

Critical Behavior of the Pseudospin Model of Order-Disorder Type Ferroelectrics

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The behavior of the specific heat, the field-dependent susceptibility, and the soft mode is considered in the neighborhood of the critical point using the spin model for hydrogen-bonded ferroelectrics with a purely dipolar interaction. Shape-independent results are obtained if one refers always to the state of zero internal field, i.e., with an external field present that just compensates the depolarizing field. The results are expressed in terms of the nonvanishing expectation values of single spin operators. These can be obtained either by solving self-consistency conditions or more crudely by using the molecular-field values. The critical coefficients are given explicitly for the latter case. For the specific heat a logarithmic singularity is obtained, while the inverse susceptibility is found to depend linearly on $|T - T_c|$. The next higher-order response functions and the corresponding behavior of the soft mode, as well as the leading power in the electric field of the susceptibility and the soft mode at $T = T_c$, have also been calculated. The predicted critical behavior agrees with experimental results surprisingly close to the critical point.

I. INTRODUCTION

RECENTLY a microscopic model for order-disorder type ferroelectrics was introduced by Blinc¹ which takes into account the tunneling of the "ferroelectric" ions [the protons forming the hydrogen bonds in substances like KH_2PO_4 (KDP)] in their double-well potentials. This model could be conveniently reformulated in terms of a pseudospin model.²⁻⁶ Even in its simplest form,^{2,3} which consists of an Ising interaction Hamiltonian with an additional tunneling term, it accounts qualitatively for many of the properties of order-disorder type ferroelectrics. In particular, in the molecular-field approximation one finds a second-order phase transition with a spontaneous dipole moment in the ordered phase, and with low-lying collective excitations exhibiting the Cochran-Landauer behavior in the neighborhood of the transition temperature.^{3,4}

As a first step in studying the critical behavior of order-disorder ferroelectrics, we have examined the simple model,^{2,3} taking only the motion of the protons into account. Since their displacements are small compared to the nearest-neighbor proton-proton distance, the interaction between the protons is approximated by a dipolar interaction. These calculations must be considered preliminary for two distinct reasons. The model may be oversimplified, and the statistical mechanical treatment may be too crude.

The model neglects the strong coupling between the protons and the other ions of the crystal⁴ as well as

three- and four-body interactions between the protons.⁵ This model has so far been applied exclusively to KDP. Mueller has, however, recently pointed out⁷ that the simple model may be expected to apply more closely to triglycine sulphate (TGS) than to KDP. In the latter crystal, each PO_4 ion is linked to four other PO_4 ions by hydrogen bonds, and the four protons forming these bonds are known to interact strongly via three- and four-body forces which give rise to the "Slater rules."⁸ In TGS, on the other hand, glycenium ions are only linked in pairs by single hydrogen bonds, and one would expect three- and four-body interactions to be much less important. Since, in addition, the lattice distortion induced by the phase transition is smaller in TGS than in KDP, one might conclude that interaction with other phonon modes is also less important in TGS. This will, however, be true only for the acoustic modes. In both crystals, the phase transition induced by the ordering of the protons gives rise to appreciable internal displacements of other ion groups in the unit cell. In TGS this results mainly in a bending of one member⁹ of the glycenium ion pair, and a shift of the unpaired glycenium ion.^{9,10} These displacements, as well as the electronic polarization of the ions, give a contribution to the spontaneous polarization of the crystal that is usually larger than the direct proton contribution and of a different direction.⁸ They will further lead to an indirect interaction between the protons that may well be larger than the direct dipolar interaction, and that is only approximately described by the interaction term of our model.

The approximation procedure used in our statistical mechanical treatment becomes invalid within a certain temperature interval ΔT around the transition temper-

¹ R. Blinc, *J. Phys. Chem. Solids* **13**, 204 (1960).

² P. G. de Gennes, *Solid State Commun.* **1**, 132 (1963).

³ R. Brout, K. A. Mueller, and H. Thomas, *Solid State Commun.* **4**, 507 (1966).

⁴ J. Villain and S. Stamenkovic, *Phys. Status Solidi* **15**, 585 (1966).

⁵ R. Blinc and S. Svetina, *Phys. Letters* **15**, 119 (1965); *Phys. Rev.* **147**, 423 (1966).

⁶ M. Tokunaga and T. Matsubara, *Progr. Theoret. Phys.* (Kyoto) **35**, 581 (1966).

⁷ K. A. Mueller (private communication).

⁸ See for example F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

⁹ S. Hoshina, Y. Okaya, and R. Pepinsky, *Phys. Rev.* **115**, 323 (1959).

¹⁰ J. L. Bjorkstam, *Phys. Rev.* **153**, 599 (1967).

ature T_c , where the critical fluctuations are large. General considerations¹¹ show ΔT to be the smaller, the larger the range of the interaction, or rather, the more concentrated the Fourier transform of the interaction is around the origin in reciprocal space. Because of the long-range nature of the dipolar interaction, one might expect ΔT to be quite small in our case, so that the approximation remains acceptable even for temperatures reasonably close to T_c . However, the Fourier transform of the dipolar interaction is not very concentrated around the origin, but has a variation over all of the Brillouin zone, which in a definite direction is qualitatively similar to that of an isotropic nearest-neighbor exchange interaction. That is, the particular angular dependence makes the dipolar interaction effectively short-ranged in real space. There exists, of course, the possibility that indirect interaction mechanisms, like the one mentioned above, have a longer effective range, but that would have to be shown in detail.

Experimental results, on the other hand, seem to agree with the results of the present approximation scheme surprisingly close to T_c . Susceptibility measurements on KDP by Craig¹² show a linear dependence on $(T-T_c)$ for the reciprocal susceptibility, in agreement with Eq. (48) below, outside an interval of $\Delta T \sim 5 \times 10^{-4} T_c$. Within this interval first-order effects complicate the phase transition.^{10,12} The inverse susceptibility in TGS depends linearly on $(T-T_c)$ outside $\Delta T \sim 2 \times 10^{-4} T_c$ on both sides of the transition point.^{12,13}

For the specific heat the situation is less clear. The specific heat of KDP was recently measured by Reese and May.¹⁴ These authors obtain a logarithmic behavior, in agreement with our Eq. (35) below, on both sides of the critical point outside an interval of $\Delta T \sim 10^{-4} T_c$. On the other hand, a recent analysis¹⁵ of some early specific-heat measurements by Stephenson *et al.*¹⁶ yielded a reciprocal square-root singularity outside $\Delta T \sim 10^{-3} T_c$, whereas a previous analysis¹⁷ of the same data suggested a logarithmic dependence. For TGS, an analysis by Grindlay¹⁸ of specific-heat measurements by Strukov¹⁹ gave evidence of a logarithmic behavior for $10^{-3} T_c \lesssim T \lesssim 10^{-2} T_c$.

The temperature dependence of the soft ferroelectric

mode frequency in KDP has recently been measured,²⁰ and its real part shows a variation, in good agreement with Eq. (26) below.

Further experiments to determine the nature of the transition particularly for TGS would be of great interest, as would the determination of the critical coefficients in the presence of an applied field, both for KDP and TGS.

In Sec. II the required spin-pair correlation functions are calculated. The specific-heat calculation is presented in Sec. III, and in Secs. IV and V the effect of an external electric field on the polarization and the Cochran mode is studied. In Sec. VI we discuss briefly the effect of the interaction of the protons with other ions.

II. MATHEMATICAL FORMULATION

For reasons of mathematical simplicity, we formulate the theory for a rigid lattice and consider only direct proton interactions. We expect, however, that the effect of the motion of the other ions can be taken approximately into account by using effective values for the interaction parameters and the dipole moment, which will leave the functional dependence of the physical properties on temperature and field unchanged.

The model is described in terms of Pauli spin operators $\sigma_i(\alpha)$ ($i=1, 2, 3$) at lattice site α . We assign a direction $\zeta(\alpha)$ to the line connecting the two valleys of the double-well potential at site α , and call the valleys on the positive and negative sides $V^+(\alpha)$ and $V^-(\alpha)$, respectively. The operator $\sigma_3(\alpha)$ describes the excess in population of the valley $V^+(\alpha)$ over that of $V^-(\alpha)$, and is thus proportional to the dipole moment of that lattice site, and $\sigma_1(\alpha)$ and $\sigma_2(\alpha)$ are operators which transfer the ion from one valley to the other. The $\sigma_i(\alpha)$ satisfy the commutation relations

$$[\sigma_i(\alpha), \sigma_j(\alpha')] = 2i\delta_{\alpha\alpha'} \epsilon_{ijk} \sigma_k(\alpha), \quad (1)$$

where ϵ is the totally antisymmetric tensor of third rank. Unless otherwise noted, the operators will be taken in the Heisenberg representation.

In the simplest case, to which we shall restrict ourselves in this paper, the system is described by a Hamiltonian containing only a tunneling term and an interaction term.^{2,3} Since we shall consider the system in the presence of an external field \mathbf{E}^{ext} , we add a term describing the interaction of the system with this field. Thus,

$$H = -\Gamma \sum_{\alpha} \sigma_1(\alpha) - \frac{1}{2} \sum_{\alpha\alpha'} v(\alpha\alpha') \sigma_3(\alpha) \sigma_3(\alpha') - \mathbf{E}^{\text{ext}} \cdot \sum_{\alpha} \mathbf{p}(\alpha) \sigma_3(\alpha). \quad (2)$$

¹¹ R. Brout, *Phase Transitions* (W. A. Benjamin, Inc., New York, 1965), Chap. 2.

¹² P. P. Craig, *Phys. Letters* **20**, 140 (1966).

¹³ S. Triebwasser, *IBM J. Res. Develop.* **1**, 212 (1958); J. J. Brophy and S. L. Webb, *Phys. Rev.* **128**, 584 (1962).

¹⁴ W. Reese and L. F. May, *Phys. Rev.* **162**, 510 (1967).

¹⁵ D. T. Teaney, *Solid State Commun.* **5**, 207 (1967).

¹⁶ C. C. Stephenson and J. C. Hooley, *J. Am. Chem. Soc.* **66**, 1397 (1944); C. C. Stephenson and A. C. Zettlemayer, *ibid.* **66**, 1402 (1944).

¹⁷ J. Grindlay, *Phys. Rev.* **139**, A1603 (1965).

¹⁸ J. Grindlay, *Phys. Letters* **18**, 239 (1965).

¹⁹ B. A. Strukov, *Fiz. Tverd. Tela* **6**, 2862 (1964) [English transl.: *Soviet Phys.—Solid State* **6**, 2278 (1965)].

²⁰ I. P. Kaminow and T. C. Damen, *Phys. Rev. Letters* **20**, 1105 (1968).

Here, 2Γ is the tunneling frequency,²¹ $\mathbf{p}(\boldsymbol{\alpha})$ is the dipole moment due to the ion at site $\boldsymbol{\alpha}$ being displaced into the valley $V^+(\boldsymbol{\alpha})$, and $\mp v(\boldsymbol{\alpha}, \boldsymbol{\alpha}')$ is the interaction energy between particles at lattice sites $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$ when they are in corresponding (−) and opposite (+) valleys of their potentials, respectively. In Appendix A, we discuss the properties of $v(\boldsymbol{\alpha}, \boldsymbol{\alpha}')$ for the case of purely dipolar interaction.

In order to obtain the susceptibility and the specific heat, we shall need the spin-spin correlation functions. For the Hamiltonian Eq. (2), both $\sigma_1(\boldsymbol{\alpha})$ and $\sigma_3(\boldsymbol{\alpha})$ will, in general, have average values $\langle\sigma_1(\boldsymbol{\alpha})\rangle$ and $\langle\sigma_3(\boldsymbol{\alpha})\rangle$ about which fluctuations will occur. We restrict ourselves, for simplicity, to the case that all double-well potentials are identical and have parallel axes, and to a ferroelectrically ordered state. Then, the average values are independent of the site $\boldsymbol{\alpha}$. We define the fluctuations $\tau_i(\boldsymbol{\alpha})$ by

$$\sigma_i(\boldsymbol{\alpha}t) = \langle\sigma_i\rangle + \tau_i(\boldsymbol{\alpha}t). \quad (3)$$

For the purpose of calculation it is most convenient to study the time-ordered correlation functions (Green's functions) of the form

$$G_{ij}(\boldsymbol{\alpha}t, \boldsymbol{\alpha}'t') = -i\langle(\tau_i(\boldsymbol{\alpha}t)\tau_j(\boldsymbol{\alpha}'t'))_+\rangle. \quad (4)$$

The $+$ denotes the Wick time-ordering operation, and $\langle \rangle$ the thermal average. These functions possess Fourier series expansions²²

$$G_{ij}(\boldsymbol{\alpha}t, \boldsymbol{\alpha}'t') = (1/N) \sum_{\mathbf{q}} \exp[i\mathbf{q}\cdot(\boldsymbol{\alpha}-\boldsymbol{\alpha}')] G_{ij}(\mathbf{q}, t-t'), \quad (5)$$

$$G_{ij}(\mathbf{q}, t-t') = (-i\beta)^{-1} \sum_{\nu} \exp[-i\omega_{\nu}(t-t')] \times G_{ij}(\mathbf{q}, \omega_{\nu}), \quad (6)$$

and a spectral representation²³

$$G_{ij}(\mathbf{q}, \omega_{\nu}) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi_{ij}''(\mathbf{q}, \omega)}{\omega_{\nu} - \omega}. \quad (7)$$

Here, N is the number of lattice sites, and $\omega_{\nu} = 2\pi\nu/(-i\beta)$ where ν is an integer. The spectral weight function $\chi_{ij}''(\mathbf{q}, \omega)$ is defined by

$$\chi_{ij}''(\mathbf{q}, \omega) = \frac{1}{2} \int dt \exp[i\omega(t-t')] \times \sum_{\boldsymbol{\alpha}} \exp[-i\mathbf{q}\cdot(\boldsymbol{\alpha}-\boldsymbol{\alpha}')] \langle[\tau_i(\boldsymbol{\alpha}t), \tau_j(\boldsymbol{\alpha}'t')] \rangle. \quad (8)$$

The Green's functions satisfy the equation of motion

$$i(\partial/\partial t)G_{ij}(\boldsymbol{\alpha}t, \boldsymbol{\alpha}'t') = \delta_{\alpha\alpha'}\delta(t-t') \langle[\tau_i(\boldsymbol{\alpha}t), \tau_j(\boldsymbol{\alpha}t)] \rangle - i\langle(i(\partial/\partial t)\tau_i(\boldsymbol{\alpha}t)\tau_j(\boldsymbol{\alpha}'t'))_+\rangle. \quad (9)$$

The equations of motion for the individual spin operators, which follow trivially from the Hamiltonian Eq. (2) using the commutation relations Eq. (1), are linearized about the average values $\langle\sigma_i\rangle$, and the resulting expressions for $\partial\tau_i(\boldsymbol{\alpha}t)/\partial t$ are substituted into Eq. (9). Then, making use of the Fourier series Eq. (6), the following set of coupled equations is obtained:

$$\omega_{\nu}G_{33}(\mathbf{q}, \omega_{\nu}) = -2i\Gamma G_{23}(\mathbf{q}, \omega_{\nu}), \quad (10)$$

$$\omega_{\nu}G_{23}(\mathbf{q}, \omega_{\nu}) = 2i\langle\sigma_1\rangle - 2i[v(0)\langle\sigma_3\rangle + pE_{\zeta}^{\text{ext}}]G_{13}(\mathbf{q}, \omega_{\nu}) + 2i[\Gamma - v(\mathbf{q})\langle\sigma_1\rangle]G_{33}(\mathbf{q}, \omega_{\nu}), \quad (11)$$

$$\omega_{\nu}G_{13}(\mathbf{q}, \omega_{\nu}) = 2i[v(0)\langle\sigma_3\rangle + pE_{\zeta}^{\text{ext}}]. \quad (12)$$

In addition, setting the static parts of the equations of motion for σ_i equal to zero yields the following relationship between the average values of σ_1 and σ_3 :

$$\Gamma\langle\sigma_3\rangle - [v(0)\langle\sigma_3\rangle + pE_{\zeta}^{\text{ext}}]\langle\sigma_1\rangle = 0. \quad (13)$$

In these equations

$$v(\mathbf{q}) = \sum_{\boldsymbol{\alpha}} v(\boldsymbol{\alpha}, \boldsymbol{\alpha}') \exp[-i\mathbf{q}\cdot(\boldsymbol{\alpha}-\boldsymbol{\alpha}')] \quad \text{and}$$

$$v(0) = \sum_{\boldsymbol{\alpha}} v(\boldsymbol{\alpha}, \boldsymbol{\alpha}'). \quad (14)$$

The Green's functions G_{33} and G_{13} will be particularly useful for the calculations that follow. From Eqs. (10)–(12) we obtain for $\nu \neq 0$

$$G_{33}(\mathbf{q}, \omega_{\nu}) = 4\Gamma\langle\sigma_1\rangle/(\omega_{\nu}^2 - \omega_{\mathbf{q}}^2), \quad (15)$$

$$G_{13}(\mathbf{q}, \omega_{\nu}) = -\frac{4[v(0)\langle\sigma_3\rangle + pE_{\zeta}^{\text{ext}}]\langle\sigma_1\rangle}{\omega_{\nu}^2 - \omega_{\mathbf{q}}^2}, \quad (16)$$

where $\omega_{\mathbf{q}}$ are the eigenfrequencies for small oscillations about the mean values $\{\langle\sigma_1\rangle, 0, \langle\sigma_3\rangle\}$,²

$$\omega_{\mathbf{q}}^2 = 4\Gamma[\Gamma - v(\mathbf{q})\langle\sigma_1\rangle] + 4[v(0)\langle\sigma_3\rangle + pE_{\zeta}^{\text{ext}}]^2. \quad (17)$$

For dipolar interaction, $v(0)$ will be shape-dependent. One obtains shape-independent physical properties if one refers to the state of zero internal field, i.e., if an external field is present that just compensates the depolarizing field. Using the expression for the required external field given by Eq. (A17) in Appendix A, we can write

$$v(0)\langle\sigma_3\rangle_0 + pE_{\zeta}^{\text{ext}} = v_{\text{eff}}\langle\sigma_3\rangle_0, \quad (18)$$

where v_{eff} is the shape-independent quantity defined in Eq. (A19), and where the subscript zero refers to the state of zero internal field. Thus, for vanishing internal field, Eq. (13) takes the form²⁴

$$[\Gamma - v_{\text{eff}}\langle\sigma_1\rangle_0]\langle\sigma_3\rangle_0 = 0. \quad (19)$$

²⁴ This relation implies that the perpendicular susceptibility χ_{\perp} for the pure Ising model is constant for $T \leq T_c$ (Γ here plays the role of a transverse field). This may be compared with exact calculations by M. E. Fisher [J. Math. Phys. 4, 124 (1963)] for the two-dimensional Ising model which shows a variation of χ_{\perp} of less than 14% for the interval $0 \leq T \leq T_c$, and in three dimensions the deviations from a constant value are expected to be less pronounced.

²¹ $\hbar = 1$ in this paper.

²² See for example, L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962), Chaps. 1–3.

²³ This holds in general only for the terms $\nu \neq 0$. The case $\nu = 0$ is discussed below.

The normal mode frequency can be written

$$\omega_q^2 = \omega_0^2 + 4\Gamma \langle \sigma_1 \rangle_0 [v_{\text{eff}} - v(\mathbf{q})], \quad (20)$$

where

$$\omega_0^2 = 4\Gamma(\Gamma - v_{\text{eff}} \langle \sigma_1 \rangle_0) + 4v_{\text{eff}}^2 \langle \sigma_3 \rangle_0^2, \quad (21)$$

and where

$$v_{\text{eff}} > v(\mathbf{q}) \quad \text{for } \mathbf{q} \neq 0 \quad (22)$$

is required as a stability condition for ferroelectric order.

It should be noted that this compensation of the depolarizing field is always necessary in order to obtain shape-independent results, whenever dipole forces are present. The procedure is the same whether or not additional short-range forces contribute to $v(\mathbf{q})$.

For $\nu=0$, the determinant of the system of Eqs. (10)–(12) vanishes, and the $\nu=0$ Fourier coefficients $G_{ij}(\mathbf{q}, 0)$ have to be determined by a different method. We obtain a relation between $G_{ij}(\mathbf{q}, 0)$ and the isothermal static susceptibility $\chi_{ij}^{\text{isoth}}(\mathbf{q})$ in the following way: We consider the system under the action of an additional static field $\varphi(\alpha)$ in pseudospin space, which adds to the Hamiltonian, Eq. (2), a term

$$H' = - \sum_{\alpha} \varphi(\alpha) \cdot \sigma(\alpha), \quad (23)$$

and obtain the isothermal susceptibility as the second derivative of the free energy with respect to this additional field $\varphi(\alpha)$. The result is

$$\chi_{ij}^{\text{isoth}}(\alpha, \alpha') = i \int_0^{-i\beta} \langle \tau_i(\alpha t) \tau_j(\alpha' 0) \rangle_{\varphi=0} dt, \quad (24)$$

which is recognized as the negative $\nu=0$ Fourier coefficient of the Green's function $G_{ij}(\alpha t, \alpha' t')$. After taking the spatial Fourier transform, we find

$$G_{ij}(\mathbf{q}, 0) = -\chi_{ij}^{\text{isoth}}(\mathbf{q}). \quad (25)$$

It can be shown that this result agrees with

$$\lim_{\omega \rightarrow 0} G_{ij}(\mathbf{q}, \omega_{\nu})$$

of Eq. (7) (regarding ω_{ν} as a continuous complex variable), only if the Green's function $G_{ij}(\alpha t, \alpha' t')$ goes to zero sufficiently rapidly for large time differences $|t-t'|$, and only then is $G_{ij}(\mathbf{q}, 0)$ given by the spectral representation Eq. (7). For the functions G_{13} and G_{33} , this is the case in the paraelectric phase, and we can therefore use Eqs. (15) and (16) also for $\omega_{\nu}=0$. In the ferroelectric phase, however, these functions approach nonvanishing values G_{ij}^{∞} for $|t-t'| \rightarrow \infty$, and we find a difference proportional to the constants G_{ij}^{∞} between the correct expression, Eq. (25), and the $\omega_{\nu}=0$ limit of Eqs. (15) and (16).

The Green's functions and the eigenfrequencies have been expressed in terms of the equilibrium values

$\langle \sigma_1 \rangle_0$ and $\langle \sigma_3 \rangle_0$ and the isothermal static susceptibility χ_{ij}^{isoth} . These quantities can either be obtained from a molecular-field approximation, or they can be determined in a self-consistent fashion analogous to the random-phase approximation for the Heisenberg Hamiltonian. In this paper, only the molecular-field values will be used, but we should like to emphasize that the results expressed in terms of $\langle \sigma_i \rangle_0$, $\langle \sigma_3 \rangle_0$, and χ_{ij}^{isoth} are more general than the molecular-field approximation.

The molecular-field values for $\langle \sigma_1 \rangle_0$ and $\langle \sigma_3 \rangle_0$ have been obtained in Refs. 3 and 4. With these values, $\omega_0(T)$ shows the Cochran-Landauer behavior for $T \approx T_c$:

$$\omega_0^2 = a_{\pm} |T - T_c| \quad (26)$$

with different coefficients a_+ above and a_- below the transition temperature.^{3,4}

The molecular-field calculation for χ_{ij}^{isoth} is presented in Appendix B. It is readily confirmed that the results Eqs. (B13) and (B14) for $\chi_{13}^{\text{isoth}}(\mathbf{q})$ and $\chi_{33}^{\text{isoth}}(\mathbf{q})$ agree with the $\omega_{\nu} \rightarrow 0$ limit of Eqs. (15) and (16) for $T > T_c$, but are different for $T < T_c$. By using the molecular-field values for $\langle \sigma_1 \rangle_0$ and $\langle \sigma_3 \rangle_0$, we find from Eqs. (B13)–(B16) for $T \approx T_c$ the critical behavior

$$\chi_{13}^{\text{isoth}}(\mathbf{q}) = - \frac{C(T_c - T)^{1/2}}{v_{\text{eff}} - v(\mathbf{q}) + b_-(T_c - T)}, \quad \text{for } T < T_c \quad (27)$$

$$\chi_{33}^{\text{isoth}}(\mathbf{q}) = [v_{\text{eff}} - v(\mathbf{q}) + b_{\pm} |T_c - T|]^{-1}, \quad \text{for } T \geq T_c. \quad (28)$$

Note that $\chi_{13}^{\text{isoth}}(\mathbf{q}) = 0$, for $T > T_c$.

III. CALCULATION OF THE SPECIFIC HEAT

The internal energy is given by

$$\langle H \rangle = -\Gamma \sum_{\alpha} \langle \sigma_1(\alpha) \rangle - \frac{1}{2} \sum_{\alpha, \alpha'} v(\alpha, \alpha') \langle \sigma_3(\alpha) \sigma_3(\alpha') \rangle - p E_{\zeta}^{\text{ext}} \sum_{\alpha} \langle \sigma_3(\alpha) \rangle. \quad (29)$$

The second term in this equation can be expressed in terms of the Green's function G_{33} . We obtain for zero internal field,

$$\langle H \rangle / N = -\Gamma \langle \sigma_1 \rangle_0 - \frac{1}{2} v_{\text{eff}} \langle \sigma_3 \rangle_0^2 - \frac{1}{2} (1/N) \sum_{\mathbf{q}} v(\mathbf{q}) i G_{33}(\mathbf{q}, t=t'). \quad (30)$$

The Fourier coefficients $G_{33}(\mathbf{q}, \omega_{\nu})$ are given by Eq. (15). Inverting the time Fourier series Eq. (6) and using the summation formula

$$(1/\beta) \sum_{\nu \neq 0} 1/(\omega - \omega_{\nu}) = n(\omega) + \frac{1}{2} - (1/\beta\omega), \quad (31)$$

where $n(\omega)$ is the Bose occupation number factor

$$n(\omega) = 1/(\exp\beta\omega - 1), \quad (32)$$

the equal-time Green's function $G_{33}(\mathbf{q}, t=t')$ may be written

$$iG_{33}(\mathbf{q}, t=t') = (4\Gamma\langle\sigma_1\rangle_0/\omega_q)[n(\omega_q) + \frac{1}{2} - (1/\beta\omega_q)] \\ + (1/\beta)\chi_{33}^{\text{isoth}}(\mathbf{q}). \quad (33)$$

When we substitute this equal-time Green's function

in the expression Eq. (30) for the internal energy, we note that only the χ^{isoth} part gives rise to a singularity of the specific heat.²⁵ On account of Eq. (28), the dominant contribution to the integral for $T \approx T_c$ comes from the small- q region. In order to determine the singular behavior near T_c , it is therefore sufficient to use the functional form for $v_{\text{eff}} - v(\mathbf{q})$ given by Eq. (A20) of Appendix A. In order to simplify the calculation, it will be assumed that ζ is a symmetry axis of the crystal. Then,

$$\chi_{33}^{\text{isoth}}(\mathbf{q}) = \frac{1}{4\pi n p^2 [q_x^2/q^2 + \frac{1}{2}(M_1 q_x^2 + M_2 q_y^2 + M_3 q_z^2)] + b_{\pm} |T - T_c|}. \quad (34)$$

The summation over the Brillouin zone in Eq. (30) is approximated by an integral over the Debye zone. The specific heat for zero internal field is obtained by differentiating the internal energy with respect to the temperature. For $T \gtrsim T_c$ we obtain for the singular term

$$C_v \approx \frac{b_{\pm}}{2\pi} \frac{v_{\text{eff}}}{n(4\pi n p^2)^2 \beta} \frac{1}{(M_1 + M_2)^{3/2}} \ln \frac{T_c}{T - T_c}. \quad (35)$$

In addition to the singular term, the $\langle\sigma_3\rangle_0^2$ and $\langle\sigma_1\rangle_0$ terms in Eq. (30), as well as the first term of Eq. (33), contribute to a finite discontinuity at $T = T_c$.

The logarithmic singularity is a consequence of the particular form of the dipolar interaction and does not depend on the presence of the tunneling term. For an isotropic interaction potential of the form

$$v_{\text{eff}} - v(q) = Aq^2 \quad \text{for } q \rightarrow 0, \quad (36)$$

a square-root singularity would be obtained for the specific heat.¹¹

For $T < T_c$, the singular term is negative. This represents a serious shortcoming of the approximation procedure for $T < T_c$. It should be emphasized that this result does not depend on the particular nature of the dipole interaction or on the presence of the tunneling term. It can be shown that the same difficulty occurs in the random-phase approximation (RPA) when this approximation is applied to the Ising model with isotropic interaction potential,¹¹ or even when applied to the Heisenberg model.²⁶ However, as far as we know, this difficulty has not been previously recognized. In both of these cases, as well as for the present model, the internal energy is a continuous function of temperature and has a cusp at $T = T_c$, from which it follows that any singular contribution to the specific heat at $T = T_c$ will have a different sign for $T > T_c$ and for $T < T_c$.

IV. FIELD-DEPENDENT SUSCEPTIBILITY

In the presence of a space- and time-varying electric field $\delta E(\alpha t)$ applied along the anisotropy axis, the following term is added to the Hamiltonian Eq. (2):

$$H^{\text{ext}} = -p \sum_{\alpha} \delta E(\alpha t) \sigma_3(\alpha t). \quad (37)$$

It is assumed that the field has been switched on at some past time t_0 such that $\delta E(\alpha t) = 0$ for $t < t_0$. This field is in addition to the static external field required to give zero internal field for $t < t_0$. The adiabatic response of the system to $\delta E(\alpha t)$ will be calculated using perturbation theory.

The linear response of the pseudospin operators to this additional field can be written

$$\delta^{(1)}\langle\sigma_i(\alpha t)\rangle = \sum_{\alpha'} \int_{-\infty}^{+\infty} dt' \chi_{i3}(\alpha t, \alpha' t') p \delta E(\alpha', t'), \quad (38)$$

where the adiabatic response function χ_{i3} has the form

$$\chi_{i3}(\alpha t, \alpha' t') = i\eta(t-t') \langle[\tau_i(\alpha t), \tau_3(\alpha' t')]\rangle_{\delta E=0}. \quad (39)$$

Here $\eta(t)$ is the step function. The Fourier transform of $\chi_{i3}(\alpha t, \alpha' t')$ is directly related to the spectral weight function $\chi_{i3}''(\mathbf{q}, \omega)$ defined by Eq. (8):

$$\chi_{i3}(\mathbf{q}, \omega) = (1/\pi) \int_{-\infty}^{\infty} \frac{\chi_{i3}''(\mathbf{q}, \omega')}{\omega' - \omega - i\epsilon} d\omega'. \quad (40)$$

The spectral weight function $\chi_{33}''(\mathbf{q}, \omega)$ is obtained from Eq. (15):

$$\chi_{33}''(\mathbf{q}, \omega) = (4\Gamma\langle\sigma_1\rangle_0/2\omega_q) \pi [\delta(\omega - \omega_q) - \delta(\omega + \omega_q)], \quad (41)$$

and the response function may be written in the form

$$\chi_{33}(\mathbf{q}, \omega) = 4\Gamma\langle\sigma_1\rangle_0/[\omega_q^2 - (\omega + i\epsilon)^2]. \quad (42)$$

²⁵ The first term is proportional to ω_q for small ω_q , as can be seen by expanding $n(\omega_q)$, and does not, therefore, contribute to the singularity.

²⁶ H. S. Bennett, Ann. Phys. (N.Y.) **39**, 127 (1966).

In our model, the electrical susceptibility tensor has only one nonvanishing component α_{FF} , which for $q \neq 0$ is given by

$$\alpha_{\text{FF}}(\mathbf{q}, \omega) = n p^2 \chi_{33}(\mathbf{q}, \omega). \quad (43)$$

Note that the other components of the pseudospin response tensor have no relation to the electrical susceptibility. Special attention is required for the $q=0$ case where the discontinuous behavior of $\omega_{\mathbf{q}}$ at $q=0$ reflects the fact that the response to a spatially uniform field is shape-dependent. For this reason, the susceptibility at $q=0$ is defined as the response to a change in the *internal* field:

$$\delta E^{\text{int}} = \delta E - 4\pi n p \delta^{(1)} \langle \sigma_3 \rangle N_{\text{FF}}. \quad (44)$$

It is therefore given by

$$\begin{aligned} \alpha_{\text{FF}}(0, \omega) &= n p^2 \chi_{33}(0, \omega) / [1 - 4\pi n p^2 N_{\text{FF}} \chi_{33}(0, \omega)] \\ &\equiv n p^2 \tilde{\chi}_{33}(\omega), \end{aligned} \quad (45)$$

which leads to the shape-independent result

$$\alpha_{\text{FF}}(0, \omega) = 4n p^2 \Gamma \langle \sigma_1 \rangle_0 / [\omega_0^2 - (\omega + i\epsilon)^2] \quad (46)$$

with ω_0 as defined by Eq. (21). It is equal to the $\mathbf{q} \rightarrow 0$ limit of $\alpha_{\text{FF}}(\mathbf{q}, \omega)$ for $\mathbf{q} \perp \zeta$. If we use the molecular-field result Eq. (26) for ω_0 , we obtain for the static limit of the adiabatic susceptibility the critical behavior

$$\alpha_{\text{FF}}(\mathbf{q}, 0) = n p^2 / [v_{\text{eff}} - v(\mathbf{q}) + c_{\pm} |T - T_c|] \quad (47)$$

and

$$\alpha_{\text{FF}}(0, 0) = n p^2 / c_{\pm} |T - T_c|, \quad (48)$$

with different coefficients c_+ above and c_- below T_c .

The isothermal susceptibility $\alpha_{\text{FF}}^{\text{isoth}}(\mathbf{q})$ is given by the same expressions Eq. (43) and Eq. (45) except that the adiabatic response function χ_{33} is replaced by the isothermal response function χ_{33}^{isoth} . The isothermal susceptibility agrees with the static limit of the adiabatic susceptibility only for $T > T_c$. From Eq. (28) it follows that the critical behavior of $\alpha_{\text{FF}}^{\text{isoth}}(\mathbf{q})$ is of the form given by Eqs. (47) and (48) with the coefficients c_{\pm} replaced by b_{\pm} where $b_+ = c_+$ but $b_- \neq c_-$.

The expression Eq. (42) for the frequency-dependent susceptibility has been previously derived by Brout, Mueller, and Thomas⁸ and later (in the $q=0$ limit) by Silverman,²⁷ who in addition considered relaxation effects. The static limit was first derived by Tokunaga and Matsubara,⁶ using the molecular-field approximation. The particular consequences of dipolar interaction were, however, not studied in these papers.

For the higher-order response functions we shall, for simplicity, consider only the isothermal response to a time-independent spatially uniform field δE^{int} . All response functions with respect to the internal field are denoted by a tilde.

The isothermal response to an additional field in the pseudospin space is considered in Appendix B. The quadratic response of the polarization $P = n p \langle \sigma_3 \rangle$ to a field in real space can be written

$$\delta^2 P = n p \tilde{\chi}_{333}^{\text{isoth}} (p \delta E^{\text{int}})^2, \quad (49)$$

where $\tilde{\chi}_{333}^{\text{isoth}}$ is given in Eq. (B30) of Appendix B. For $T < T_c$, we obtain the critical behavior

$$\tilde{\chi}_{333}^{\text{isoth}} = \text{const} / (T_c - T) \quad (T < T_c). \quad (50)$$

We give here also the result for $\tilde{\chi}_{133}^{\text{isoth}}$. From Eq. (B29) we find

$$\tilde{\chi}_{133}^{\text{isoth}} = \text{const} / (T - T_c)^2 \quad (T < T_c). \quad (51)$$

For $T > T_c$, the second-order response $\delta^2 P$ is zero, since the polarization is an odd function of the field. In this case, it is possible to obtain the third-order response

$$\delta^3 P = n p \tilde{\chi}_{3333}^{\text{isoth}} (p \delta E^{\text{int}})^3 \quad (52)$$

from the second-order response coefficient $\tilde{\chi}_{133}^{\text{isoth}}$ by means of Eq. (13), which may be written in the form

$$[\Gamma - v_{\text{eff}} \langle \sigma_1 \rangle] \langle \sigma_3 \rangle = p \delta E^{\text{int}} \langle \sigma_1 \rangle. \quad (53)$$

If we insert the power series in δE^{int} for $\langle \sigma_1 \rangle$ and $\langle \sigma_3 \rangle$ and compare the coefficients, we find

$$\tilde{\chi}_{3333}^{\text{isoth}} = [\Gamma / (\Gamma - v \langle \sigma_1 \rangle_0)^2] \tilde{\chi}_{133}^{\text{isoth}}. \quad (54)$$

For $\tilde{\chi}_{133}^{\text{isoth}}$, we obtain from Eq. (B29) the critical behavior

$$\tilde{\chi}_{133}^{\text{isoth}} = \text{const} / (T - T_c)^2, \quad (T > T_c) \quad (55)$$

which gives for the third-order response

$$\tilde{\chi}_{3333}^{\text{isoth}} = \text{const} / (T - T_c)^4, \quad (T > T_c). \quad (56)$$

For $T = T_c$, there exists no power-series expansion for the response. For both $|\beta - \beta_c|$ and $p \delta E^{\text{int}}$ small, but one not necessarily small compared to the other, an equation of state can be derived from the molecular-field equations of the form

$$\langle \sigma_3 \rangle^3 - A \langle \sigma_3 \rangle \Delta - B (p \delta E^{\text{int}} / v_{\text{eff}}) = 0, \quad (57)$$

$$\langle \sigma_1 \rangle = (\Gamma / v_{\text{eff}}) - (\langle \sigma_3 \rangle^2 / A) + \Delta, \quad (58)$$

where

$$\Delta = \tanh \Gamma \beta - \tanh \Gamma \beta_c \approx [1 - (\Gamma^2 / v_{\text{eff}}^2)] \Gamma (\beta - \beta_c) \quad (59)$$

and

$$\begin{aligned} B &= (\Gamma / v_{\text{eff}}) A \\ &= 2 \frac{\Gamma^2 / v_{\text{eff}}^2}{1 - \beta_c v_{\text{eff}} (1 - \Gamma^2 / v_{\text{eff}}^2)}. \end{aligned} \quad (60)$$

The solution of Eq. (57) can be written

$$\begin{aligned} \langle \sigma_3 \rangle &= \left\{ \frac{1}{2} B p \delta E / v_{\text{eff}} + \left[\left(\frac{1}{2} B p \delta E / v_{\text{eff}} \right)^2 - \left(\frac{1}{3} A \Delta \right)^3 \right]^{1/2} \right\}^{1/3} \\ &+ \left\{ \frac{1}{2} B p \delta E / v_{\text{eff}} - \left[\left(\frac{1}{2} B p \delta E / v_{\text{eff}} \right)^2 - \left(\frac{1}{3} A \Delta \right)^3 \right]^{1/2} \right\}^{1/3}. \end{aligned} \quad (61)$$

²⁷ B. D. Silverman, Phys. Rev. Letters **20**, 443 (1968).

For $T = T_c$, i.e., $\Delta = 0$, one obtains

$$\langle \sigma_3 \rangle = B^{1/3} [p \delta E^{\text{int}} / v_{\text{eff}}]^{1/3} \quad (62)$$

and

$$\langle \sigma_1 \rangle = (\Gamma / v_{\text{eff}}) \{ 1 - B^{-1/3} [p \delta E^{\text{int}} / v_{\text{eff}}]^{2/3} \}. \quad (63)$$

V. FIELD DEPENDENCE OF THE NORMAL MODE FREQUENCY

The normal mode frequency in an arbitrary uniform field is given by Eq. (17) and may be written in the form

$$\omega_q^2 = 4\Gamma [\Gamma - v(\mathbf{q}) \langle \sigma_1 \rangle] + 4[v_{\text{eff}} \langle \sigma_3 \rangle + p \delta E^{\text{int}}]^2. \quad (64)$$

We make use of the results of the preceding section in order to obtain the field dependence of ω_q . For $T > T_c$, we find a shift of second order in the field:

$$\omega_q^2(\delta E^{\text{int}}) = \omega_q^2(0) + 4[(1 + v_{\text{eff}} \tilde{\chi}_{33}^{\text{isoth}})^2 - \Gamma v(\mathbf{q}) \tilde{\chi}_{133}^{\text{isoth}}] (p \delta E^{\text{int}})^2, \quad (65)$$

which leads to the critical behavior

$$\omega_q^2(\delta E^{\text{int}}) = a_+(T - T_c) + 4\Gamma \langle \sigma_1 \rangle_0 [v_{\text{eff}} - v(\mathbf{q})] + \frac{[g_+ + h_+ v(\mathbf{q})]}{(T - T_c)^2} (p \delta E^{\text{int}})^2, \quad (T > T_c). \quad (66)$$

For $T < T_c$, the shift is linear in δE^{int} :

$$\omega_q^2(\delta E^{\text{int}}) = \omega_q^2(0) + 4[2v_{\text{eff}} \langle \sigma_3 \rangle_0 (1 + v_{\text{eff}} \tilde{\chi}_{33}^{\text{isoth}}) - \Gamma v(\mathbf{q}) \tilde{\chi}_{133}^{\text{isoth}}] (p \delta E^{\text{int}}) \quad (67)$$

and we find the critical behavior

$$\omega_q^2(\delta E^{\text{int}}) = a_-(T_c - T) + (4\Gamma^2 / v_{\text{eff}}) [v_{\text{eff}} - v(\mathbf{q})] + \frac{[g_- + h_- v(\mathbf{q})]}{(T_c - T)^{1/2}} p \delta E^{\text{int}}, \quad (T < T_c). \quad (68)$$

Finally, for $T = T_c$, we obtain for the normal mode frequency

$$\omega_q^2(\delta E^{\text{int}}) = (4\Gamma^2 / v_{\text{eff}}) [v_{\text{eff}} - v(\mathbf{q})] + [g_0 + h_0 v(\mathbf{q})] (p \delta E^{\text{int}})^{2/3}, \quad (T = T_c). \quad (69)$$

VI. CONCLUDING REMARKS

In the preceding sections, we have obtained the specific heat, the response to external electric fields, and the normal mode frequency for the case of a rigid lattice. As discussed in the Introduction, there is good qualitative agreement with available experimental results. For a quantitative comparison with experiments it will be necessary to take into account the displacements of the other ions in the crystal and their electronic polarizability. These effects give rise to an indirect interaction between the protons, and to a contribution to the total polarization of the crystal.

In order to incorporate these effects at least approximately in the model discussed in this paper, we assume that the displacement of any of the other ions is proportional to the local electric field at its lattice site, and that all the frequencies considered are below the optical phonon frequencies of the crystal. Then indirect dipole interactions between the protons as well as possible short-range contributions can be taken into account by replacing by effective values the parameters in the interaction energy, Eq. (A14), which will not change the form of the functional dependence on q . The total electric polarization of the crystal can be written in the form

$$P^{\text{total}} = (1 + \gamma) \cdot P^{\text{proton}} + \chi^{\text{host}} \cdot E^{\text{int}},$$

where γ depends on the polarizability of the other ions and on the proton-other-ion interactions as well as on the interactions of the other ions among themselves, and χ^{host} is the electric susceptibility of the crystal in the absence of the protons. Under the stated assumptions, we therefore expect that the form of the temperature and field dependence of the spontaneous polarization, the soft mode frequency, the specific heat, and the response coefficients in the critical region is well represented by the rigid lattice model.

APPENDIX A: DIPOLAR INTERACTION

The interaction energy between two dipoles $\mathbf{u}(\alpha)$ and $\mathbf{u}(\alpha')$ at sites α and α' has the form

$$U(\alpha \alpha') = \mathbf{u}(\alpha) \cdot \mathbf{D}(\alpha - \alpha') \cdot \mathbf{u}(\alpha'), \quad (A1)$$

where

$$\mathbf{D}(\mathbf{x}) = (1/x^5) [3\mathbf{x}\mathbf{x} - x^2 \mathbf{1}] \quad (A2)$$

is the dipolar interaction tensor.

For our pseudospin model,

$$\mathbf{u}(\alpha) = \mathbf{p}(\alpha) \sigma_3(\alpha), \quad (A3)$$

where $\mathbf{p}(\alpha)$ is the dipole moment due to the ion at site α being displaced to one side. We thus find an interaction term as in Eq. (2) with

$$v(\alpha \alpha') = \mathbf{p}(\alpha) \cdot \mathbf{D}(\alpha - \alpha') \cdot \mathbf{p}(\alpha'). \quad (A4)$$

We shall assume for simplicity that all the ferroelectric ions sit in identical double-well potentials with axes all parallel to a common direction \hat{e}_z . Then,

$$\mathbf{p}(\alpha) = p \hat{e}_z \quad (A5)$$

and

$$v(\alpha \alpha') = p^2 D_{zz}(\alpha - \alpha'). \quad (A6)$$

We are interested in the small- q behavior of the Fourier transform

$$v(\mathbf{q}) = p^2 D_{zz}(\mathbf{q}), \quad (A7)$$

where

$$\mathbf{D}(\mathbf{q}) = \sum_{\alpha} \mathbf{D}(\alpha - \alpha') \exp[-i\mathbf{q} \cdot (\alpha - \alpha')]. \quad (\text{A8})$$

The matrix element $D_{\kappa\lambda}(\mathbf{q})$ can be considered as the κ component of the field at site α' produced by dipoles of magnitude $\exp[-i\mathbf{q} \cdot (\alpha - \alpha')]$ in the λ direction at sites α ($\kappa, \lambda = \xi, \eta, \zeta$). We can write this field as a sum of two terms, the first of which is produced by a continuous polarization distribution

$$\mathbf{P}(\mathbf{x}) = n \exp(-i\mathbf{q} \cdot \mathbf{x}) \hat{e}_{\lambda} \quad (\text{A9})$$

(where n is the density of ferroelectric ions), and the second of which is produced by the difference between the actual discrete distribution and $\mathbf{P}(\mathbf{x})$.

The field due to the polarization distribution Eq. (A9) is given by

$$\mathbf{E}(\mathbf{x}) = -4\pi(\mathbf{q} \cdot \mathbf{P}/q^2), \quad (\text{A10})$$

and we obtain for the first part of $\mathbf{D}(\mathbf{q})$,

$$D_{\kappa\lambda}^{(1)}(\mathbf{q}) = -4\pi n(q_{\kappa}q_{\lambda}/q^2). \quad (\text{A11})$$

The long range of the dipole interaction is reflected in the discontinuous behavior of $D_{\kappa\lambda}^{(1)}$ for small q ; the $q=0$ limit depends on the direction from which the point $q=0$ is approached.

The second part will be analytic at $q=0$, because the contributions to the field at site α' from the dipole at α and from the polarization $-P(\mathbf{x})$ in the cell at α cancel each other for large distances $|\alpha - \alpha'|$. Since the Taylor expansion in powers of \mathbf{q} will contain only even powers, we can write

$$D_{\kappa\lambda}^{(2)}(\mathbf{q}) = 4\pi n \left\{ L_{\kappa\lambda} + \frac{1}{2} \sum_{\mu\nu} M_{\kappa\lambda\mu\nu} q_{\mu}q_{\nu} + O(q^4) \right\}, \quad (\text{A12})$$

where $L_{\kappa\lambda}$ and $M_{\kappa\lambda\mu\nu}$ depend on the lattice structure. The tensor $L_{\kappa\lambda}$ is just the Lorentz local-field factor. Since $\text{tr}\mathbf{D}=0$ and $\text{tr}\mathbf{D}^{(1)} = -4\pi n$, \mathbf{L} satisfies

$$\text{tr}\mathbf{L} = L_{\xi\xi} + L_{\eta\eta} + L_{\zeta\zeta} = 1. \quad (\text{A13})$$

We thus obtain to second order in q

$$v(\mathbf{q}) = 4\pi n p^2 \left\{ L_{\zeta\zeta} - (q_{\zeta}^2/q^2) - \frac{1}{2} \sum_{\mu\nu} M_{\zeta\zeta\mu\nu} q_{\mu}q_{\nu} \right\}. \quad (\text{A14})$$

One could take indirect interactions approximately into account by assuming larger values for $L_{\zeta\zeta}$ than Eq. (A13) permits as in Slater's theory of displacive ferroelectrics.²⁸ If ζ is a symmetry axis of the crystal, then we can find axes ξ and η such that the quadratic expression takes the form

$$-\frac{1}{2}(M_1 q_{\xi}^2 + M_2 q_{\eta}^2 + M_3 q_{\zeta}^2). \quad (\text{A15})$$

The ferroelectric structure will be stable only if this quadratic form is positive-definite.

Special consideration is required for the $q=0$ Fourier component $\mathbf{D}(0)$. As is well known, the sum in Eq. (A8) is only conditionally convergent for $q=0$, which means that $\mathbf{D}(0)$ depends on the shape of the sample.^{29,30} This shape dependence is related to the occurrence of depolarization effects. If there exists a spontaneous polarization $n p \langle \sigma_3 \rangle \hat{e}_{\zeta}$, it gives rise to a depolarizing field

$$\mathbf{E}^d = -4\pi n p \langle \sigma_3 \rangle \mathbf{N} \cdot \hat{e}_{\zeta}, \quad (\text{A16})$$

where \mathbf{N} is the depolarization tensor (we confine ourselves to samples of ellipsoidal shape). We can eliminate all shape dependence from our theory if we always compare states with the same macroscopic internal field.

In order to obtain the state of zero internal field, we have to apply an external field determined by

$$\mathbf{E}^{\text{int}} = \mathbf{E}^{\text{ext}} + \mathbf{E}^d = \mathbf{E}^{\text{ext}} - 4\pi n p \langle \sigma_3 \rangle \mathbf{N} \cdot \hat{e}_{\zeta} = 0, \quad (\text{A17})$$

in which case the molecular field acting in the pseudo spin space has the form

$$\mathbf{F} = \{\Gamma, 0, [v(0) + 4\pi n p^2 N_{\zeta\zeta}] \langle \sigma_3 \rangle\}. \quad (\text{A18})$$

We thus see that the transition from zero external field to zero internal field is effected by replacing the shape-dependent $v(0)$ by the shape-independent quantity $v(0) + 4\pi n p^2 N_{\zeta\zeta}$, which by construction is equal to the Lorentz local-field contribution:

$$v_{\text{eff}} = v(0) + 4\pi n p^2 N_{\zeta\zeta} = 4\pi n p^2 L_{\zeta\zeta}. \quad (\text{A19})$$

Comparison with Eq. (A14) shows that v_{eff} is equal to the $q=0$ limit of $v(\mathbf{q})$ for $\mathbf{q} \perp \zeta$, and we can write

$$v_{\text{eff}} - v(\mathbf{q}) = 4\pi n p^2 \left\{ (q_{\zeta}^2/q^2) + \frac{1}{2} \sum_{\mu\nu} M_{\zeta\zeta\mu\nu} q_{\mu}q_{\nu} \right\}. \quad (\text{A20})$$

APPENDIX B: ISOTHERMAL RESPONSE IN THE MOLECULAR FIELD APPROXIMATION

We want to calculate the isothermal response to an additional field $\varphi(\alpha)$ in pseudospin space, which adds to the Hamiltonian, Eq. (2), a term

$$H' = - \sum_{\alpha} \varphi(\alpha) \cdot \delta(\alpha). \quad (\text{B1})$$

We define the response $\mathbf{s}(\alpha)$ as the deviation from the $\varphi=0$ value $\langle \delta \rangle_0$,

$$\langle \delta(\alpha) \rangle = \langle \delta \rangle_0 + \mathbf{s}(\alpha), \quad (\text{B2})$$

²⁹ A discussion of the problems associated with the shape dependence and the conditional convergence of Fourier sums has been given by M. Lax, J. Chem. Phys. **20**, 1351 (1952).

³⁰ Actually, for a finite sample such shape dependence exists for \mathbf{q} vectors within a pathological region around the origin of extent $\Omega^{-1/3}$, where Ω is the volume of the sample as discussed by M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955). We shall here need only the behavior at $q=0$.

²⁸ J. C. Slater, Phys. Rev. **78**, 748 (1950).

and write to first order in the field φ ,

$$\mathbf{s}^{(1)}(\boldsymbol{\alpha}) = \sum_{\boldsymbol{\alpha}'} \mathbf{x}^{\text{isoth}}(\boldsymbol{\alpha}, \boldsymbol{\alpha}') \cdot \varphi(\boldsymbol{\alpha}'). \quad (\text{B3})$$

This equation defines the linear isothermal response tensor $\mathbf{x}^{\text{isoth}}$.³¹ The additional field $\varphi(\boldsymbol{\alpha})$ gives rise to a change $\mathbf{f}(\boldsymbol{\alpha})$ in the molecular field \mathbf{F} in pseudospin space:

$$\mathbf{F}(\boldsymbol{\alpha}) = \mathbf{F}_0 + \mathbf{f}(\boldsymbol{\alpha}). \quad (\text{B4})$$

Here, \mathbf{F}_0 is the molecular field in the absence of $\varphi(\boldsymbol{\alpha})$:

$$\mathbf{F}_0 = \{\Gamma, 0, v_{\text{eff}}\langle\sigma_3\rangle_0\} \quad (\text{B5})$$

and $\mathbf{f}(\boldsymbol{\alpha})$ is given by

$$\mathbf{f}(\boldsymbol{\alpha}) = \sum_{\boldsymbol{\alpha}'} \mathbf{v}(\boldsymbol{\alpha}, \boldsymbol{\alpha}') \cdot \mathbf{s}(\boldsymbol{\alpha}') + \varphi(\boldsymbol{\alpha}), \quad (\text{B6})$$

where the only nonvanishing component of the tensor $\mathbf{v}(\boldsymbol{\alpha}, \boldsymbol{\alpha}')$ is

$$v_{33}(\boldsymbol{\alpha}, \boldsymbol{\alpha}') = v(\boldsymbol{\alpha}, \boldsymbol{\alpha}'). \quad (\text{B7})$$

From the molecular-field equation

$$\boldsymbol{\delta}(\boldsymbol{\alpha}) = [\mathbf{F}(\boldsymbol{\alpha})/F(\boldsymbol{\alpha})] \tanh\beta F(\boldsymbol{\alpha}), \quad (\text{B8})$$

we obtain the linear response to the change in the molecular field as

$$\mathbf{s}^{(1)}(\boldsymbol{\alpha}) = \mathbf{A} \cdot \mathbf{f}(\boldsymbol{\alpha}) \quad (\text{B9})$$

with

$$\mathbf{A} = \langle\langle\sigma_1\rangle_0/\Gamma\rangle \mathbf{1} - [\langle\langle\sigma_1\rangle_0/\Gamma\rangle - \beta(1 - \langle\sigma\rangle_0^2)] \times \langle\langle\boldsymbol{\delta}\rangle_0\langle\boldsymbol{\delta}\rangle_0/\langle\sigma\rangle_0^2\rangle. \quad (\text{B10})$$

Taking Fourier transforms of Eqs. (B6) and (B9) and solving for $\mathbf{s}^{(1)}(\mathbf{q})$ gives

$$\mathbf{s}^{(1)}(\mathbf{q}) = \mathbf{x}^{\text{isoth}}(\mathbf{q}) \cdot \varphi(\mathbf{q}) \quad (\text{B11})$$

with

$$\mathbf{x}^{\text{isoth}}(\mathbf{q}) = [\mathbf{1} - \mathbf{A} \cdot \mathbf{v}(\mathbf{q})]^{-1} \cdot \mathbf{A}. \quad (\text{B12})$$

Of special interest are the components χ_{13}^{isoth} and χ_{33}^{isoth} ,

$$\chi_{13}^{\text{isoth}}(\mathbf{q}) = A_{13}/[1 - A_{33}v(\mathbf{q})], \quad (\text{B13})$$

$$\chi_{33}^{\text{isoth}}(\mathbf{q}) = A_{33}/[1 - A_{33}v(\mathbf{q})], \quad (\text{B14})$$

where

$$A_{13} = -\langle\langle\sigma_1\rangle_0\langle\sigma_3\rangle_0/\langle\sigma\rangle_0^2\rangle [\langle\langle\sigma_1\rangle_0/\Gamma\rangle - \beta(1 - \langle\sigma\rangle_0^2)] \quad (\text{B15})$$

and

$$A_{33} = (1/\langle\sigma\rangle_0^2) [\langle\langle\sigma_1\rangle_0^2/\Gamma\rangle + \beta\langle\sigma_3\rangle_0^2(1 - \langle\sigma\rangle_0^2)]. \quad (\text{B16})$$

We note that in the limit $\Gamma \rightarrow 0$, we recover the RPA

³¹ $(\mathbf{x})_{ij} = \chi_{ij}$.

result for the pure Ising model¹¹:

$$\lim_{\Gamma \rightarrow 0} \chi_{33}^{\text{isoth}}(\mathbf{q}) = \beta(1 - \langle\sigma\rangle_0^2) / [1 - \beta v(\mathbf{q})(1 - \langle\sigma\rangle_0^2)]. \quad (\text{B17})$$

In the case of a uniform field φ , the above results become shape dependent. This shape dependence is again eliminated by calculating the response to the additional "internal" field φ^{int} defined by

$$\varphi^{\text{int}} = \varphi - 4\pi n p^2 N s_3 \hat{e}_3. \quad (\text{B18})$$

The change in the molecular field, Eq. (B6), then takes the form

$$\mathbf{f} = \mathbf{v}_{\text{eff}} \cdot \mathbf{s} + \varphi^{\text{int}}, \quad (\text{B19})$$

and the linear response to φ^{int} is given by

$$\tilde{\mathbf{x}}^{\text{isoth}} = [\mathbf{1} - \mathbf{A} \cdot \mathbf{v}_{\text{eff}}]^{-1} \cdot \mathbf{A}. \quad (\text{B20})$$

We shall finally derive the quadratic isothermal response for the case of a uniform field φ . From Eq. (B8), we obtain to second order in \mathbf{f} ,

$$\mathbf{s} = \mathbf{A} \cdot \mathbf{f} - \langle\boldsymbol{\delta}\rangle_0 (\mathbf{f} \cdot \mathbf{B} \cdot \mathbf{f}) \quad (\text{B21})$$

with

$$\mathbf{B} = \frac{1}{2} (\langle\sigma_1\rangle_0/\Gamma) [\langle\sigma_1\rangle_0/\Gamma - \beta(1 - \langle\sigma\rangle_0^2)] \mathbf{1} + [\frac{3}{4} \langle\langle\sigma_1\rangle_0^2/\Gamma^2\rangle + \beta(1 - \langle\sigma\rangle_0^2) (\frac{1}{4} \langle\langle\sigma_1\rangle_0/\Gamma\rangle - \beta\langle\sigma\rangle_0^2)] \langle\langle\boldsymbol{\delta}\rangle_0\langle\boldsymbol{\delta}\rangle_0/\langle\sigma\rangle_0^2\rangle. \quad (\text{B22})$$

In order to obtain shape-independent results, we use Eq. (B19) to express \mathbf{f} in terms of φ^{int} . In the quadratic term of Eq. (B21), we can replace \mathbf{f} by its linear approximation

$$\mathbf{f}^{(1)} = [\mathbf{1} + \mathbf{v}_{\text{eff}} \cdot \tilde{\mathbf{x}}^{\text{isoth}}] \cdot \varphi^{\text{int}}. \quad (\text{B23})$$

Then, solving Eq. (B21) for \mathbf{s} , we obtain to second order in φ^{int} ,

$$\mathbf{s} = \tilde{\mathbf{x}}^{\text{isoth}} \cdot \varphi^{\text{int}} - \rho (\varphi^{\text{int}} \cdot \mathbf{B}' \cdot \varphi^{\text{int}}). \quad (\text{B24})$$

Here, $\tilde{\mathbf{x}}^{\text{isoth}}$ is given by Eq. (B20). Further,

$$\rho = (\mathbf{1} - \mathbf{A} \cdot \mathbf{v}_{\text{eff}})^{-1} \cdot \langle\boldsymbol{\delta}\rangle_0, \quad (\text{B25})$$

and

$$\mathbf{B}' = [\mathbf{1} + \mathbf{v}_{\text{eff}} \cdot \tilde{\mathbf{x}}^{\text{isoth}}] \cdot \mathbf{B} \cdot [\mathbf{1} + \mathbf{v}_{\text{eff}} \cdot \tilde{\mathbf{x}}^{\text{isoth}}]. \quad (\text{B26})$$

Of special interest is the response to a field $\varphi^{\text{int}} = (0, 0, \varphi_3^{\text{int}})$, which is given by

$$s_1 = \tilde{\chi}_{13}^{\text{isoth}} \varphi_3 + \tilde{\chi}_{133}^{\text{isoth}} \varphi_3^2, \quad (\text{B27})$$

$$s_3 = \tilde{\chi}_{33}^{\text{isoth}} \varphi_3 + \tilde{\chi}_{333}^{\text{isoth}} \varphi_3^2, \quad (\text{B28})$$

where

$$\tilde{\chi}_{133}^{\text{isoth}} = -[(B_{13}A_{13}v_{\text{eff}} + B_{33})/(1 - A_{33}v_{\text{eff}})^2] \times \langle\langle\sigma_1\rangle_0 + \tilde{\chi}_{13}^{\text{isoth}}v_{\text{eff}}\langle\sigma_3\rangle_0\rangle \quad (\text{B29})$$

and

$$\tilde{\chi}_{333}^{\text{isoth}} = -[(B_{13}A_{13}v_{\text{eff}} + B_{33})/(1 - A_{33}v_{\text{eff}})^2] \langle\sigma_3\rangle_0. \quad (\text{B30})$$