Ising model in a transverse tunneling field and proton-lattice interaction in H-bonded ferroelectrics

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The addition of a $B_{ij}S_i^xS_j^x$-type coupling between the tunneling motion of one proton and the tunneling motion of another to the Ising model in a transverse-field Hamiltonian, or the addition of the probably larger $S_i^xF_i^xQ_i$-type pseudospin phonon coupling (describing the modulation of the distance between the two equilibrium sites in an O–H · · · O bond by nonpolar phonons), results in a temperature-dependent renormalization of the proton tunneling integral. This is important close to T_C, where the soft-mode frequency vanishes, $\omega_{\text{crit}} \to 0$. This may lead to large isotope shifts in T_C on deuteration even for small values of the tunneling intergal and may explain some phenomena recently observed in $PbHPO_4$ and squaric acid as well as the dependence of the effective proton-lattice interaction constant on hydrostatic pressure in KH_2PO_4-type systems. This last effect may be also due to the presence of a $S_i^xD_i^xQ_i^2$ term in addition to the Kobayashi $S_i^zF_i^zQ_i$ term when coupling with polar optic phonons is taken into account. When the lattice motion is so anharmonic that the lattice ions move in a double-well potential, and the proton-lattice coupling so strong that the protons can tunnel in only one out of the two possible lattice configurations, two Curie temperatures may appear.

I. INTRODUCTION

The pseudospin-$\frac{1}{2}$ Ising model in a transverse field (IMTF) has been extensively used to describe structural and, in particular, ferroelectric phase transitions in hydrogen-bonded systems, where the transition is triggered by the ordering of protons into one out of the two equilibrium sites in the O–H · · · O bonds.[1–4] The fact that the spontaneous polarization often appears in a direction which is perpendicular to the H bonds has been accounted for by Kobayashi[5] by introducing the coupling of the pseudospin proton tunneling modes with polar optic phonons. The IMTF Hamiltonian is just a first approximation to the true physical situation in systems like KH_2PO_4, where four-body Slater-type interactions[6–8] (which are in KH_2PO_4 equivalent to introducing a pseudospin-$\frac{15}{2}$ Hamiltonian) have to be included for a complete quantitative fit[6–8] of the thermal and dielectric properties. Nevertheless, it has been remarkably successful in providing a consistent, simple, and qualitatively correct description of both dynamic and static aspects of structural phase transitions in widely different classes of H-bonded solids such as KH_2PO_4,[4] and $NaH_3(SeO_3)_2$,[9] pseudo-two-dimensional squaric acid,[10] and pseudo-one-dimensional[11,12] $PbHPO_4$. One of the most remarkable features of the IMTF Hamiltonian is the prediction of the simultaneous occurrence of: (i) a soft proton tunneling mode[13,14] the frequency of which decreases on deuteration and vanishes at T_C; (ii) an increase in the Curie temperature T_C on deuteration[4]; (iii) a decrease in T_C with increasing hydrostatic pressure[15]—or, what is the same, increased tunneling probability[16]—leading to a vanishing of ferroelectricity at high pressures.[15,16] In deuterated isomorphs, where the tunneling term is smaller, ferroelectricity should vanish at much higher hydrostatic pressure[15,16] than in undeuterated systems.

In all H-bonded systems studied so far these three phenomena, which result from the presence of the "tunneling" term, have been indeed found to coexist, though the proton tunneling mode is, except at high pressures,[17] usually overdamped.

Recent far-infrared,[18] submillimeter dielectric,[19] and Raman[20] scattering experiments in $PbHPO_4$ and squaric acid,[21] however, seem to show some new facts which cannot be, even qualitatively, explained within the simple IMTF framework or the modification introduced by Kobayashi.[15] Whereas it follows from the IMTF Hamiltonian that a significant isotope shift in T_C on deuteration should be found only in those systems where the frequency of the proton tunneling mode is comparable—though smaller—than kT_C, this rule seems to be broken in $PbHPO_4$.[18–20] Here T_C shifts from $T_{C,H} = 37\,^\circ\text{C}$ to $T_{C,D} = 187\,^\circ\text{C}$ on deuteration, whereas the frequency of the "soft" proton mode ($\sim 1\ \text{cm}^{-1}$) is by more than two orders of magnitude smaller[20,21] than kT_C. At the same time

another "hard" temperature-dependent proton tunneling mode has been observed below (but not above) T_C.[20] The situation is similar in squaric acid, where $T_{C,H}=97\,^{\circ}\mathrm{C}$, $T_{C,D}=243\,^{\circ}\mathrm{C}$ and the soft-mode frequency is rather low.[21]

The purpose of this paper is to investigate whether the above phenomena can be understood within an extension of the IMTF Hamiltonian where the effects of the tunneling motion of one proton on the tunneling motion of another, either directly or via pseudospin-lattice coupling, are taken into account.

In Sec. II a model Hamiltonian is derived which takes into account the direct effect of the tunneling motion of one H-bonded proton on the tunneling motion of another, as well as the indirect coupling between the tunneling motions via nonpolar and polar optical phonons. The case of lattice motion so strongly anharmonic that the protons can tunnel only in one out of the two possible lattice configurations is also considered. In Secs. III–VI the static and dynamic properties of the above model Hamiltonians are discussed in the molecular-field and random-phase approximations.

It should be noted that the modulation of the tunneling integral and the pseudospin coupling constant by acoustic phonons in H-bonded systems have already been discussed.[22,23]

II. MODEL HAMILTONIAN

A. Proton-phonon coupling

The total Hamiltonian of the coupled proton-phonon system we are investigating is the sum of a protonic term, a lattice term, and a proton-lattice interaction term[4,5]

$$H = H_p + H_L + H_I \quad . \tag{1}$$

The Hamiltonian H_p of the "bare" O–H $\cdots$ O proton system in a rigid lattice can be written in the usual pseudospin-$\frac{1}{2}$ operator formalism[1–4]

$$H_p = -\Omega \sum_i S_i^x - \tfrac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \tfrac{1}{2} \sum_{i,j} B_{ij} S_i^x S_j^x \quad , \tag{2}$$

where Ω is the proton tunneling frequency, J_{ij} is the pseudospin-pseudospin Ising interaction constant, and B_{ij} measures the effect of the tunneling motion of one proton on the tunneling motion of another. It should be noted that the first two terms in expression (2) represent just the usual IMTF Hamiltonian.[1–4] Whereas the tunneling term Ω is proportional to the overlap integral $s<1$ between the protonic wave functions at the two equilibrium sites in the O–H $\cdots$ O bond, B is proportional to the square of the overlap, s^2.

H_L represents the usual Hamiltonian of lattice vibrations

$$H_L = \tfrac{1}{2} \sum_{q,p} (P_{q,p} P_{-q,p} + \omega_{q,p}^2 Q_{q,p} Q_{-q,p}) \quad , \tag{3}$$

where $Q_{q,p}$, $P_{q,p}$, and $\omega_{q,p}$ are the normal coordinate, momentum, and frequency of the pth lattice mode with wave vector q.

The pseudospin-phonon interaction consists of three different contributions

$$H_I = H_I^{(a)} + H_I^{(b)} + H_I^{(c)} \quad . \tag{4}$$

Here

$$H_I^{(a)} = -\sum_i S_i^z F_{i,p}^z Q_{p,i} \quad , \tag{5a}$$

describes the well-known interaction[5] of the pseudospins with polar optical phonons, which makes the two potential wells for proton motion unequivalent.

$H_I^{(b)}$, on the other hand, describes the modulation of the distance 2ξ between the two equilibrium sites in the O–H $\cdots$ O bonds, and the resulting modulation of the tunneling term Ω by nonpolar optic phonons

$$H_I^{(b)} = -\sum_i S_i^x F_i^x Q_i \quad . \tag{5b}$$

This term provides an indirect coupling between the tunneling motion of one proton and the tunneling motion of another, which may be larger than the direct $S_i^x S_j^x$ interaction.

Expanding the tunneling integral Ω in powers of the lattice coordinates Q

$$\Omega(Q) = \Omega(0) + \left(\frac{\partial \Omega}{\partial Q}\right)_0 Q + \cdots , \tag{6}$$

we see that

$$F^x = \left(\frac{\partial \Omega}{\partial Q}\right)_0 \quad . \tag{7}$$

If one, for the sake of simplicity, represents the O–H $\cdots$ O bond potential by a sum of two harmonic potentials, displaced by 2ξ, one finds Ω as

$$\Omega = E_0 \frac{4q}{\sqrt{\pi}} \exp(-q^2) \quad . \tag{8a}$$

Here

$$q^2 = 2mE_0\xi^2/\hbar^2 \quad , \tag{8b}$$

where m stands for the proton mass and E_0 is the protonic vibrational zero-point energy in a given harmonic potential well in the absence of tunneling. If we further assume that the distance between the two wells linearly depends on the phonon coordinates

$$\xi = \xi_0 + cQ \quad , \tag{8c}$$

one finds that F^x is proportional to the tunneling in-

tegral Ω

$$F^x=\left(\frac{\partial\Omega}{\partial\xi}\right)\left(\frac{\partial\xi}{\partial Q}\right)=-(2q^2-1)\frac{\Omega c}{\xi} \quad . \tag{9}$$

F^x is thus proportional to the overlap s and not to s^2 as the "direct" $S^x S^x$ coupling constant. F^x is positive if the lattice vibration results in a compression of the O–O bond distance so that $c<0$. It should be noted that F^xQ may be in some cases comparable to $\Omega(0)$.

The third term in expression (3), $H_l^{(c)}$ represents the coupling of the tunneling motion with polar optic phonons. For crystals, which are not polar above T_C, symmetry requires this coupling to be an even function of Q

$$H_l^{(c)}=-\sum_i S_i^x D_{i,p} Q_{i,p}^2 \quad . \tag{10a}$$

Polar optic phonons thus make the two potential minima in the O–H · · · O bond nonequivalent [Eq. (5a)] and in addition produce a deformation of the intervening potential barrier resulting in expression (10a).

The deformation in the shape of the potential well produces a fluctuation in E_0 such as

$$E_0=E_0(0)+dQ_p^2 \quad , \tag{10b}$$

so that one finds that $\partial\Omega/\partial Q_p=0$, $\partial^2\Omega/\partial Q_p^2=2D$ where

$$D=-(2q^2-3)\frac{\Omega d}{2E_0} \quad . \tag{10c}$$

B. Proton-lattice pseudospin coupling

Here we wish to present the model Hamiltonian for the case where the lattice motion is so strongly anharmonic that the lattice ions move in a double-well potential and the proton-lattice coupling is so strong that the protons can tunnel only in one out of the two possible lattice configurations. In this case it is convenient to describe the lattice motion in terms of Pauli pseudospin-$\frac{1}{2}$ matrices

$$\sigma^z=\begin{pmatrix}\frac{1}{2} & 0\\ 0 & -\frac{1}{2}\end{pmatrix}$$

and

$$\sigma^x=\begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}$$

and we can write the Hamiltonian of the coupled proton-lattice pseudospin system

$$H=-\Omega\sum_i S_i^x(\tfrac{1}{2}-\sigma_i^z)-\tfrac{1}{2}\sum_{i,j}J_{ij}S_i^zS_j^z +\Delta\sum_i\sigma_i^z-\Gamma^R\sum_i\sigma_i^x \quad . \tag{11}$$

In the above expression Γ^R stands for the lattice ion tunneling integral which should be much smaller than its proton counterpart Ω, whereas Δ measures the possible asymmetry in the lattice double-well potential.

In the following let us separately analyze the effects of the new terms we introduced in the model Hamiltonians (2), (5b), (10a), and (11).

III. DIRECT $S_i^xS_j^x$ COUPLING

Let us first investigate the IMTF Hamiltonian with the addition of the "direct" $S_i^xS_j^x$ interaction term. The Hamiltonian given by expression (2), can be in the molecular-field approximation (MFA) replaced by[4]

$$H_{p,i}^{\mathrm{MFA}}=-\vec{\mathrm{H}}_i\cdot\vec{\mathrm{S}}_i \quad . \tag{12}$$

The molecular field $\vec{\mathrm{H}}_i$ represents a vector in the pseudospin space $\vec{\mathrm{H}}_i=(H_x,0,H_z)$ with components

$$H_x=\Omega+\sum_j B_{ij}\langle S_j^x\rangle=\Omega+B_0\langle S^x\rangle \quad , \tag{13a}$$

$$H_z=\sum_j J_{ij}\langle S_j^z\rangle=J_0\langle S^z\rangle \quad . \tag{13b}$$

In contrast to the usual IMTF not only H_z but also H_x is temperature dependent.

The thermal expectation values of the pseudospin operators are now determined from the self-consistency equations[4]

$$\langle S^x\rangle=\frac{1}{2}\frac{H_x}{H}\tanh\left(\frac{\beta H}{2}\right) \quad , \tag{14a}$$

$$\langle S^z\rangle=\frac{1}{2}\frac{H_z}{H}\tanh\left(\frac{\beta H}{2}\right) \quad , \tag{14b}$$

where $H=(H_x^2+H_z^2)^{1/2}$ and $\beta=1/kT$. Nonzero solutions for the spontaneous polarization, which is proportional to $\langle S^z\rangle$, are stable below the transition temperature T_C. This is given by

$$\frac{2(\Omega+B_0\langle S^x\rangle_C)}{J_0}=\tanh[\tfrac{1}{2}\beta_C(\Omega+B_0\langle S^x\rangle_C)] \quad , \tag{15a}$$

where $\beta_C=1/kT_C$ and $\langle S_x\rangle_C=\langle S_x\rangle_{T_C}$.

Eliminating $\langle S^x\rangle_C$ with the help of Eq. (14a), we can rewrite Eq. (15a)

$$\frac{2\Omega}{J_o-B_0}=\tanh\left(\frac{\beta_C\Omega}{2}\frac{J_0}{J_0-B_0}\right) \quad . \tag{15b}$$

The dependence of the transition temperature T_C on B_0 is shown in Fig. 1 for two representative cases: (i) $2\Omega_{\mathrm{H}}<J_0$ (undeuterated system) and (ii) $2\Omega_{\mathrm{D}}\ll J_0$ (deuterated system). The transition temperature of the undeuterated system $T_{C,\mathrm{H}}$ decreases continuously with increasing B_0 and ferroelectricity

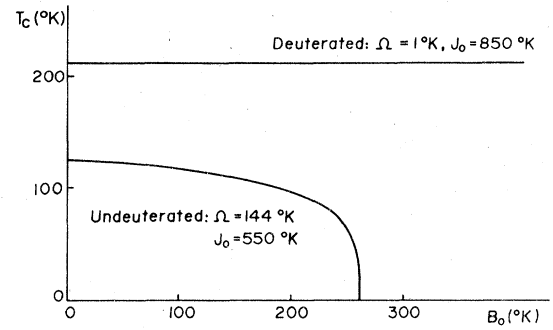

FIG. 1. Dependence of T_C on the $B_{ij}S_i^xS_j^x$ pseudospin coupling constant $B_0=\sum_j B_{ij}$.

vanishes ($T_C\to 0$) for

$$B_0 \geqslant J_0 - 2\Omega \quad . \tag{16a}$$

In the same range of B_0 values $T_{C,D}$ does not depend on B_0 so that the isotope shift in the Curie temperatures $(T_{C,D}-T_{C,H})/T_{C,D}$ continuously increases with increasing B_0 and reaches the value of 1 for $B_0 = J_0 - 2\Omega_H$. It should be noted that Fig. 1 closely resembles the experimentally observed dependence of T_C on hydrostatic pressure[15] in KH_2PO_4 and KD_2PO_4. In KH_2PO_4 $T_{C,H}\to 0$ at $\sim$16 kbar, whereas no vanishing of $T_{C,D}$ was observed in KD_2PO_4 even at much higher pressures.[15] We shall see later that a similar effect is produced by the indirect $S_i^xS_j^x$ coupling via phonons ($F^x \neq 0$).

It should be noted that the presence of the S^xS^x coupling term amounts to a temperature-dependent renormalization of the tunneling frequency

$$\Omega' = \Omega + B_0\langle S^x\rangle \quad . \tag{16b}$$

The renormalization is not significant at high temperatures, $T\to\infty$. For $T \leqslant T_C$, however, we find

$$\Omega' = \Omega\frac{J_0}{J_0 - B_0} \quad . \tag{16c}$$

Expression (16c) shows that the S^xS^x term may result in a significant increase of the effective tunneling integral close to T_C if B_0 is positive and close to J_0. In such a case there will be a large isotope shift in T_C even for a small value of Ω.

Let us now study the dynamic properties of the above system.

Introducing collective variables as Fourier transform of the pseudospin operators,[1,3,4] we can rewrite expression (2)

$$H_p = -\Omega S_0^x - \tfrac{1}{2}\sum_q J_q S_q^z S_{-q}^z - \tfrac{1}{2}\sum_q B_q S_q^x S_{-q}^x \tag{17}$$

and obtain the linearized random-phase approximation (RPA) Heisenberg equations of motion for the spin deviation operators $\delta\vec{S}_q e^{i\omega t} = \vec{S}_q - \langle\vec{S}\rangle$ as

$$i\omega\delta S_q^x = J_o\langle S^z\rangle\delta S_q^y \quad , \tag{18a}$$

$$i\omega\delta S_q^y = (-J_0\langle S^z\rangle + B_q\langle S^z\rangle)\delta S_q^x + (\Omega' - J_q\langle S^x\rangle)\delta S_q^z \quad , \tag{18b}$$

$$i\omega\delta S_q^z = -\Omega'\delta S_q^y \quad , \tag{18c}$$

where $J_q = \sum_j J_{ij}e^{i\vec{q}\cdot(\vec{r}_j-\vec{r}_i)}$ as well as $B_q = \sum_j B_{ij}e^{i\vec{q}\cdot(\vec{r}_j-\vec{r}_i)}$.

The homogeneous system of linear Eqs. (18a)–(18c) has a nontrivial solution only if the corresponding secular determinant is identically equal to zero. The resulting equation for the eigenfrequencies is

$$i\omega[-\omega^2 + \Omega'(\Omega' - J_q\langle S^x\rangle) + J_0\langle S^z\rangle^2(J_0 - B_q)] = 0 \quad . \tag{19}$$

One solution which corresponds to longitudinal excitations[14] is

$$\omega_1 = 0 \quad . \tag{20a}$$

The frequency of transverse excitations which represent the free precession of the pseudospins around the molecular field,[4] is, on the other hand, obtained as

$$\omega_{2,3}^2 = \Omega'(\Omega' - J_q\langle S^x\rangle) + J_0\langle S^z\rangle^2(J_0 - B_q) \tag{20b}$$

and approaches zero as $q\to 0$, $T\to T_C$, where T_C is given by expression (15). It should be noted that the $B_qS_q^xS_{-q}^x$ term renormalizes the soft-mode frequency (20b). The renormalization effects are significant only close to T_C where they, as discussed above, increase the isotope shifts in T_C.

For $T > T_C$ we get

$$\omega_{2,3}^2 = \Omega'(\Omega' - J_q\langle S^x\rangle), \quad T > T_C \quad , \tag{20c}$$

which is the same as in the IMTF model except for Ω' instead of Ω. At high enough temperatures

$$\Omega' = \Omega\left(1 + \frac{B_0}{4kT}\right) \to \Omega \tag{21}$$

so that the soft-mode frequency is the same as in the absence of the $BS_i^xS_j^x$ term though T_C is different.

IV. $S_{-q}^xF_q^xQ_q$ COUPLING

Let us now discuss the coupling of the pseudospin tunneling motion with nonpolar optical phonons, which results in an indirect $S_i^xS_j^x$ coupling. The coupling of S^z with polar optical phonons[5] is taken into account.

The Hamiltonian of our problem is now

$$H = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \sum_q S_{-q}^x F_q^x Q_q^{(1)} - \sum_q S_{-q}^z F_q^z Q_q^{(2)} + \frac{1}{2} \sum_q \sum_{p=1}^{2} (P_q^{(p)} P_{-q}^{(p)} + \omega_{q,p}^2 Q_q^{(p)} Q_{-q}^{(p)}) \quad , \tag{22}$$

where $Q_q^{(1)}$ is the normal coordinate of a nonpolar optic phonon, interacting with S^x and $Q_q^{(2)}$ the normal coordinate of a polar optic phonon interacting with S^z.

The thermal expectation values of the pseudospin operators are—within the MFA—again determined by the self-consistency equations (14a) and (14b). The components H_x and H_z of the molecular field are, however, now given by

$$H_x = \Omega + F_0^x \langle Q^{(1)} \rangle \quad , \tag{23a}$$

$$H_z = J_0 \langle S^z \rangle + F_0^z \langle Q^{(2)} \rangle \quad , \tag{23b}$$

where

$$\langle Q^{(1)} \rangle = (F_0^x / \omega_{1,0}^2) \langle S^x \rangle \tag{23c}$$

and

$$\langle Q^{(2)} \rangle = (F_0^z / \omega_{2,0}^2) \langle S^z \rangle \quad . \tag{23d}$$

Nonzero solutions for the spontaneous polarization, which is proportional to $\langle S^z \rangle$, are stable below the transition temperature T_C. This is given by

$$\frac{2\Omega}{J_0 + b - a} = \tanh\left(\frac{\beta_C \Omega}{2} \frac{J_0 + b}{J_0 + b - a} \right) \quad , \tag{24}$$

where $\beta_C = 1/kT_C$ and $a = |F_0^x|^2/\omega_{1,0}^2$, $b = |F_0^z|^2/\omega_{2,0}^2$. Equation (24) is analogous to Eq. (15b). Expression (24) shows that at T_C proton-phonon interactions renormalize the tunneling integral $\Omega \rightarrow \Omega(J_0 + b)/(J_0 + b - a)$. For $a = b = 0$, we obtain the equation for T_C of the IMTF Hamiltonian.[4] Since a is proportional to the square of the tunneling integral, the renormalization of Ω is mass and pressure dependent. A nonvanishing solution for T_C exists only if

$$2\Omega < J_0 + b - a \quad . \tag{25}$$

Introducing, as before, Fourier-transformed collective variables, we find [using expression (22)] for the linearized pseudospin and phonon deviation operators

$$i\omega \delta S_q^x = (J_0 \langle S^z \rangle + F_0^z \langle Q^{(2)} \rangle) \delta S_q^y \quad , \tag{26a}$$

$$i\omega \delta S_q^y = -(J_0 \langle S^z \rangle + F_0^z \langle Q^{(2)} \rangle) \delta S_q^x + (\Omega - J_q \langle S^x \rangle + F_0^x \langle Q^{(1)} \rangle) \delta S_q^z - F_q^z \langle S^x \rangle \delta Q_q^{(2)} + F_q^x \langle S^z \rangle \delta Q_q^{(1)} \quad , \tag{26b}$$

$$i\omega \delta S_q^z = -(\Omega + F_0^x \langle Q^{(1)} \rangle) \delta S_q^y \quad , \tag{26c}$$

$$i\omega \delta Q_q^{(1)} = \delta P_q^{(1)} \quad , \tag{26d}$$

$$i\omega \delta Q_q^{(2)} = \delta P_q^{(2)} \quad , \tag{26e}$$

$$i\omega \delta P_q^{(1)} = -\omega_{1,q}^2 \delta Q_q^{(1)} + F_{-q}^x \delta S_q^x \quad , \tag{26f}$$

$$i\omega \delta P_q^{(2)} = -\omega_{2,q}^2 \delta Q_q^{(2)} + F_{-q}^z \delta S_q^z \quad . \tag{26g}$$

The above system of linear equations has nontrivial solutions if the corresponding secular determinant vanishes. The resulting equation for the eigenfrequencies of the coupled proton-phonon modes can be written in the form

$$(\omega^2 - \omega_{1,q}^2)(\omega^2 - \omega_{2,q}^2)(\omega^2 - \omega_{B'}^2) - \omega_A^4 (\omega^2 - \omega_{1,q}^2) - \omega_C^4 (\omega^2 - \omega_{2,q}^2) = 0 \quad , \tag{27}$$

where

$$\omega_{B'}^2 = \omega_B^2 + g^2 \quad , \tag{28a}$$

$$\omega_B^2 = \Omega''(\Omega'' - J_q \langle S^x \rangle) \quad , \tag{28b}$$

$$\Omega'' = \Omega + F_0^x \langle Q^{(1)} \rangle \quad , \tag{28c}$$

$$g = J_0 \langle S^z \rangle + F_0^z \langle Q^{(2)} \rangle \quad , \tag{28d}$$

$$\omega_A^4 = \Omega'' |F_q^z|^2 \langle S^x \rangle \quad , \tag{28e}$$

$$\omega_C^4 = g |F_q^x|^2 \langle S^z \rangle \quad . \tag{28f}$$

The frequency of the longitudinal excitations, i.e., fluctuations parallel to the molecular field is zero both above and below T_C.

For $T > T_c$, $\langle S^z \rangle = \langle Q^{(2)} \rangle = \omega_C^4 = 0$, and we find

$$\omega^2 = \omega_{1,q}^2 \tag{29a}$$

and

$$\omega^4 - \omega^2(\omega_B^2 + \omega_{2,q}^2) + \omega_B^2 \omega_{2,q}^2 - \omega_A^4 = 0 \quad . \tag{29b}$$

The dispersion relation (29b) is equal to the Kobayashi[5] result if only Ω is replaced by the temperature-dependent renormalized frequency Ω''. The frequencies of the two coupled transverse modes are given by

$$\omega_{\pm}^2 = \tfrac{1}{2} \{ (\omega_{2,q}^2 + \omega_B^2) \pm [(\omega_{2,q}^2 - \omega_B^2)^2 + 4\omega_A^4]^{1/2} \} \quad , \quad T > T_C \quad , \tag{30}$$

where ω_B is the soft-mode frequency of the "renormalized" protonic system given by Eqs. (28b) and (28c).

The ω_- mode describes the in-phase motion of the pseudospin system and the lattice, whereas in the "hard" ω_+ mode the two systems move with opposite phase. It should be noted that the coupling with the polar phonons occurs via the F^z term, whereas the nonpolar phonons are above T_C decoupled from the proton modes.

The stability limit of the paraelectric phase is determined by the temperature T_C [expression (24)]

where ω_- vanishes.

If $F_q^z = 0$, we find for $T > T_C$ that $\omega_+ = \omega_{2,q}$ and $\omega_- = \omega_B$. Below T_C we obtain in this case

$$\omega^2 = \omega_{2,q}^2 \tag{31a}$$

and

$$\omega_\pm^2 = \tfrac{1}{2}\{(\omega_{1,q}^2 + \omega_{B'}^2) \pm [(\omega_{1,q}^2 - \omega_{B'}^2)^2 + 4\omega_C^4]^{1/2}\}, \quad T < T_C \ , \tag{31b}$$

where $\omega_{B'}$ and ω_C are given by expressions (28a) and (28f). The frequency of the ω_- mode approaches zero at T_C for $q = 0$, whereas the ω_+ mode varies only weakly with temperature.

The above results show that the $S_{-q}^x F_q^x Q_q^{(1)}$ coupling renormalizes the frequency of the "proton-like" mode ω_- both above and below T_C, but makes the "nonpolar-optic-phonon-like" mode frequency, ω_+, different from $\omega_{1,q}$ only below T_C where $\langle S^z \rangle$, and hence ω_C, are different from zero. This is quite different from the $S_{-q}^z F_q^z Q_q^{(2)}$ coupling[5] where the "polar-optic-phonon-like" frequency ω_+ is different from $\omega_{2,q}$ for $T > T_C$ as well as $T < T_C$. The difference is the result of the fact that $\langle S^z \rangle \neq 0$ only below T_C, whereas $\langle S^x \rangle \neq 0$ both above and below T_C.

In looking for $S_{-q}^x F_q^x Q_q^{(1)}$ effects on the lattice vibrations we should thus study the temperature dependence of the lattice modes[20] below T_C and not, as in case of $S_{-q}^z F_q^z Q_q^{(2)}$ coupling, above T_C.

The temperature dependence of the "soft" ω_- and "hard" ω_+ modes is presented in Figs. 2(a) and 2(b) for $F^z = 0$, whereas Fig. 2(c) shows the temperature dependence of the spontaneous polarization, $\langle S^z \rangle$.

The dependence of the paraelectric soft-mode frequency ω_- on the strength of the F^x coupling is shown in Figs. 3(a) and 3(b) both for a deuterated ($\Omega_D = 1\,^\circ\text{K}$, $T_{C,D} = 213\,^\circ\text{K}$) and an undeuterated system ($\Omega_H = 144\,^\circ\text{K}$, $T_{C,H} = 122\,^\circ\text{K}$).

The strength of the F^x coupling is measured in terms of the parameter $a = J_0 (F^x)^2 / 4\omega_I^2 \Omega^2$ which should be—in view of the proportionality of F^x to Ω—mass independent. Whereas the F^x coupling practically does not affect the soft-mode frequency and T_C in the deuterated system, it affects ω_- of the undeuterated system close to $T_{C,H}$ and $T_{C,H}$ itself even for rather small values of a. For $a = 1$, $(\omega_-)_H \neq 0$ down to $T = 0$, whereas (ω_-) and $T_{C,D}$ are not changed at all. The high-temperature value of $(\omega_-)_H$ is as well only insignificantly higher than for $a = 0$.

The dependence of $T_{C,H}$ and $T_{C,D}$ on F^x is presented in Fig. 4 whereas Fig. 5 shows the dependence of the normalized isotope shift $(T_{C,D} - T_{C,H})/T_{C,D}$ on $\alpha = |F_x|^2 4\Omega^2 \omega_I^2$ for $\Omega_D = 1\,^\circ\text{K}$, $J_H = J_D = 850\,^\circ\text{K}$ and different values of Ω_H.

The F_x coupling thus provides a mechanism which allows for large isotope shifts in T_C even in systems

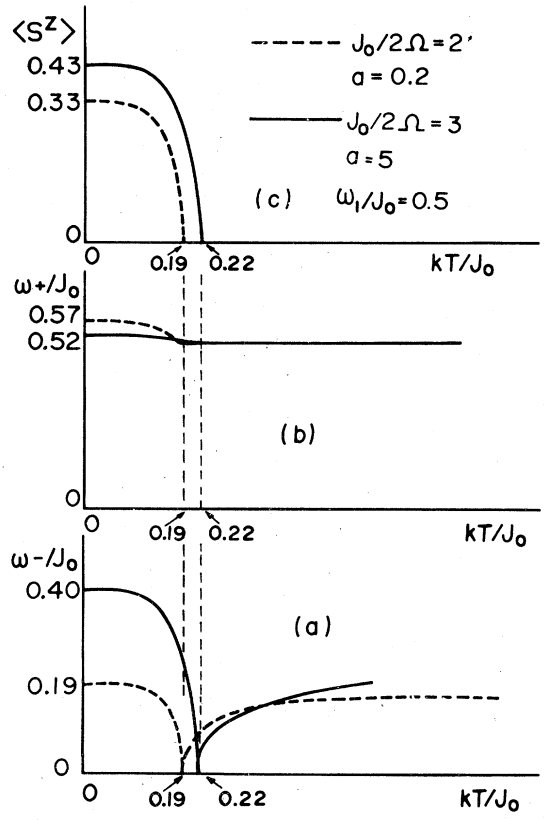

FIG. 2. Temperature dependence of ω_-, ω_+ and $\langle S^z \rangle$ in case of $S_i^x F^x Q_i$ pseudospin phonon coupling. Here a is $a = J_0 |F^x|^2 / (4\omega_I^2 \Omega^2)$.

with relatively low Ω and low proton-tunneling-mode frequencies. At the same time it could also account for the observed rather different dependences of $T_{C,H}$ and $T_{C,D}$ on pressure.

The effects on T_C are qualitatively similar to those

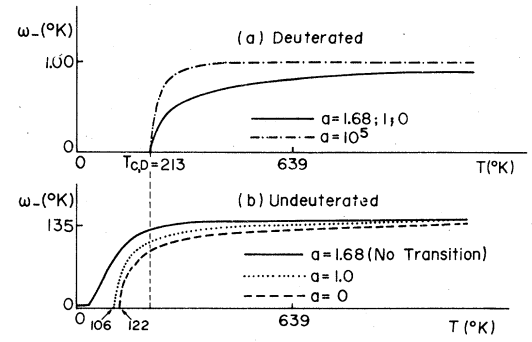

FIG. 3. Dependence of ω_- on temperature and strength of the $S_i^x F^x Q_i$ pseudospin phonon coupling $a = J_0 |F^x|^2 / 4\omega_I^2 \Omega^2$ for a deuterated ($\Omega_D = 1\,^\circ\text{K}$, $J_0 = 850\,^\circ\text{K}$) and an undeuterated system ($\Omega_H = 144\,^\circ\text{K}$, $J_0 = 544\,^\circ\text{K}$).

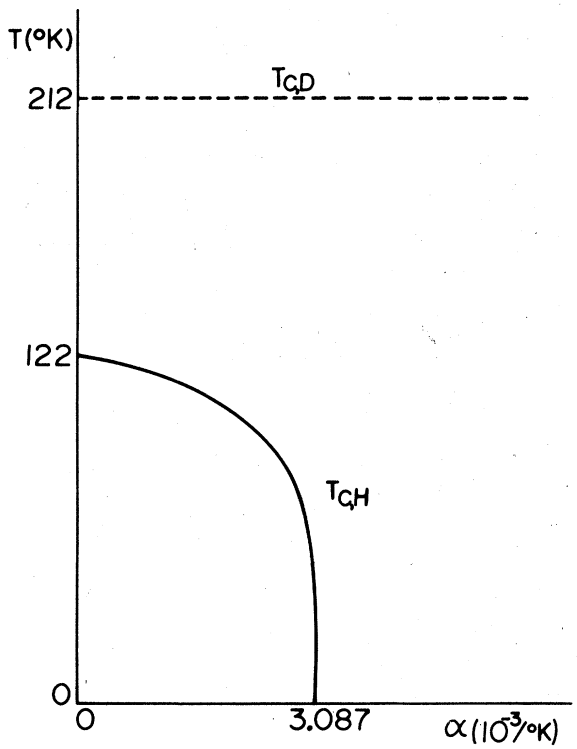

FIG. 4. Dependence of $T_{C,H}$ ($\Omega_H = 144\,°K$, $J_0 = 544\,°K$) and $T_{C,D}$ ($\Omega_D = 1\,°K$, $J_0 = 850\,°K$) on the normalized strength of the $S_i^x F^x Q_i$ pseudospin phonon coupling $\alpha = |F_x^2|/4\omega_1^2\Omega^2$.

provided by the "direct" $S_i^x S_j^x$ coupling but are probably more significant in view of the larger magnitude of the $S_{-q}^x F_q^x Q_q^{(1)}$ term as compared to the $BS_q^x S_{-q}^x$ term. The proton-lattice coupling again results in a temperature-dependent renormalization of the tunneling integral

$$\Omega' = \Omega + \frac{F_0^{x\,2}}{\omega_{1,0}^2}\langle S^x\rangle \quad , \tag{31c}$$

so that the term $F_0^{x\,2}/\omega_{1,0}^2$ plays the role of B_0 in expression (16b). It should be noted that here the proton-lattice coupling always increases the effective tunneling integral.

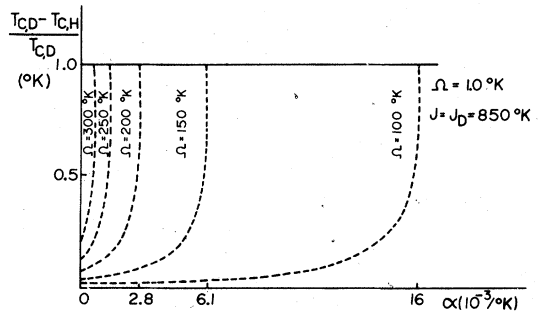

FIG. 5. Dependence of the reduced isotope shift $(T_{C,D} - T_{C,H})/T_{C,D}$ on $\alpha = |F_x^2|/4\omega_1^2\Omega^2$ for different values of Ω.

V. $S_j^x D_j Q_j^2$ COUPLING

For the sake of completeness let us now also look into the coupling of the tunneling motion with polar optical phonons. In crystals with a nonpolar high-temperature phase, this coupling is of the form $S_j^x D_j Q_j^2$. The linear coupling term vanishes due to symmetry as $S_j^x \to S_j^x$, $Q_j \to -Q_j$, $S_j^z \to -S_j^z$ on inversion.

The Hamiltonian of our problem can be thus written

$$H = -\Omega\sum_i S_i^x - \frac{1}{2}\sum_{i,j} J_{ij} S_i^z S_j^z - \sum_i S_i^z F_i^z Q_i - \sum_i S_i^x D_i Q_i^2 + \frac{1}{2}\sum_i (P_i^2 + \omega_{ph}^2 Q_i^2) \quad . \tag{32}$$

Within the molecular-field approximation we now find that

$$H_i^{MFA} = -\vec{H}_i\cdot\vec{S}_i - F_i^z\langle S^z\rangle Q_i + \tfrac{1}{2}[P_i^2 + (\omega_{ph}^2 - 2D\langle S^x\rangle)Q_i^2] \quad , \tag{33a}$$

where

$$H_x = \Omega + D\langle Q^2\rangle \approx \Omega + D\langle Q\rangle^2 \tag{33b}$$

and

$$H_z = J_0\langle S^z\rangle + F_0^z\langle Q\rangle \quad . \tag{33c}$$

In expression (33b), the fluctuations in the polar phonon coordinates are neglected. The expectation value of the polar phonon coordinate is now obtained as

$$\langle Q\rangle = \frac{F_0^z\langle S^z\rangle}{\omega_{ph}^2 - 2D\langle S^x\rangle} \quad . \tag{33d}$$

The expression for T_C is given by

$$\frac{2\Omega}{\tilde{J}_{0,C}} = \tanh(\tfrac{1}{2}\beta_C\Omega) \quad , \tag{34}$$

where $\tilde{J}_{0,C}$ stands for the renormalized pseudospin interaction constant

$$\tilde{J}_0 = J_0 + \frac{(F_0^z)^2}{\omega_{ph}^2 - 2D\langle S^x\rangle} \tag{35}$$

at $T = T_C$. The proton-phonon interactions thus renormalize the Ising pseudospin interaction constant $J_0 \to \tilde{J}_0$. Since both D and $\langle S^x\rangle$ are proportional to Ω, the renormalization is strongly mass and temperature dependent. This might be at least in part responsible for the fact that $(J)_H \neq (J)_D$ in H-bonded ferroelectrics. The mass-dependent renormalization disappears in the Kobayashi model where $D = 0$.

The resulting equation for the eigenfrequencies of the coupled "transverse" proton-polar optic phonon modes is

$$\omega_{\pm}^2 = \tfrac{1}{2}\{(\tilde{\omega}_{\rm ph}^2 + \tilde{\omega}_B^2) \pm [(\tilde{\omega}_{\rm ph}^2 - \tilde{\omega}_B^2)^2 + 4(\omega_A^4 + \omega_C^4 - \omega_D^4)]^{1/2}\} \ , \quad (36a)$$

where

$$\tilde{\omega}_{\rm ph}^2 = \omega_{\rm ph}^2 - 2D\langle S^x\rangle \ , \quad (36b)$$

$$\tilde{\omega}_B^2 = \tilde{\Omega}(\tilde{\Omega} - J_0\langle S^x\rangle) + (\tilde{J}_0\langle S^z\rangle)^2 \ , \quad (36c)$$

$$\tilde{\Omega} = \Omega + D\langle Q\rangle^2 \ , \quad (36d)$$

$$\omega_A^4 = \tilde{\Omega}|F_0^z|^2\langle S^x\rangle \ , \quad (36e)$$

$$\omega_C^4 = 4D^2\tilde{J}_0\langle S^z\rangle^2\langle Q\rangle^2 \ , \quad (36f)$$

$$\omega_D^4 = 2DF_0^z(\tilde{\Omega} + \tilde{J}_0\langle S^x\rangle)\langle S^z\rangle\langle Q\rangle \ . \quad (36g)$$

Expression (36a) is valid both for $T > T_C$ and $T < T_C$. Above T_C our result is equivalent to the one obtained by Kobayashi except for the mass and temperature-dependent renormalization of the phonon frequency $\omega_{\rm ph}^2 \to \omega_{\rm ph}^2 - 2D\langle S^x\rangle$. There is, however, a considerable difference below T_C. The coupling term $\omega_A^4 + \omega_C^4 - \omega_D^4$ is in the Kobayashi model given by $\Omega|F_0^z|^2\langle S^x\rangle$, whereas it is in the present case obtained as

$$\omega_A^4 + \omega_C^4 - \omega_D^4 = \langle S^x\rangle\tilde{\Omega}\left[|F_0^z|^2 + \frac{4D^2}{\tilde{\Omega}\langle S^x\rangle}\tilde{J}_0\langle S^z\rangle^2\langle Q\rangle^2 - \frac{2F_0^zD}{\tilde{\Omega}}\left(\tilde{J}_0 + \frac{\tilde{\Omega}}{\langle S^x\rangle}\right)\langle S^z\rangle\langle Q\rangle\right] \ . \quad (37)$$

The renormalization of the coupling term is critically temperature dependent and vanishes at $T \geq T_C$. In addition it is also dependent on the mass of the tunneling particle and on hydrostatic pressure thus explaining the strong dependence of this term on pressure in KH_2PO_4-type crystals below T_C.[24]

VI. $\Omega S_i^x(\frac{1}{2} - \sigma_i^z)$ COUPLING

Let us finally investigate the case where the motion of the lattice ions which couples to the proton tunneling is so strongly anharmonic that we have a double-minimum-type single-particle lattice potential. Limiting ourselves to the two lowest-lattice energy states, we can express the relevant lattice Hamiltonian in terms of pseudospin-$\frac{1}{2}$ Pauli matrices σ^z, σ^y, and σ^x. We thus deal with two interacting pseudospin systems instead of with a proton-phonon system as before.

If we further assume that the coupling between these two systems is so strong that the protons can tunnel only in one out of the two possible lattice configurations, we can write the Hamiltonian of our problem in the form

$$H = -\Omega\sum_i S_i^x(\tfrac{1}{2} - \sigma_i^z) - \tfrac{1}{2}\sum_{i,j} J_{ij}S_i^zS_j^z + \Delta\sum_i \sigma_i^z - \Gamma^R\sum_i \sigma_i^x \ . \quad (38)$$

In the MFA, expression (38) decomposes into a "proton"

$$H_{S,i} = -\Omega(\tfrac{1}{2} - \langle\sigma^z\rangle)S_i^x - J_0\langle S^z\rangle S_i^z \quad (39a)$$

and a "lattice" part

$$H_{\sigma,i} = -\Gamma^R\sigma_i^x + (\Omega\langle S^x\rangle + \Delta)\sigma_i^z \ , \quad (39b)$$

where $J_0 = \sum_i J_{ij}$. It should be noted that the lattice motion will be always biased (i.e., $\langle\sigma^z\rangle \neq 0$) in view of the coupling with S^x even if the intrinsic asymmetry in the lattice double-well potential Δ is zero. The lattice pseudospins introduced above thus represent a nonpolar optic lattice mode in crystals with a nonpolar high-temperature phase.

Expressions (39a) and (39b) can be rewritten

$$H_S = -H_{x,S}S^x - H_{z,S}S^z \quad (40a)$$

and

$$H_\sigma = -H_{x,\sigma}\sigma^x - H_{z,\sigma}\sigma^z \ , \quad (40b)$$

with

$$H_{x,S} = \Omega(\tfrac{1}{2} - \langle\sigma^z\rangle) \ , \quad (41a)$$

$$H_{z,S} = J_0\langle S^z\rangle \ , \quad (41b)$$

$$H_{x,\sigma} = \Gamma^R \ , \quad (41c)$$

$$H_{z,\sigma} = -(\Delta + \Omega\langle S^x\rangle) \ . \quad (41d)$$

The thermal expectation values of the pseudospin operators are now determined from the self-consistency equations

$$\langle S^z\rangle = \frac{1}{2}\frac{H_{z,S}}{H_S}\tanh(\tfrac{1}{2}\beta H_S) \ , \quad (42a)$$

$$\langle S^x\rangle = \frac{1}{2}\frac{H_{x,S}}{H_S}\tanh(\tfrac{1}{2}\beta H_S) \ , \quad (42b)$$

$$\langle\sigma^z\rangle = \frac{1}{2}\frac{H_{z,\sigma}}{H_\sigma}\tanh(\tfrac{1}{2}\beta H_\sigma) \ , \quad (42c)$$

$$\langle\sigma^x\rangle = \frac{1}{2}\frac{H_{x,\sigma}}{H_\sigma}\tanh(\tfrac{1}{2}\beta H_\sigma) \ , \quad (42d)$$

where

$$H_S = (H_{z,S}^2 + H_{x,S}^2)^{1/2}$$

and

$$H_\sigma = (H_{z,\sigma}^2 + H_{x,\sigma}^2)^{1/2} \ .$$

Expressions (42a)–(42d) and (41a)–(41d) show that we are dealing with a strongly temperature-dependent renormalization of the tunneling frequency. The paraelectric-ferroelectric transition temperature T_C determines the boundary of the region where a nonzero value of $\langle S^z \rangle$ becomes stable. Since the static properties of the system are not significantly affected, if we put $\Delta = \Gamma^R = 0$, let us determine T_C for this case. From Eq. (42a) we find the equation for T_C

$$\frac{2\Omega(\frac{1}{2} - \langle \sigma^z \rangle_C)}{J_0} = \tanh\left[\frac{\Omega\beta_C}{2}(\tfrac{1}{2} - \langle \sigma^z \rangle_C)\right],$$

$$\beta_C = 1/kT_C \ , \tag{43a}$$

where $\langle \sigma^z \rangle_C$ has to be determined from Eq. (42c)

$$\langle \sigma^z \rangle_C = -\tfrac{1}{2}\tanh\left[\frac{\beta_c \Omega^2}{2J_0}(\tfrac{1}{2} - \langle \sigma^z \rangle_C)\right] \ . \tag{43b}$$

We thus deal with a system of two self-consistency equations for β_C. The solutions of this system are shown in Fig. 6, where kT_C/J_0 and $\langle \sigma^z \rangle_C$ are plotted as functions of $J_0/2\Omega$.

For $J_0/2\Omega > 1$, there is a single T_C separating the high-temperature paraelectric from the low-temperature ferroelectric phase.

For $J_0/2\Omega = 1$ ferroelectricity appears below $kT_C = 0.2J_0$ but the ferroelectric phase becomes unstable at $T = 0$. This is a consequence of the fact that Eq. (43b) has now two solutions for $\langle \sigma^z \rangle_C$

$$\langle \sigma^z \rangle_{C\mathrm{I,II}} = -\tfrac{1}{2} \ \text{ and } \ -(\sqrt{2}-1)/2 \ , \tag{44a}$$

corresponding to

$$(kT_C/J_0)_{\mathrm{I,II}} = 0 \ \text{ and } \ \sqrt{2}/[8\ln(1+\sqrt{2})] \ . \tag{44b}$$

For $0.922 \leq J_0/2\Omega \leq 1$ we have two Curie temperatures, $T_{C\mathrm{I}}$ and $T_{C\mathrm{II}}$, and the ferroelectric phase is intermediate between a high-temperature paraelectric and a low-temperature paraelectric phase. With increasing Ω the upper T_C decreases and the lower T_C increases so that the ferroelectricity disappears at $J_0/2\Omega = 0.922$ where

$$(2\Omega_{\mathrm{eff}})_{T=T_C} = 2\Omega(\tfrac{1}{2} - \langle \sigma^z \rangle) = J_0 \ .$$

For $J_0/2\Omega < 0.922$ there is no solution for T_C and the paraelectric phase is stable at all temperatures.

The temperature dependence of $\langle S^z \rangle$, which is proportional to the spontaneous polarization, is presented in Fig. 7 for $J_0/2\Omega = 1.5$, $J_0/2\Omega = 1$, and $J_0/2\Omega = 0.95$. The existence of two second-order transition temperatures, $T_{C\mathrm{I}}$ and $T_{C\mathrm{II}}$, separating the polarized phase from two disordered phases is clearly seen for $J_0/2\Omega = 0.95$.

Introducing Fourier-transformed collective variables, we find the linearized RPA Heisenberg equations of motion for the pseudospin fluctuations around the MFA solutions as

$$i\omega\delta S_q^x = J_0 \langle S^z \rangle \delta S_q^y \ , \tag{45a}$$

$$i\omega\delta S_q^y = (\Omega/2 - \Omega\langle \sigma^z \rangle - J_q \langle S^x \rangle)\delta S_q^z - J_0 \langle S^z \rangle \delta S_q^x - \Omega \langle S^z \rangle \delta\sigma_q^z \ , \tag{45b}$$

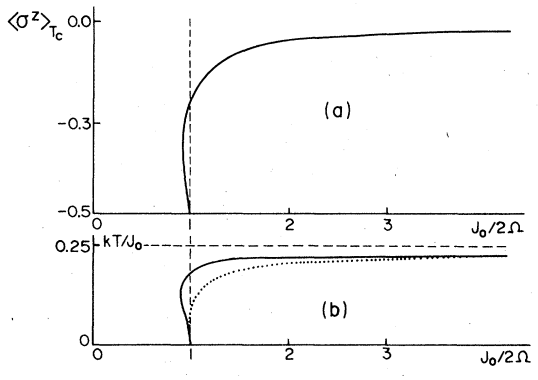

FIG. 6. Dependence of kT_C/J_0 and $\langle \sigma^z \rangle_{T_C}$ on $J_0/2\Omega$ in case of $\Omega S^x(\frac{1}{2} - \sigma^z)$ proton-lattice coupling. The dotted line shows the dependence of kT_C/J_0 on $J_0/2\Omega$ for the simple IMTF Hamiltonian.

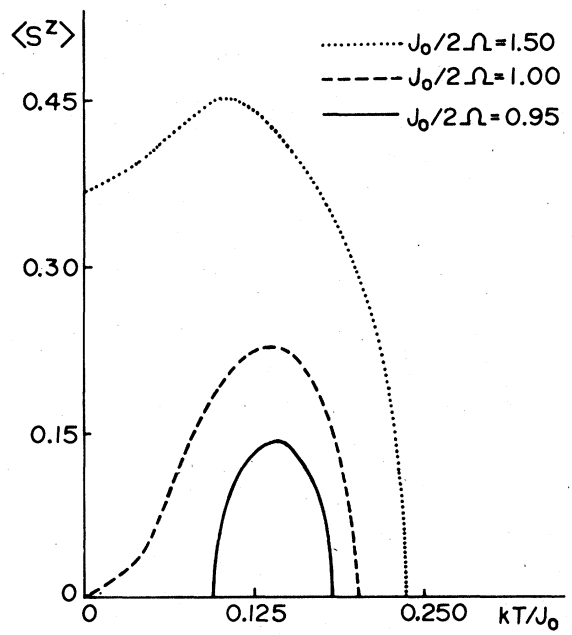

FIG. 7. Temperature dependence of $\langle S^z \rangle$ in case of $\Omega S^x(\frac{1}{2} - \sigma^z)$ proton-lattice coupling for $J_0/2\Omega = 1.5$, 1.0, and 0.95.

$$i\omega\delta S_q^z = -(\Omega/2 - \Omega\langle\sigma^z\rangle)\delta S_q^y \ , \tag{45c}$$

$$i\omega\delta\sigma^x = -(\Omega\langle S^x\rangle + \Delta)\delta\sigma_q{}^y \ , \tag{45d}$$

$$i\omega\delta\sigma^y = (\Omega\langle S^x\rangle + \Delta)\delta\sigma_q^x + \Gamma^R\delta\sigma_q^z + \Omega\langle\sigma^x\rangle\delta S_q^x \ , \tag{45e}$$

$$i\omega\delta\sigma_q^z = -\Gamma^R\delta\sigma_q^x \ . \tag{45f}$$

The two longitudinal-mode frequencies are again zero, $\omega_{1,2}=0$, both above as well as below T_C. The frequencies of the four coupled transverse modes are obtained as

$$\omega_\pm^2 = \tfrac{1}{2}\{(\omega_A^2+\omega_B^2) \pm [(\omega_B^2-\omega_A^2)^2+4C]^{1/2}\} \ , \tag{46a}$$

where now

$$\omega_A^2 = (J_0\langle S_0^z\rangle)^2 + \Omega'(\Omega' - J_0\langle S^x\rangle) \ , \tag{46b}$$

$$\omega_B^2 = (\Gamma^R)^2 + (\Omega\langle S^x\rangle + \Delta)^2 \ , \tag{46c}$$

and

$$C = J_0\Omega^2(\Gamma^R)^2\langle S^z\rangle^2\langle\sigma^x\rangle \ , \tag{46d}$$

with Ω' standing for the renormalized tunneling frequency

$$\Omega' = \Omega(\tfrac{1}{2} - \langle\sigma^z\rangle) \ . \tag{46e}$$

For $T > T_C$, $\langle S^z\rangle = C = 0$, and we get a soft "proton-like" and a hard "lattice-like" mode

$$\omega_-^2 = \omega_A^2 \propto T - T_C \tag{47a}$$

and

$$\omega_+^2 = \omega_B^2 \ . \tag{47b}$$

The temperature dependence of the "hard" ω_+ and "soft" ω_- modes from expression (46a) is shown in Fig. 8 for $J_0/2\Omega = 1.5$, 1.0, and 0.95. For sake of simiplicity we assumed that $\Gamma^R = \Delta = 0$. It should be noted that ω_+ corresponds to an "out of phase" and ω_- to an "in-phase" motion of the proton and lattice systems.

For $J_0/2\Omega = 1.5$, ω_- vanishes at $kT_C = 0.2375J_0$, and increases with decreasing temperatures close to T_C in ferroelectric phase. For $J_0/2\Omega = 1$, ω_- vanishes both at $kT_C = 0.2J_0$ and $T = 0$, whereas it vanishes for $J_0/2\Omega = 0.95$ at $kT_{C\mathrm{I}} = 0.18J_0$ and $kT_{C\mathrm{II}} = 0.95J_0$, but is nonzero at $T = 0$. The frequency of the hard mode, ω_+ increases with decreasing temperature in all three cases discussed above and shows no critical temperature dependence.

VII. CONCLUSIONS

The obtained results show that:

(i) The introduction of "direct" $B_{ij}S_i^xS_j^x$ coupling between the tunneling motion of one proton and the tunneling motion of another, or the introduction of the probably larger "indirect" coupling of this type via $S_i^xF^xQ_i$ pseudospin-phonon interaction describing the modulation of the distance between the two equilibrium sites in an O–H · · · O bond by nonpolar optical phonons, may lead to a situation where large isotope shifts in T_C occur on deuteration though the unrenormalized tunneling integral Ω and the renormalized frequency of the proton tunneling modes are low even far away from T_C. This is qualitatively different from the predictions of the pure IMTF Hamiltonian and may perhaps explain some phenomena recently observed in $PbHPO_4$ type systems[18–20] and squaric acid.[21] The physical reason for this effect is the fact that the mass and temperature-dependent renormalization of the proton tunneling integral is important only close to T_C where $\omega_- \to 0$ and not far away from T_C.

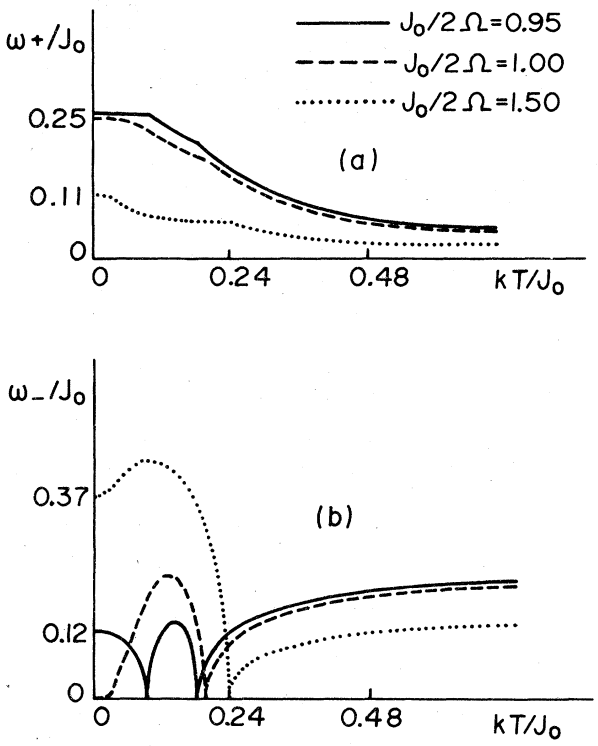

FIG. 8. Temperature dependence of ω_+ and ω_- in case of $\Omega S^x(\frac{1}{2} - \sigma^z)$ proton-lattice coupling for $J_0/2\Omega = 1.5$, 1.0, and 0.95.

(ii) The increase in the "coupling constants" B_{ij} or F^x—which are both functions of the tunneling integral and thus very sensitive to the shape of the O–H · · · O bond potential—with increasing hydrostatic pressure leads to a decrease in $T_{C,\mathrm{H}}$ and an eventual vanishing of ferroelectricity in undeuterated systems, whereas $T_{C,\mathrm{D}}$ of a deuterated system is, for the same range of B_{ij} or F^x values, not affected at all. The corresponding $T_{C,\mathrm{H}}$ vs F^x or B_{ij} curves are similar to the T_C versus hydrostatic pressure curves ob-

served in many H-bonded systems.[15]

(iii) The S^xF^xQ and S^xDQ^2 couplings lead to a significant change in the dynamics of the coupled proton-phonon system below T_C and could be the reason for the observed large pressure dependence of the proton polar optic phonon interaction constant in KH_2PO_4-type crystals.[17,21] This might also explain the presence of the "hard" proton tunneling mode ω_+ [expression (31b) or (36)] observed in $PbHPO_4$ below T_C.[20]

(iv) When the lattice motion is so anharmonic that the lattice ions move in a double-well potential, and the proton-lattice coupling so strong that the protons can tunnel only in one out of the two possible lattice configurations, two Curie temperatures may appear for $0.922 < J_0/2\Omega < 1$ as a result of the T-dependent renormalization of the tunneling frequency so that the ferroelectric phase is bounded by a high-temperature paraelectric and a low-temperature paraelectric phase.

It should be noted that all above results have been obtained in the MFA and RPA approximations and that the finite width of the soft modes and damping effects[25] have not been taken into account. A recent continued fraction calculation[26] has however shown that the MFA and RPA represent useful first approximations for the statics and dynamics of the Ising model in a transverse tunneling field Hamiltonian so that the above results are still qualitatively meaningful. The basic predictions agree with those recently obtained by a variational treatment of the proton-phonon system in KH_2PO_4.[27]

ACKNOWLEDGMENTS

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