+d & 1-d & 1-d\\ 1-2a+d & Z_4/2 & 1-d & 1-d\\ 1-d & 1-d & Z_4/2 & 1-2a+d\\ 1-d & 1-d & 1-2a+d & Z_4/2 \end{pmatrix} \tag{26}$$

where $Z_4=2+4a+8b+2d$, $a=e^{-\beta\epsilon_0}$, $b=e^{-\beta\epsilon_1}$,

$d = e^{-\beta(4\epsilon_1 - 2\epsilon_0)}$. Since $\epsilon_1 >> \epsilon_0$, the Boltzmann factor d of the two highest levels may be ignored in the following. The matrix

$$M_{ij}^{-1}(q) = M_{ij}^{-1} \cos\vec{q}\cdot(\vec{R}_i - \vec{R}_j)$$

is given by

$$M^{-1}(q) = \frac{Z_4}{2}\begin{pmatrix} C_0 & C_1 & C_2 & C_3 \\ C_1 & C_0 & C_4 & C_5 \\ C_2 & C_4 & C_0 & C_6 \\ C_3 & C_5 & C_6 & C_0 \end{pmatrix}, \tag{27}$$

where

$$\begin{aligned} &C_0 = \alpha, \quad C_1 = \gamma\cos\pi q_x \ , \\ &C_2 = \delta\cos\tfrac{1}{2}\pi(q_x - q_y + q_z) \ , \\ &C_3 = \delta\cos\tfrac{1}{2}\pi(q_x + q_y + q_z) \ , \\ &C_4 = \delta\cos\tfrac{1}{2}\pi(q_x + q_y - q_z) \ , \\ &C_5 = \delta\cos\tfrac{1}{2}\pi(q_x - q_y - q_z), \quad C_6 = \gamma\cos\pi q_y \ , \end{aligned} \tag{28}$$

and

$$\begin{aligned} &\alpha = \frac{2}{R}(2a + 6b + 4ab + 8b^2), \quad \gamma = \frac{4}{R}(a - b + 2ab) \ , \\ &\delta = -\frac{4}{R}(a + b), \quad R = 64b(a + b)(1 + b) \ . \end{aligned} \tag{29}$$

In (28) and in the following, we denote for simplicity $\frac{1}{2}\pi(q_x\bar{a}, q_y\bar{a}, q_z\bar{c})$ as $\vec{q} = (q_x, q_y, q_z)$ where $\bar{a}$ and $\bar{c}$ are the KDP lattice constants. Diagonalizing $M^{-1}(\vec{q})$ yields via (14) (with $c = \frac{1}{2}$) four susceptibilities

$$\chi_\nu(\vec{q}) = \tfrac{1}{2}\beta/[\lambda_\nu(\vec{q}) - \tfrac{1}{2}], \quad \nu = 1, \ldots, 4 \ . \tag{30}$$

The corresponding eigenvectors $a_\nu(\vec{q})$ define four distinct polarization fluctuation modes. The $\nu = 1$ mode corresponds in the limit $q \to 0$ to the B_2 mode,[7,8] $\nu = 2, 3$ to the E mode[17] and $\nu = 4$ to the A mode.[22,23] The B_2 mode susceptibility $\chi_{B_2}(\vec{q})$ becomes critical when $T \to T_c$ and $q \to 0$.

The expressions for $\lambda_\nu(\vec{q})$ for general $\vec{q}$ are rather complicated and have been evaluated numerically. In the following, we discuss the analytical results in the special case of the plane (q,q,q_z). In this case, the eigenvalues are

$$\begin{aligned} \lambda_{1,2}(\vec{q}) &= \frac{Z_4}{2}\left[\alpha + \frac{C_3 + C_4 \mp [(C_3 - C_4)^2 + 4(C_1 + C_2)^2]^{1/2}}{2}\right] , \\ \lambda_{3,4}(\vec{q}) &= \frac{Z_4}{2}\left[\alpha + \frac{-(C_3 + C_4) \mp [(C_3 - C_4)^2 + 4(C_1 - C_2)^2]^{1/2}}{2}\right] , \end{aligned} \tag{31}$$

where $\vec{q} = (q,q,q_z)$. Since mode 1 is associated with the critical susceptibility, we examine it in some detail. Along the $\vec{q}_z$ and $\vec{q}_x = \vec{q}_y$ directions, (31) yields

$$\chi_1(q_z) = \beta\Big/\left\{\frac{1 + 2a + 4b}{2b(1 + b)}\left[b + \sin^2\left(\frac{q_z\pi}{2}\right)\right] - 1\right\}, \quad \vec{q} = (0,0,q_z) \ , \tag{32}$$

$$\chi_1(q) = \beta\Big/\left\{\frac{1 + 2a + 4b}{2(a + b)(1 + b)}\left[(a + b) + (1 - a)\sin^2\left(\frac{q\pi}{2}\right)\right] - 1\right\}, \quad \vec{q} = (q,q,0) \ . \tag{33}$$

Equations (32) and (33) reduce for $q = 0$ to the known expression of the electric susceptibility in the longitudinal ($\hat{z}$) direction χ_{B_2}.[7,8] On the other hand, (33) reduces at $\vec{q} = \frac{1}{2}\pi$ to the known result of the electric susceptibility in the transverse direction ($\hat{x}$ or $\hat{y}$), χ_E, confirming our previous identification of this susceptibility with antiferroelectriclike ordering of the hydrogen bonds.[17] In Fig. 3, we present a plot of $\chi_1(q)$ in the (q,q,q_z) plane using the known values for the Slater energies in KD_2PO_4: $\epsilon_0 = 92$ K, $\epsilon_1 = 907$ K at $T - T_c = 5$ K, where $T_c = 220$ K.[24]

In Fig. 4, the contour lines of $\chi_1(\vec{q}) = \text{const}$ are shown for the same temperature and energies. The most marked feature of these results is the strong anisotropy, with $\chi_1(\vec{q})$ decreasing with increasing $\vec{q}$ along $(0,0,q)$ direction much more rapidly than along the perpendicular direction. Physically, the origin of this anisotropy lies in the fact that polarization fluctuations in the (q_x,q_y) plane involve only configurations with low energies ϵ_0, whereas those along the $\hat{q}_z$ direction necessarily involve configurations with high energies of the order ϵ_1. An estimate of this anisotropy can be found by expanding (32) and (33) for small q and q_z,

$$\begin{aligned} &\chi_1^{-1}(q_z) \sim \chi_1^{-1}(0) + Aq_z^2, \quad \vec{q} = (0,0,q_z) \ , \\ &\chi_1^{-1}(q) \sim \chi_1^{-1}(0) + Bq^2, \quad \vec{q} = (q,q,0) \ , \end{aligned} \tag{34}$$

where

$$B/A = 2b(1 - a)/(a + b) \ , \tag{35}$$

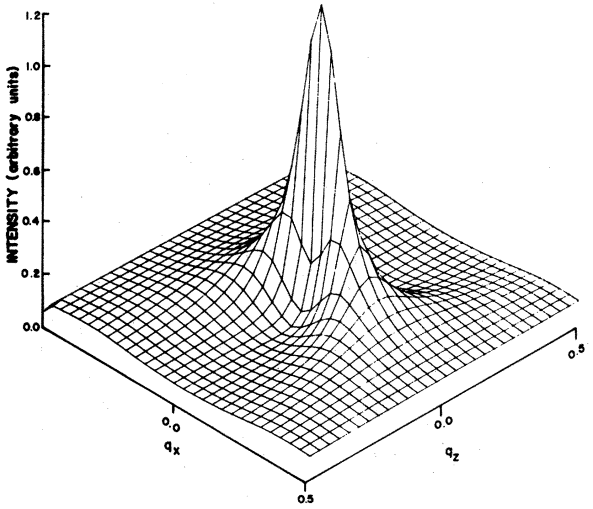

FIG. 3. Plot of $\chi_1(q)$ in the (q,q,q_z) plane using the known Slater energies $\epsilon_0 = 92$ K, $\epsilon_1 = 907$ K for KD_2PO_4 at $T - T_c = 5$ K.

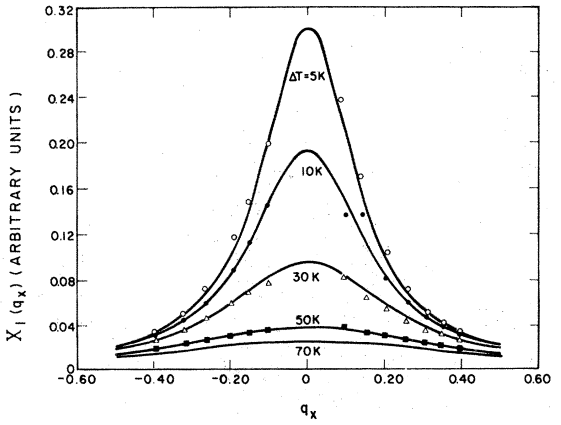

FIG. 5. Plot of $\chi_1(q)$ along $(q_x, 0, 0)$ for different values of temperature. The points are experimental data (Ref. 14).

which means $B/A \ll 1$ (recall that $b/a \ll 1$). Using the above values for ϵ_0 and ϵ_1, we obtain $B/A \sim 0.02$ at $T \simeq T_c = 220$ K and $B/A \sim 0.03$ at $T = 300$ K. Qualitatively similar anisotropy has been found for the same model using a mean-field approximation, although in that approximation the ratio B/A is independent of temperature.[12] However, due to the use of the bare competing interaction constants U and V, the mean-field treatment predicts a completely incorrect transition temperature and cannot be used for comparison with the observed temperature dependence of the susceptibilities. By contrast, the present results [e.g., (32) and (33)] are known to be in good agreement with the observed $q = 0$ susceptibilities in KD_2PO_4, and hence can be used with the same parameters for comparison with the available $q \neq 0$ scattering measurements. Indeed, neutron scattering measurements for KD_2PO_4 reveal a strong anisotropy in the (q_x,q_z) plane and give contour lines[13,14] which are closely reproduced by the theoretical result which is plotted in Fig. 4.

A quantitative comparison between the predictions of (33) and the experimental results at several temperatures is shown in Fig. 5. As can be seen, the finite-q cluster results are indeed in good agreement with the data.[14] For comparison, we present in Fig. 6 the predicted decrease of $\chi_1(q)$ along the $\hat{q}_z$ directions for the same set of temperatures.

In conclusion, the quantitative agreement between the results of the present approach and experiment

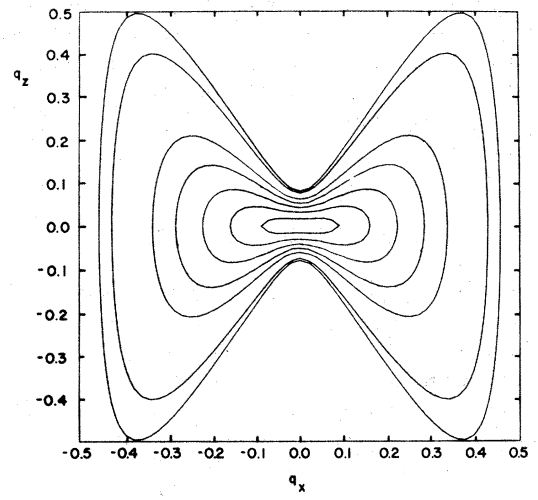

FIG. 4. Solution of the equation $\chi_1(q) = \text{const}$ in the (q_x,q_z) plane for different values of $\chi_1(q)$ at $T - T_c = 5$ K.

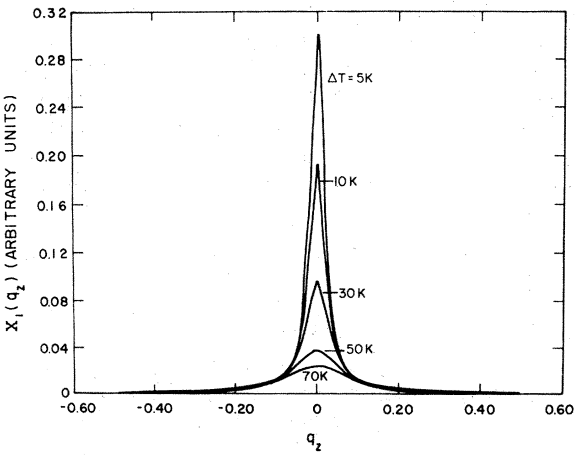

FIG. 6. Plot of $\chi_1(q)$ along $(0,0,q_z)$ for different values of temperature.

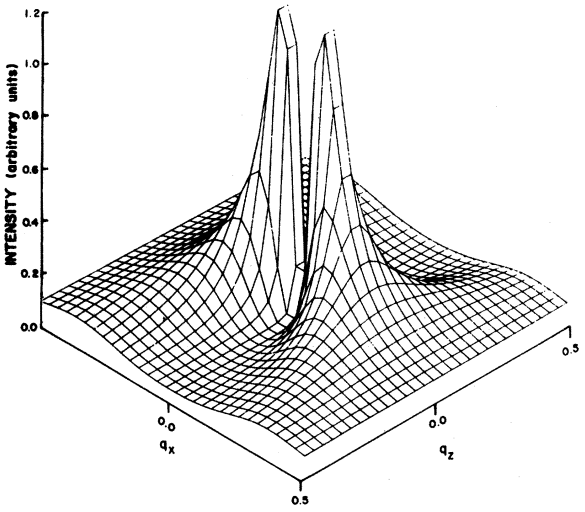

FIG. 7. Plot of $\chi_1(q)$, given in Eq. (30), in the plane (q,q,q_z) for the ice-rule limit, $\epsilon_0=92$ K, $\epsilon_1=\infty$ at $T-T_c=5$ K.

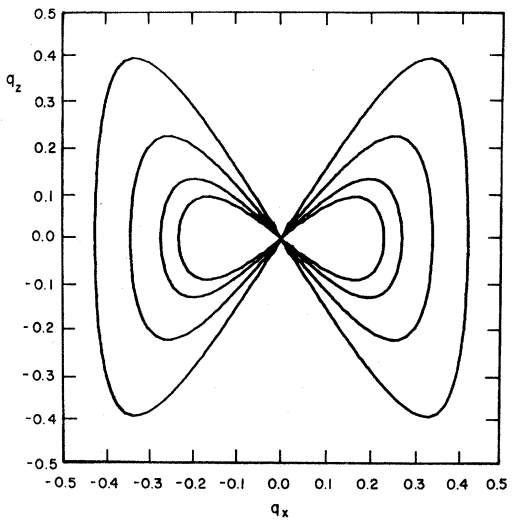

FIG. 8. Contours of $\chi_1(q)$ in the plane (q,q,q_z) for the ice-rule limit, $\epsilon_0=92$ K, $\epsilon_1=\infty$ at $T-T_c=5$ K.

strongly indicates that the short-range interactions, rather than the long-range dipolar forces,[13] may play the dominant role in producing the strongly anisotropic fluctuations in KDP-type crystals.

IV. ICE-RULE SYSTEMS

Ice-rule systems are described by bond configurations in which all the groups have exactly two hydrogens adjacent to them. This amounts to excluding all the energy levels except for the two ground states and the four levels with energy ϵ_0 (see Fig. 2). The ice-rule limit is included in the general model (24) by taking $V\to\infty$ and $U+V=$const or, equivalently, $\epsilon_1\to\infty$, $\epsilon_0=$const [see (25)]. From the discussion in Sec. III, it follows that the anisotropy is expected to be enhanced in this limit. In Fig. 7, we plot $\chi_1(\vec{q})$ as given in (30) in the plane (q,q,q_z) for the case $\epsilon_0=92$ K, $\epsilon_1=\infty$ at $T-T_c=5$ K. Contours of $\chi_1(q)$ for the same set of parameters are plotted in Fig. 8. These results show a dipolar-type singularity near the origin. The singular dependence on $\vec{q}$ can be extracted from (31), which yields for $\epsilon_1=\infty$ and small q,

$$\chi_1^{-1}(q)\simeq\chi_1^{-1}(0)+B\frac{q_z^2}{2q_\perp^2+q_z^2}\ , \tag{36}$$

with $\chi_1^{-1}(0)=(a-\frac{1}{2})/\beta$ and $B=(1+2a)\times(a^{-1}-1)/2\beta$. A similar singularity appears in the mean-field treatment.[12] However, in that case $\chi_1^{-1}(0)$ diverges in the ice-rule limit, whereas in the cluster approximation both B and $\chi_1^{-1}(0)$ remain finite. It should be noted that the predicted dipolar singularity (36), in the ice-rule systems qualitatively agrees with the exact result for the correlations in the special case of a six-vertex model.[16] Finally, the same type of singularity has been observed in neutron scattering measurements of copper formate tetrahydrate which is known to satisfy the ice-rule constraints. Using a different approach, Youngblood *et al.*[15] argued that a singularity of the type given in (36) exists in ice-rule systems. The present approach, however, provides a systematic treatment of the anisotropy in both the ice-rule systems and in systems for which these rules are not strictly obeyed. Also, our predictions contain both the $q=0$ critical susceptibilities and the q-dependent parts, thus enabling us to make a quantitative comparison with the scattering data using only the parameters which are determined via the uniform static measurements. Finally, we obtain an explicit expression for the susceptibility which is valid not only in the asymptotic region $\vec{q}\to 0$ limit but for finite $\vec{q}$ as well.

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