

Low-Temperature Effects of the Tunneling Integral in Hydrogen-Bonded Ferroelectrics

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The coupling of proton tunneling to acoustic phonons in hydrogen-bonded ferroelectrics is studied. The resultant collective modes are obtained. The presence of proton tunneling in renormalized acoustic phonons leads to a T^4 dependence of the low-temperature growth of the disorder in the ferroelectric. Also, the acoustic phonons velocities are decreased by coupling to proton tunneling; this suggests that undeuterated ferroelectrics will have a smaller acoustic-phonon velocity than the deuterated ferroelectrics. The low-temperature decrease of the spontaneous polarization is shown to have a leading term, T^4 , which results from two physical causes: anharmonicity of the lattice forces and the decrease with temperature of the proton order parameter.

INTRODUCTION

IN recent years several workers have studied KH_2PO_4 -type ferroelectrics using a model that incorporates a proton-tunneling Hamiltonian term. In this view the protons exist in a double-minimum potential well, with there existing a tunneling matrix element between the two equilibrium sites.

de Gennes¹ has studied the collective proton-flip modes of a model Hamiltonian that includes the tunneling integral plus long- and short-range proton-proton interactions. He finds energy bands of elementary excitations. But the excitation energies do not go down to zero in the $k=0$ limit, as is the case in ferromagnets. These modes have also been studied by Blinc and Svetina.²

Blinc and Svetina,^{3,4} using the same type of model Hamiltonian, have performed a high-temperature cluster series expansion for the ferroelectric's partition function. They find that the tunneling integral term produces a spontaneous polarization curve that rises less rapidly with decreasing temperature below the critical temperature than models without the tunneling term. This is because the tunneling term is a quantum-mechanical force tending to have the protons share their time equally between the two sites. The tunneling integral also offers an explanation of the substantial difference between the critical temperatures of the deuterated and undeuterated ferroelectrics.⁴ Also, the drastic difference in domain-wall mobility ($\mu_H/\mu_D \simeq 10^6$) can be understood in terms of the large ratio of the tunneling integrals ($\Gamma_H/\Gamma_D \simeq 10^3$).⁴

In this paper we investigate some independent consequences of a tunneling integral term in the model ferroelectric Hamiltonian. In particular we look at effects on the ferroelectric at low temperatures ($T \ll T_c$). The coupling of proton-flip modes to acoustic phonons will play a central role in producing our effects, so a combined proton and lattice-vibration Hamiltonian must be considered.

HAMILTONIAN

The zeroth-order Hamiltonian for our ferroelectric crystal is assumed to be

$$H_0 = \sum_{\gamma k} \frac{1}{2} M_{\gamma} (\dot{X}_{\gamma}^2(k) + \omega_{\gamma}^2(k) X_{\gamma}^2(k)) + \sum_{\gamma\gamma'k} C_{\gamma\gamma'}(k) X_{\gamma}(0) X_{\gamma'}^2(k) - \Gamma \sum_i (\sigma_x)_i - \sum_{i \neq j} J_{ij} (\sigma_z)_i (\sigma_z)_j. \quad (1)$$

The first term in (1) represents the normal modes of vibration of the crystal in the harmonic approximation. The sum over k extends over the primary Brillouin zone, the sum over γ runs over the $3N$ normal modes (N is the number of atoms in the unit cell). Three of the vibration modes will be acoustic modes with

$$\lim_{k \rightarrow 0} \omega_{\gamma}(k) \rightarrow ks_{\gamma}.$$

The second term in (1) represents a particular part of the anharmonic corrections to the lattice Hamiltonian, these particular anharmonic terms playing a special role in our development.

The third term of (1) is the proton-tunneling contribution to the Hamiltonian, while the fourth term represents a proton-proton interaction, which favors an ordered (ferroelectric) arrangement of the crystal ($J_{ij} > 0$). The sums i and j go over all the protons of a KH_2PO_4 -type crystal. The two states of the Pauli spin operators represent the two possible positions a proton is assumed to be able to take in its bond.

We now add a most general coupling of the lattice distortions to the proton. First there is a term

$$V = \sum_{i\gamma k} D_{ij}(k) (\sigma_z)_i X_{\gamma}(k), \quad (2)$$

which represents a direct shift of the energies of the two proton positions due to a lattice deformation.

The lattice deformation may also produce a correction to the proton-proton interaction energies. Therefore we allow the replacement

$$J_{ij} \rightarrow J_{ij} + \sum_{\gamma k} J_{ij\gamma}(k) X_{\gamma}(k) + \dots \quad (3)$$

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

² R. Blinc and S. Svetina, *Phys. Letters* **15**, 119 (1965).

³ R. Blinc and S. Svetina, *Phys. Rev.* **147**, 423 (1966).

⁴ R. Blinc and S. Svetina, *Phys. Rev.* **147**, 430 (1966).

Finally, the tunneling integral Γ will be altered by a lattice deformation

$$\Gamma \rightarrow \Gamma \left(1 + \sum_{\gamma k} G_{i\gamma}(k) X_\gamma(k) + \dots \right). \quad (4)$$

The correction to Γ is assumed proportional to Γ , since Γ is roughly proportional to $\exp[-(2m\Delta V)^{1/2}a/\hbar] = e^{-\xi}$, where ΔV is a potential barrier of thickness a , and m is the mass of the tunneling particle. Then $\delta\Gamma \simeq -\Gamma\delta\xi$.

Collecting all of the above lattice-proton interactions yields the total interaction potential

$$V = \sum_{ij\gamma k} [D_{i\gamma}(k)(\sigma_x)_i - J_{ij\gamma}(k)(\sigma_x)_i(\sigma_x)_j - \Gamma G_{i\gamma}(k)(\sigma_x)_i] X_\gamma(k). \quad (5)$$

GROUND STATE

Following Blinc and Sventina,³ we account for the effect of the tunneling-integral contribution to (1) by assuming a $T=0$ ground state of the system, which has all the protons "aligned" to some direction in the abstract (σ_x, σ_z) space. Physically, this means the tunneling integral always leads to a ground state with the protons spending some part of their time at each site of their bond. This ground state can most easily be handled by rotating our abstract coordinate system in the (σ_x, σ_z) space. Then we have the transformation

$$\begin{aligned} \sigma_x &\rightarrow \cos\theta \sigma_x + \sin\theta \sigma_z, \\ \sigma_z &\rightarrow \cos\theta \sigma_z - \sin\theta \sigma_x, \end{aligned} \quad (6)$$

where θ is the rotation angle in the abstract space. θ is to be varied to minimize the ground-state energy. Also, due to the anharmonic contributions to the lattice Hamiltonian and the couplings to protons positions,

there will be $X_\gamma(k=0) \neq 0$ static deformations of the lattice. The $X_\gamma(0)$ are therefore additional parameters to be varied in order to find a minimum-energy ground state for the system.

At $T=0$ all of the protons are put in a spin-up state; the evaluation of the expected value of H then gives

$$\begin{aligned} \langle H \rangle &= \sum_\gamma \frac{1}{2} M_\gamma \omega_\gamma^2(0) X_\gamma^2(0) \\ &- \Gamma \sin\theta \left[1 + \sum_{i,\gamma} G_{i\gamma}(0) X_\gamma(0) \right] + \cos\theta \sum_{i\gamma} D_{i\gamma}(0) X_\gamma(0) \\ &- \cos^2\theta \sum_{ij\gamma} [J_{ij} + J_{ij\gamma}(0) X_\gamma(0)]. \end{aligned} \quad (7)$$

We have neglected a zero-point lattice-vibration contribution coming from the anharmonic lattice Hamiltonian term in (1).

Neglecting the lattice deformations $X_\gamma(0)$ in (7) yields the results of Blinc and Sventina³:

$$\partial \langle H \rangle / \partial \theta = - (d/d\theta) [\cos^2\theta \sum_{i \neq j} J_{ij} + \Gamma \sin\theta \sum_i] = 0, \quad (8)$$

which gives

$$\sin\theta = \Gamma/2 \sum_j J_{ij} \quad (9)$$

and

$$E_0 = -N(qJ + \Gamma^2/4Jq), \quad (10)$$

where J is defined as the average proton-proton coupling constant. Letting q be the number of proton-proton neighbors retained in our model, then J is defined as

$$J = (1/q) \sum_{j=1}^q J_{ij}. \quad (11)$$

Solving (7), however, for the equilibrium deformation gives

$$X_\gamma(0) = [M_\gamma \omega_\gamma^2(0)]^{-1} [\cos^2\theta \sum_{ij} J_{ij\gamma}(0) + \Gamma \sin\theta \sum_i G_{i\gamma}(0) - \cos\theta \sum_i D_{i\gamma}(0)]. \quad (12)$$

Inserting this result back into (7) gives a corrected equation for the ground-state energy:

$$\langle H \rangle = -\Gamma \sin\theta \sum_i - \cos^2\theta \sum_{ij} J_{ij} - \frac{1}{2} \sum_\gamma \{ [\cos^2\theta \sum_{ij} J_{ij\gamma}(0) + \Gamma \sin\theta \sum_i G_{i\gamma}(0) - \cos\theta \sum_i D_{i\gamma}(0)]^2 / M_\gamma \omega_\gamma^2(0) \}. \quad (13)$$

The rotation angle which minimizes $\langle H \rangle$ is now somewhat altered. For example, if one assumed that $D_{i\gamma}(0)$ terms dominated the last term in (13), one would have as a result a renormalized proton-proton coupling constant:

$$J'_{ij} = J_{ij} + \sum_\gamma \frac{D_{i\gamma}(0) D_{j\gamma}(0)}{2M_\gamma \omega_\gamma^2(0)}. \quad (14)$$

In any case, regardless of the relative size of the terms in

(13), it is seen that the rotation angle θ goes linearly with the tunneling integral Γ for small Γ . If $\Gamma=0$, then $\theta=0$. The tunneling integral is the driving mechanism for the protons to find an optimum state with $\theta \neq 0$.

ELEMENTARY EXCITATIONS OF THE SYSTEM

In order to obtain the low-temperature dependence of system parameters, the elementary excitations of the

Hamiltonian (1), corrected by the interaction (5), are now obtained.

The lattice-vibration Hamiltonian becomes a quantum-mechanical operator by the prescription

$$X_\gamma(k) = [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} [A_\gamma^\dagger(k) + A_\gamma(-k)] \quad (15)$$

with $A_\gamma^\dagger(k)$ being a boson-creation operator for a "bare" phonon of wave number k and mode γ .

Keeping all the interaction terms from (5) which are linear in $X_\gamma(k)$ and $(\sigma_x)_i$ gives a total interaction

$$V_{\text{int}} = \Gamma \sum_{i\gamma k} H_{i\gamma}(k) X_\gamma(k) (\sigma_x)_i, \quad (16)$$

where

$$H_{i\gamma}(k) = (1/\Gamma) [2 \sin\theta \cos\theta \sum_j J_{ij\gamma}(k) - \sin\theta D_{i\gamma}(k) - \cos\theta \Gamma G_{i\gamma}(k)]. \quad (17)$$

Using (9), it is seen that, for small Γ , $H_{i\gamma}(k)$ is independent of Γ and is a sum of interaction coupling constants between the protons and the lattice vibrations.

We can then write a quantum-mechanical Hamil-

tonian

$$H = \sum_{k\gamma} \hbar\omega_\gamma(k) [\frac{1}{2} + A_\gamma^\dagger(k) A_\gamma(k)] + \Gamma \sum_{i\gamma k} H_{i\gamma}(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} (\sigma_x)_i \times [A_\gamma^\dagger(k) + A_\gamma(-k)] - \Gamma \cos\theta \sum_i (\sigma_x)_i - \sum_{ij} J_{ij} (\cos\theta \sigma_x - \sin\theta \sigma_z)_i (\cos\theta \sigma_x - \sin\theta \sigma_z)_j. \quad (18)$$

We now search for the operator that creates the elementary excitations of (18) by assuming for that operator a linear mixture of lattice-vibration operators and proton-flip operators

$$P^\dagger = \sum_\gamma [\alpha_\gamma A_\gamma^\dagger(k) + \beta_\gamma A_\gamma(-k)] + \sum_i [c_i (\sigma_-)_i + d_i (\sigma_+)_i], \quad (19)$$

which satisfies the equation of motion

$$[H, P^\dagger] = EP^\dagger. \quad (20)$$

$\alpha_\gamma, \beta_\gamma, c_i$, and d_i are coefficients to be found and E is the elementary excitation energy. σ_\pm are the usual raising and lowering matrices $\frac{1}{2}(\sigma_x \pm i\sigma_y)$.

Calculating several commutators gives⁵

$$[H, A_\gamma^\dagger(k)] = \hbar\omega_\gamma(k) A_\gamma^\dagger(k) + \Gamma \sum_i H_{i\gamma}^*(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} (\sigma_x)_i, \quad (21a)$$

$$[H, A_\gamma(-k)] = -\hbar\omega_\gamma(k) A_\gamma(-k) - \Gamma \sum_i H_{i\gamma}(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} (\sigma_x)_i, \quad (21b)$$

$$[H, (\sigma_-)_i] = (4 \cos^2\theta \sum_j J_{ij} + 2 \sin\theta \Gamma) (\sigma_-)_i - 2 \sin^2\theta \sum_j J_{ij} (\sigma_x)_j + \Gamma \sum_\gamma \sum_k H_{i\gamma}(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} [A_\gamma^\dagger(k) + A_\gamma(-k)], \quad (22a)$$

and

$$[H, (\sigma_+)_i] = -(4 \cos^2\theta \sum_j J_{ij} + 2 \sin\theta \Gamma) (\sigma_+)_i + 2 \sin^2\theta \sum_j J_{ij} (\sigma_x)_j - \Gamma \sum_\gamma \sum_k H_{i\gamma}(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} [A_\gamma^\dagger(k) + A_\gamma(-k)]. \quad (22b)$$

From the commutators above we can obtain equations relating the coefficients in (19) in order to solve (20):

$$[E - \hbar\omega_\gamma(k)] \alpha_\gamma = \Gamma [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} \sum_i H_{i\gamma}(k) (c_i - d_i), \quad (23a)$$

$$[E + \hbar\omega_\gamma(k)] \beta_\gamma = \Gamma [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} \sum_i H_{i\gamma}(k) (c_i - d_i), \quad (23b)$$

$$[E - \epsilon] c_i = -2 \sin^2\theta \sum_j J_{ij} (c_j - d_j) + \Gamma \sum_\gamma \sum_k H_{i\gamma}^*(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} (\alpha_\gamma - \beta_\gamma), \quad (23c)$$

$$[E + \epsilon] d_i = -2 \sin^2\theta \sum_j J_{ij} (c_j - d_j) + \Gamma \sum_\gamma \sum_k H_{i\gamma}^*(k) [\hbar/M_\gamma\omega_\gamma(k)]^{1/2} (\alpha_\gamma - \beta_\gamma). \quad (23d)$$

⁵ We use in (21a) the property $H_{i\gamma}(-k) = H_{i\gamma}^*(k)$.

The energy unit ϵ is defined by

$$\begin{aligned}\epsilon &= 4 \cos^2\theta \sum_j J_{ij} + 2 \sin\theta \Gamma \\ &= 2(qJ + \Gamma^2/4Jq).\end{aligned}\quad (24)$$

Solving (23a)–(23d) with the proton-lattice coupling neglected gives, of course, the unaltered phonon modes, but it also leads to collective proton-flip modes first obtained by de Gennes.¹ Letting

$$c_i = \exp(i\mathbf{k} \cdot \mathbf{R}_i) \tilde{c}_i, \quad (25a)$$

where \mathbf{R}_i is the position of the i th proton, and

$$J_{ij} \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] = J_{ij}(k) \quad (\text{a Hermitian matrix}), \quad (25b)$$

then⁶

$$(E - \epsilon) \tilde{c}_i = -[4\epsilon/(E + \epsilon)] \Gamma^2 \sum_j J_{ij}(k) \tilde{c}_j. \quad (26)$$

Letting the eigenvalues of the matrix $4\Gamma^2 J_{ij}(k)$ be called $\epsilon_\lambda(k)$ with eigenvectors $v_j^\lambda(k)$,

$$\sum_j [4\Gamma^2 J_{ij}(k)] v_j^\lambda(k) = \epsilon_\lambda(k) v_i^\lambda(k), \quad (27)$$

then the elementary excitation of the coupled protons have energies given by

$$E_\lambda = [\epsilon^2 - \epsilon\epsilon_\lambda(k)]^{1/2} \quad (28)$$

in agreement with de Gennes.¹ The collective proton-flip modes of (28), though differing in energy from the single proton-flip energy ϵ , do not differ fundamentally in the energy spectrum, since (28) still gives elementary excitation energies which are finite as $k \rightarrow 0$. (This is unlike the ferromagnetic case.)

The coupling of lattice vibrations to proton-flip modes will, however, lead to interesting effects. Following the redefinitions (25a) and (25b), we also define

$$H_{i\gamma}(k) \exp(i\mathbf{k} \cdot \mathbf{R}_i) = \tilde{H}_{i\gamma}(k). \quad (29)$$

Using the eigenvectors of (27), we change variables to

$$\tilde{c}_i = \sum_\lambda v_i^\lambda c_\lambda' \quad (30)$$

and finally redefine the matrix element of (29):

$$\sum_j \tilde{H}_{j\gamma}(k) v_j^\lambda \equiv h_{\lambda\gamma}(k). \quad (31)$$

These redefinitions give, finally,

$$\begin{aligned}& [E^2 - \epsilon^2 + \epsilon\epsilon_\eta] c_\eta' \\ &= 4\epsilon\tilde{\hbar}\Gamma^2 \sum_\gamma \frac{h_{\eta\gamma}^*(k)}{M_\gamma [E^2 - \tilde{\hbar}^2\omega_\gamma^2(k)]} \left[\sum_{\eta'} h_{\eta'\gamma}(k) c_{\eta'}' \right].\end{aligned}\quad (32)$$

Looking at the shift of lattice vibration energies to order Γ^2 only gives

$$E_\gamma^2 = \tilde{\hbar}^2\omega_\gamma^2(k) + \frac{4\epsilon\tilde{\hbar}\Gamma^2}{M_\gamma} \sum_\eta \frac{|h_{\eta\gamma}(k)|^2}{E^2 - \epsilon^2 + \epsilon\epsilon_\eta(k)}. \quad (33)$$

The coupling constants $h_{\eta\gamma}(k)$ are proportional to k for the acoustic-phonon modes, so (33) represents a decrease in the acoustic-phonon velocities due to their coupling to the proton-flip modes.

For the acoustic phonons, (33) can be simplified in the long-wavelength limit to

$$E_\gamma^2 = [\tilde{\hbar}\omega_\gamma(k)]^2 - \frac{4\tilde{\hbar}\Gamma^2}{M_\gamma} \sum_\eta \frac{|h_{\eta\gamma}(k)|^2}{\epsilon - \epsilon_\eta(0)}. \quad (34)$$

PROTON-FLIP AMPLITUDE IN ACOUSTIC PHONONS

Because of the coupling between acoustic phonons and proton-flip modes the true elementary excitations become a mixture of these phenomena. Therefore, accompanying the thermal presence of acoustic phonons, there will be a depolarization of the ordered protons which has a T^n temperature dependence rather than a $\exp(-T_0/T)$ temperature dependence characteristic of a finite energy gap for the excitations.

Starting with Eqs. (23c) and (23d), and making the change of variables defined in (25a) and (30) gives

$$\begin{aligned}& [E - \epsilon + \epsilon\epsilon_\eta(k)/(E + \epsilon)] c_\eta' \\ &= \Gamma [\tilde{\hbar}/M_\gamma\omega_\gamma(k)]^{1/2} h_{\eta\gamma}^*(k) (\alpha_\gamma - \beta_\gamma).\end{aligned}\quad (35)$$

But from (23a) and (23b) we have

$$\beta_\gamma = \{ [E - \tilde{\hbar}\omega_\gamma(k)] / [E + \tilde{\hbar}\omega_\gamma(k)] \} \alpha_\gamma. \quad (36)$$

The normalization of the elementary excitation defined by (19) requires that

$$\alpha_\gamma^2 - \beta_\gamma^2 = 1 \quad (37)$$

in the $k \rightarrow 0$ limit, where the c_i and d_i contributions go to zero. This leads to $\alpha_\gamma - \beta_\gamma = [\hbar\omega_\gamma(k)/E]^{1/2}$, so (35) becomes

$$[E_\gamma - \epsilon + \epsilon\epsilon_\eta/(E_\gamma + \epsilon)] c_\eta' = \Gamma [\tilde{\hbar}/M_\gamma E_\gamma]^{1/2} h_{\eta\gamma}^*(k). \quad (38)$$

Neglecting E_γ on the left side of (38), we have

$$|c_\eta'|^2 = \Gamma^2 (\tilde{\hbar}/M_\gamma E_\gamma) |h_{\eta\gamma}(k)|^2 (1/|\epsilon - \epsilon_\eta|^2). \quad (39)$$

From the change of variables (30) and the orthogonality properties of eigenvectors of Hermitian matrices, it is evident that

$$\sum_{\eta=1}^q |c_\eta'|^2 = \sum_{i=1}^q |\tilde{c}_i|^2 = \sum_{i=1}^q |c_i|^2. \quad (40)$$

The squares $|c_i|^2$ represent the probability of the i th proton being flipped when an acoustic phonon is present, so the average depolarization of a proton in the presence of the γ acoustic phonon is

$$\delta\langle\sigma_z\rangle = -\frac{2}{q} \sum_{\eta=1}^q \frac{\Gamma^2 \tilde{\hbar}^2}{M_\gamma E_\gamma(k)} |h_{\eta\gamma}(k)|^2 \frac{1}{|\epsilon - \epsilon_\eta|^2}. \quad (41)$$

Comparison with (34) yields a connection between the acoustic-phonon velocity change and the proton de-

⁶ d_i has been eliminated from (26) by use of (23d).

polarization. Let δs_γ be the velocity decrease of an acoustic-phonon mode. Then

$$\delta\langle\sigma_z\rangle\cong(1/q)\delta E_\gamma/\epsilon, \quad (42)$$

where $\delta E_\gamma = -\hbar k \delta s_\gamma$. So

$$\delta\langle\sigma_z\rangle = -\lambda_\gamma k \quad (43)$$

with $\lambda_\gamma \cong -\hbar \delta s_\gamma / \epsilon q$. At low temperature, the acoustic phonons are present with a density

$$n_\gamma(k) = [\exp(\beta\hbar k s_\gamma) - 1]^{-1} \cong \exp(-\beta\hbar k s_\gamma). \quad (44)$$

The total depolarization of the ordered protons is then

$$\delta\langle\sigma_z\rangle = -\sum_\gamma \lambda_\gamma \sum_k k \exp(-\beta\hbar k s_\gamma). \quad (45)$$

Evaluating this at low temperatures gives

$$\delta\langle\sigma_z\rangle = -\frac{3}{\pi^2} \left(\sum_{\gamma=1}^3 \frac{\lambda_\gamma}{s_\gamma^4} \right) \frac{(k_B T)^4}{\hbar^3} = -c T^4. \quad (46)$$

We conclude that the ordering parameter $\langle\sigma_z\rangle$ should therefore obey a T^4 temperature law for the low-temperature growth of disorder.

TEMPERATURE DEPENDENCE OF THE SPONTANEOUS POLARIZATION

The protons themselves probably contribute very little to the polarization of the crystal. This is because the movement of the protons along their O-H...O bonds is almost perpendicular to the axis of the observed spontaneous polarization of the crystal. The polarization is most likely due to movement of the K and P ions under the influence of the ordered protons.

Without knowing in detail which ions contribute most to the spontaneous polarization, we can in general write an expression for the polarization,

$$\mathbf{p} = \sum_i e_i \mathbf{x}_i. \quad (47)$$

But the \mathbf{x}_i can be reexpressed in terms of the normal vibration modes, and (47) can then be written as

$$\mathbf{p} = \sum_\gamma X_\gamma(0) \boldsymbol{\pi}_\gamma. \quad (48)$$

Knowing the static deformation of the crystal yields the polarization. To obtain the low-temperature dependence of the $X_\gamma(0)$, we must return to the energy expression (7). When (7) was minimized it gave (12) for the static deformation parameters.

We must modify (7) to include the anharmonic term of the Hamiltonian. To (7) we must add the $\langle\sigma_z\rangle$ factors which were suppressed when evaluating at $T=0$. Equation (12) is then

$$\begin{aligned} X_\gamma(0) = & [M_\gamma \omega_\gamma^2(0)]^{-1} \left[+ \sum_{\gamma' \neq \gamma} C_{\gamma\gamma'}(k) \langle X_{\gamma'}(k)^2 \rangle \right. \\ & \left. - \cos^2\theta \sum_{ij} J_{ij} \langle \sigma_z \rangle_i \langle \sigma_z \rangle_j + \cos\theta \sum_i D_{ij}(0) \langle \sigma_z \rangle_i + \dots \right]. \end{aligned} \quad (49)$$

The first term in (49) is evaluated using (15):

$$\langle X_{\gamma'}^2(k) \rangle = [2\hbar/M_{\gamma'} \omega_{\gamma'}(k)] \left[\frac{1}{2} + n_{\gamma'}(k) \right]. \quad (50)$$

Since $C_{\gamma\gamma'}(k)$ is the coefficient for a Hamiltonian term representing the γ' normal coordinate squared, if γ' represents an acoustic mode, then $C_{\gamma\gamma'}(k)$ must be quadratic in k for small k . Using $\omega_{\gamma'} = k s_{\gamma'}$, we have

$$n_{\gamma'}(k) \cong \exp(-\beta\hbar k s_{\gamma'}) \quad (51)$$

for the acoustic phonons; the anharmonic contribution to $X_\gamma(0)$ is then seen to lead to T^4 temperature dependence. We have already shown in (46) that $\langle\sigma_z\rangle$ decreases as $-cT^4$, so the additional terms in (49) yield also a T^4 temperature dependence of the spontaneous polarization.

CORRECTION TO GROUND STATE

The Hamiltonian (18) has a term

$$V' = -\sin^2\theta \sum_{i \neq j} J_{ij} \langle \sigma_z \rangle_i \langle \sigma_z \rangle_j. \quad (52)$$

This perturbation can excite pairs of protons from the totally aligned state. However, it is seen that V' is of second order in θ and therefore of second order in Γ . Consequently (52) produces a correction to the order parameter which is of order Γ^4 . This correction does not change our previously obtained low-temperature results for $\langle\sigma_z\rangle$, $\langle\mathbf{p}\rangle$, etc.

SUMMARY OF RESULTS

The essential purpose of this work was to study the general consequences of coupling the proton flip modes in a hydrogen-bonded ferroelectric to the acoustic phonons. Considering the general coupling of this type we obtained the following results:

(1) The acoustic-phonon frequencies are decreased by an amount proportional to Γ^2 , where Γ is the proton-tunneling integral between the two hypothesized sites available to each proton in the crystal.

(2) The ferroelectric order parameter $\langle\sigma_z\rangle$, which represents the fraction of protons properly positioned in their bonds, has a low-temperature dependence $1 - cT^4$ with c proportional to Γ^2 .

(3) The spontaneous polarization of the ferroelectric is dependent on both the order parameter $\langle\sigma_z\rangle$ and on the anharmonicity of the crystal forces. Both these influences on $\langle\mathbf{p}\rangle$ lead to a T^4 low-temperature quenching of the polarization.

These theoretical results suggest certain investigations in the normal and deuterated ferroelectrics.

Due to the fact that the tunneling integral is exponentially dependent on the hydrogen mass, it is presently believed that $\Gamma_D \cong 0$, while Γ_H may be of moderate size ($\Gamma_H \cong 0.1J$). Therefore, effects discussed above should be absent in deuterated ferroelectrics. Comparison of the acoustic-phonon velocities in the two isotopic varieties of ferroelectrics could provide a

test of the Γ model of ferroelectrics. (The usual isotopic effect on phonons predicts a decrease of 1 part in 138 of the phonon frequency in the deuterated case.)

The T^4 law for the order parameter could possibly be experimentally checked by doing nuclear magnetic resonance on the protons, looking for the NMR lines resulting from protons in the "wrong" sites.⁷ These lines should grow as T^4 at low temperatures.

Low-temperature measurement of the spontaneous

⁷ Techniques for narrowing proton NMR lines will probably be needed for such an experiment; see S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) **90**, 1019 (1962).

polarization in the ferroelectric would yield less direct information, as we have shown that both anharmonicity and the order parameter influence $\langle \mathbf{p} \rangle$ with the same T^4 dependence. However, our prediction is that the T^4 -dependent decrease of $\langle \mathbf{p} \rangle$ will be greater in undeuterated ferroelectrics because the order parameter has no T^4 dependence in the deuterated case.

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Temperature-Dependent Internal Field Distribution and Magnetic Susceptibility of a Dilute Ising Spin System*

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The temperature-dependent probability distribution of internal exchange fields, \vec{H} , is obtained for a set of randomly distributed Ising-model spins using a modified form of the statistical model of Margenau. The impurities are assumed to interact via a convergent long-range potential which alternates in sign as a function of position. When spin correlations between the magnetic impurities are neglected and a *mean-random-field* (MRF) approximation is used, the probability distribution $P(\vec{H})$ is given by a nonlinear integral equation. For a $1/r^3$ potential, the self-consistent probability distribution is, in the MRF approximation, a Lorentzian with a temperature- and concentration-dependent width $\Delta(\beta)$, where $\beta = 1/(k_B T)$ and T is the temperature. The function $\Delta(\beta)$ is also given by a nonlinear integral equation which is solved for very high and very low temperatures. Using $P(\vec{H})$ derived for a $1/r^3$ potential, the magnetic susceptibility $\chi(\beta)$ and the specific heat $C_v(\beta)$ are obtained for all temperatures. The model gives a magnetic susceptibility which exhibits a maximum as a function of temperature for all nonzero (but sufficiently small) impurity concentrations. The temperature of the maximum is proportional to the impurity concentration. Possible applications of the model to the temperature and concentration dependence of $\chi(\beta)$ and $C_v(\beta)$ of dilute magnetic alloys are discussed.

1. INTRODUCTION

THE method of random molecular fields has been used to discuss the thermodynamic properties of various magnetic impurities interacting via a long-range potential. Marshall¹ has introduced this concept to obtain the low-temperature specific heat of magnetic impurities interacting via a Ruderman-Kittel-Yosida² (RKY) interaction. Later Klein and Brout³ obtained the probability distribution of the random Ising-model internal field for a system interacting via the RKY interaction in the limit as the temperature approaches 0°K. An attempt to describe the variation of the probability distribution of the internal field with temperature

as one departs from $T=0$ has been made by the author.^{4,4a} However, the validity of this approach has not been satisfactorily shown. The purpose of this paper is to use a modified form of the statistical model of Margenau⁵ to derive the temperature-dependent internal field distribution for a set of randomly distributed Ising-model impurity spins which interact via a convergent long-range potential which alternates in sign as a function of position. In the model used the formal expression for the probability distribution of the internal field, $P(\vec{H}_0)$, at a particular site 0 is given in terms of the effective internal fields at all other impurity sites in the solid. To evaluate the expression for $P(\vec{H}_0)$, a *mean-random-field* (MRF) approximation is used in which, when calculating the probability distribution of the internal field at site 0, all functions of the internal field at sites other than 0 are replaced by their mean

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³ M. W. Klein and R. Brout, Phys. Rev. **132**, 2412 (1963).

⁴ M. W. Klein, Phys. Rev. **136**, 1156 (1964).

^{4a} A similar approach to the one taken here was independently developed by T. A. Kitchens and W. L. Trousdale (to be published) to treat impurities in palladium.

⁵ H. Margenau, Phys. Rev. **48**, 755 (1935).