Soft-mode dynamics of partially deuterated KH_2PO_4-type crystals

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The dynamics of isotopically disordered ferroelectric crystals of $K(H_{1-x}D_x)_2PO_4$ type is discussed on the basis of the coupled proton-deuteron tunneling-lattice optic-mode model. It is shown that one of the collective modes of the disordered system exhibits a soft-mode behavior at the ferroelectric transition temperature. The collective mode frequencies and their pressure derivatives are calculated by a modified random-phase approximation as a function of deuteron concentration and compared with recent low-temperature Raman data of Peercy. The theory allows an estimate of the various parameters of the model and provides strong support for the proton tunneling picture of hydrogen-bonded ferroelectrics.

I. INTRODUCTION

Whereas a large effort has been made in recent years to understand the lattice dynamics of KH_2PO_4-type crystals,[1,2] relatively little attention has been paid to the dynamical behavior of isotopically disordered mixed $K(H_{1-x}D_x)_2PO_4$ systems. It is the purpose of this paper to discuss the soft-mode dynamics of such systems on the basis of the coupled proton-deuteron tunneling-lattice optic-mode model. The frequencies of the collective modes and their pressure derivatives have been calculated and compared with the results of recent[3,4] low-temperature Raman experiments of Peercy. We hoped that mixed crystals might provide a more stringent test of various proton-lattice dynamical models of KH_2PO_4 order-disorder-type ferroelectrics than pure KH_2PO_4 or KD_2PO_4.

In Sec. II the Hamiltonian of our problem is defined. In Sec. III the behavior of the coupled proton-deuteron system is discussed. In Sec. IV, the interaction of the proton-deuteron system with the lattice is taken into account. In Sec. V the obtained results are compared with the experimental data.

II. HAMILTONIAN

Our analysis will be based on the Hamiltonian for the coupled proton-deuteron–lattice system which is written in the usual pseudospin formalism[1,2] as

$$\mathcal{H} = -\sum_{i,\alpha} \Omega_\alpha C_i^\alpha S_{i\alpha}^x - \frac{1}{2}\sum_{\substack{i,j\\ \alpha,\beta}} J_{ij}^{\alpha\beta} C_i^\alpha C_j^\beta S_{i\alpha}^z S_{j\beta}^z + \frac{1}{2}\sum_q (\omega_q^2 Q_q Q_{-q} + P_q P_{-q}) - \frac{1}{2}\sum_{\substack{q,i\\ \alpha}} F_q [Q_q, S_i^z]_+ e^{i\vec{q}\cdot\vec{R}_i} C_i^\alpha - E_k e^{-i\omega t}\left(\mu \sum_{i,\alpha} C_i^\alpha S_{i\alpha}^z e^{i\vec{k}\cdot\vec{R}_i} + Q_{-k}\rho_k\right). \quad (1)$$

Here α, β mean p (for protons) or d (for deuterons), and $C_i^p = 1$, $C_i^d = 0$ if the ith O-H- -O bond contains a proton, and $C_i^p = 0$, $C_i^d = 1$ otherwise. Thus, $C_i^p + C_i^d = 1$. The tunneling frequency Ω_α has two values, Ω_p and $\Omega_d \ll \Omega_p$. For the sake of simplicity we assumed that there is just one O-H- -O bond per unit cell. The interaction term $J_{ij}^{\alpha\beta}$ has three different values, J_{ij}^{pp}, J_{ij}^{dd}, and $J_{ij}^{pd} = J_{ij}^{dp}$, describing the proton-proton, deuteron-deuteron, and proton-deuteron coupling. The mass dependence of the interaction term may be due to a renormalization of $J_{ij}^{\alpha\beta}$ due to strong proton-deuteron coupling with the O- - -O vibration.[5] The third term in expression (1), which is independent of the isotope composition, represents the Hamiltonian for the polar optic lattice mode, which couples to the pseudospin system as described by the fourth term. The brackets $[\ ,\ ]_+$ designate an anticommutator. The last term in Eq. (1) describes the interaction of the system with an oscillating external electric field $E_k e^{i(\vec{k}\cdot\vec{R}_i - \omega t)}$. Here μ stands for the dipole moment of an O-H- -O bond and ρ_k for the appropriate Fourier component of the ionic charge distribution in the unit cell.

III. PROTON-DEUTERON SYSTEM

The proton-deuteron part of the Hamiltonian (1) can be written in explicit form as

$$\mathcal{H}_{p-d} = -\Omega_p \sum_i p_i^x (1 - C_i^d) - \Omega_d \sum_i d_i^x C_i^d - \frac{1}{2}\sum_{i,j} J_{ij}^{pp} p_i^z p_j^z (1 - C_i^d)(1 - C_j^d) - \frac{1}{2}\sum_{i,j} J_{ij}^{dd}$$

$$\times d_i^z d_j^z C_i^d C_j^d - \sum_{i,j} J_{ij}^{pd} p_i^z d_j^z (1 - C_i^d) C_j^d \ , \qquad (2)$$

where $\vec{S}_p = (p^x, p^y, p^z)$ and $\vec{S}_d = (d^x, d^y, d^z)$ are the Pauli spin matrices for protons and deuterons, respectively. In the molecular-field approximation, expression (2) decomposes into a proton,

$$\mathcal{H}_{p,i} = -\Omega_p p_i^x - \sum_j J_{ij}^{pp} \langle p_j^z (1 - C_j^d) \rangle p_i^z - \sum_j J_{ij}^{pd} \langle d_j^z C_j^d \rangle p_i^z \qquad (3a)$$

and a deuteron part

$$\mathcal{H}_{d,i} = -\Omega_d d_i^x - \sum_j J_{ij}^{dd} \langle d_j^z C_j^d \rangle d_i^z - \sum_j J_{ij}^{pd} \langle p_j^z (1 - C_j^d) \rangle d_i^z \ . \qquad (3b)$$

As the system is isotopically disordered and thus not translationally invariant, the hydrogen ordering will be different in different parts of the crystal. In view of the long-range nature of the interaction, however, it is not too bad an approximation to assume that each hydrogen "sees" only the average and not the true local distribution of the protons and deuterons. In this case we have

$$\langle p_j^z (1 - C_j^d) \rangle \approx \langle p^z \rangle (1 - C^d) \ , \qquad (4a)$$

$$\langle d_j^z C_j^d \rangle \approx \langle d^z \rangle C^d \ , \qquad (4b)$$

where $C^d = \langle C_i^d \rangle$ is the deuteron concentration, and $\langle\ \rangle$ includes a configurational average. Within this approximation each proton interacts with a molecular field which is the same at all protonic sites

$$\mathcal{H}_p = -\Omega_p p^x - H_{pz} p^z \ , \qquad (5a)$$

and the same is true for the deuterons,

$$\mathcal{H}_d = -\Omega_d d^x - H_{dz} d^z \ . \qquad (5b)$$

Here we have

$$H_{pz} = J_0^{pp} (1 - C^d) \langle p^z \rangle + J_0^{pd} C^d \langle d^z \rangle \ , \qquad (6a)$$

$$H_{dz} = J_0^{dd} C^d \langle d^z \rangle + J_0^{pd} (1 - C^d) \langle p^z \rangle \ , \qquad (6b)$$

with

$$J_0^{\alpha\beta} = \sum_j J_{ij}^{\alpha\beta} \ . \qquad (6c)$$

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

$$\langle p^z \rangle = \tfrac{1}{2} (H_{pz}/H_p) \tanh(\tfrac{1}{2}\beta H_p) \ ,$$

$$\langle p^x \rangle = \tfrac{1}{2} (\Omega_p/H_p) \tanh(\tfrac{1}{2}\beta H_p) \ , \qquad (7a)$$

$$\langle d^z \rangle = \tfrac{1}{2} (H_{dz}/H_d) \tanh(\tfrac{1}{2}\beta H_d) \ ,$$

$$\langle d^x \rangle = \tfrac{1}{2} (\Omega_d/H_d) \tanh(\tfrac{1}{2}\beta H_d) \ , \qquad (7b)$$

where $\beta = 1/kT$ and $H_\alpha^2 = \Omega_\alpha^2 + H_{\alpha z}^2$ with $\alpha = p, d$. Linearizing the equations for $\langle p^z \rangle$ and $\langle d^z \rangle$, we find the dependence of the transition temperature T_c on the deuteron concentration from

$$1 - J_0^{dd} C^d \tanh(\tfrac{1}{2}\beta_C \Omega_d)/2\Omega_d - J_0^{pp} (1 - C^d) \tanh(\tfrac{1}{2}\beta_C \Omega_p)/2\Omega_p + [J_0^{pp} J_0^{dd} - (J_0^{pd})^2] C^d (1 - C^d) \tanh(\tfrac{1}{2}\beta_C \Omega_p) \times \tanh(\tfrac{1}{2}\beta_C \Omega_d)/4\Omega_p \Omega_d = 0 \ , \qquad (8)$$

where $\beta_C = 1/kT_c$.

Depending on the sign and the relative values of J_0^{pp}, J_0^{dd}, and J_0^{pd}, there are two possibilities for a low-temperature homogeneous ordering of the proton and deuteron subsystems: a parallel "ferroelectric" ordering with $\langle p^z \rangle / \langle d^z \rangle > 0$ and an "antiparallel" ordering of the two subsystems with $\langle p^z \rangle / \langle d^z \rangle < 0$. In the following we shall concentrate ourselves on the parallel ferroelectric ordering which seems to be the one realized in $K(H_{1-x}D_x)_2PO_4$.

Since the statics of isotopically disordered ferroelectrics has already been discussed by Holakovsky,[5] we will focus here on the dynamic properties of the system. Dividing the expectation values of the pseudospin operators into a static part, which is equal to the thermal average value, and a fluctuating part[1,2]

$$\langle \vec{S}_\alpha \rangle_t = \langle \vec{S}_\alpha \rangle + \delta \langle \vec{S}_\alpha \rangle e^{-i\omega t} \ , \qquad (9)$$

we find from the Heisenberg equations $dA/dt = i[\mathcal{H}, A]$ the six coupled equations of motion for the fluctuations $\delta\langle \vec{S}_\alpha \rangle$ around the mean-field approximation solution. In the random-phase approximation we get

$$-i\omega \delta\langle d^x \rangle = H_{dz} \delta\langle d^y \rangle \ , \qquad (10a)$$

$$-i\omega \delta\langle d^y \rangle = \Omega_d \delta\langle d^z \rangle - H_{dz} \delta\langle d^x \rangle - \langle d^x \rangle [J_0^{dd} C^d \delta\langle d^z \rangle + J_0^{pd} (1 - C^d) \delta\langle p^z \rangle] \ , \qquad (10b)$$

$$-i\omega \delta\langle d^z \rangle = -\Omega_d \delta\langle d^y \rangle \ , \qquad (10c)$$

$$-i\omega \delta\langle p^x \rangle = H_{pz} \delta\langle p^y \rangle \ , \qquad (10d)$$

$$-i\omega \delta\langle p^y \rangle = \Omega_p \delta\langle p^z \rangle - H_{pz} \delta\langle p^x \rangle - \langle p^x \rangle \times [J_0^{pp} (1 - C^d) \delta\langle p^z \rangle + J_0^{pd} C^d \delta\langle d^z \rangle] \ , \qquad (10e)$$

$$-i\omega \delta\langle p^z \rangle = -\Omega_p \delta\langle p^y \rangle \ . \qquad (10f)$$

Above T_c, $\langle p^z \rangle = \langle d^z \rangle = H_{pz} = H_{dz} = 0$ so that $\delta\langle d^x \rangle = \delta\langle p^x \rangle = 0$ and we are left with four equations describing the transverse excitations, i.e., the elliptic precession of p and d around the x axis. The eigenfrequencies $\omega = \pm\omega_1, \pm\omega_2$ of these modes are obtained as solutions of the equation

$$\omega^4-\omega^2\{\Omega_p[\Omega_p-\langle p_x\rangle J_0^{pp}(1-C^d)]+\Omega_d(\Omega_d-\langle d^x\rangle J_0^{dd}C^d)\}+(\Omega_d\Omega_p)^2\times\left(1-\frac{\langle d^x\rangle J_0^{dd}C^d}{\Omega_d}-\frac{\langle p^x\rangle J_0^{pp}(1-C^d)}{\Omega_p}+\frac{\langle d^x\rangle\langle p^x\rangle C^d(1-C^d)[J_0^{dd}J_0^{pp}-(J_0^{pd})^2]}{\Omega_d\Omega_p}\right)=0\ . \quad (11)$$

The above equation can be rewritten as $\omega^4-b\omega^2+c=0$, so that we find

$$\omega_{1,2}^2=\tfrac{1}{2}[b\pm(b^2-4c)^{1/2}]\ , \quad (12)$$

where the coefficients b and c are defined by expression (11). The c term vanishes at T_c as it is proportional to expression (8). For $\Omega_p\neq 0$, $\Omega_d\neq 0$ one ($\pm\omega_1$) of the above eigenfrequencies exhibits a soft-mode behavior at the ferroelectric transition temperature

$$\omega_1^2(T=T_c)=0\ , \quad (13a)$$

whereas the other ($\pm\omega_2$) stays finite at T_c:

$$\omega_2^2(T=T_c)\neq 0\ . \quad (13b)$$

The ω_1 mode corresponds to a ferroelectric in-phase motion of the proton and deuteron subsystems, whereas ω_2 corresponds to an out-of-phase antiferroelectric motion of the two subsystems which should be—in view of $|\langle p^z\rangle|\neq|\langle d^z\rangle|$—better described as a ferrielectric mode.

The above behavior of ω_1 and ω_2 is characteristic of the case where the ferroelectric state is stable at low temperatures. If, however, the signs of the interaction parameters were such that the "antiparallel" ordering of the proton and deuteron subsystems would represent a stable state, then ω_2 would become soft first and ω_1 would be the "hard" mode. In the following, only the ferroelectric case will be treated.

For $\Omega_d=0$ the ω_1 mode becomes a "deuteronlike" pure diffusive relaxational mode characteristic of an Ising model, where the real part of the eigenfrequency is zero at all temperatures. The eigenfrequency of the "protonlike" ω_2 mode is in this case given by

$$\omega_2^2=\Omega_p^2\left(1-\frac{\tanh(\frac{1}{2}\beta\Omega_p)}{\tanh(\frac{1}{2}\beta_{C0}\Omega_p)}(1-C^d)\right),\quad T>T_c\ , \quad (14)$$

where β_{C0} is given by the transition temperature of the "pure" protonic system:

$$\tanh(\tfrac{1}{2}\beta_{C0}\Omega_p)=2\Omega_p/J_0^{pp}\ . \quad (15)$$

For zero concentration of deuterium $C^d=0$, i.e., in the absence of the deuteron subsystem, the ω_2 mode becomes the well-known soft mode of the protonic system: $\omega_2^2\propto T-T_c$.

It should be noted that in view of the presumably very small value of Ω_d, the frequency $\omega_1\propto\Omega_d$ should be rather low above T_c and hard to observe. Another feature, which should be stressed, is that the frequency of the "easily" observable protonlike ω_2 mode should *increase* with increasing concentration of deuterium.

Below T_c $\langle d^z\rangle$ and $\langle p^z\rangle$ are both different from zero and the molecular field points along a general direction in the x-z plane. All six equations of motion are now coupled. The frequencies of the two longitudinal excitations are however still zero. The eigenfrequencies of the four excitations which are transverse to the molecular field, $\omega=\pm\omega_1$, $\pm\omega_2$, are now obtained from

$$\omega^4-\omega^2[H_p^2-\Omega_p\langle p^x\rangle J_0^{pp}(1-C^d)+H_d^2-\Omega_d\langle d^x\rangle J_0^{dd}C^d]+\{H_p^2H_d^2-H_p^2\Omega_d\langle d^x\rangle J_0^{dd}C^d-H_d^2\Omega_p\langle p^x\rangle J_0^{pp}(1-C^d)+C^d(1-C^d)\Omega_p\Omega_d\langle p^x\rangle\langle d^x\rangle[J_0^{pp}J_0^{dd}-(J_0^{pd})^2]\}=0. \quad (16)$$

For $\Omega_d\to 0$, the expressions for ω_1^2 and ω_2^2 become relatively simple. The frequency of the deuteronlike mode is given by

$$\omega_1^2=[J_0^{dd}\langle d^z\rangle C^d+J_0^{pd}\langle p^z\rangle(1-C^d)]^2\ , \quad (17a)$$

whereas the frequency of the protonlike mode becomes

$$\omega_2^2=[J_0^{pp}\langle p^z\rangle(1-C^d)+J_0^{pd}\langle d^z\rangle C^d]^2+\Omega_p[\Omega_p-\langle p^x\rangle J_0^{pp}(1-C^d)]\ . \quad (17b)$$

It should be noted that whereas the frequencies of the ω_1 and ω_2 modes should be for $T<T_c$—in contrast to the situation above T_c—relatively close to each other, the intensities should be rather different. The ω_2 mode becomes the normal protonic soft mode of the ferroelectric phase for $C_d\to 0$.

A discussion of these expressions is postponed until the interaction with the polar optic lattice mode is taken into account.

IV. COUPLED PROTON-DEUTERON-LATTICE MODES

For a discussion of the coupled proton-deuteron–lattice modes, we have to consider the full Hamiltonian as given by expression (1).

The equations of motion for spin fluctuations $\delta\langle\vec{S}_{i\alpha}\rangle$, which are obtained by eliminating $\delta\langle Q_q\rangle$, $\delta\langle P_q\rangle$ from the linearized random-phase-approximation (RPA) equations of motion for $\vec{S}_{i\alpha}$, Q_q, P_q are

$$-i\omega\delta\langle S_{i\alpha}^x\rangle=\sum_{j\beta}\tilde{J}_{ij}^{\alpha\beta}(0)C_j^\beta\langle S_{j\beta}^z\rangle\delta\langle S_{i\alpha}^y\rangle\ , \quad (18a)$$

$$-i\omega\delta\langle S_{i\alpha}^y\rangle=-\sum_{j\beta}\tilde{J}_{ij}^{\alpha\beta}(0)C_j^\beta\langle S_{j\beta}^z\rangle\delta\langle S_{i\alpha}^x\rangle+\sum_{j\beta}[\Omega_\beta C_j^\beta\delta_{i,j}\delta_{\alpha,\beta}-\tilde{J}_{ij}^{\alpha\beta}(\omega)C_j^\beta\langle S_{i\alpha}^x\rangle]\times\delta\langle S_{j\beta}^z\rangle-\langle S_{i\alpha}^x\rangle[\mu+F_k\rho_k/(\omega_k^2-\omega^2)]E_k e^{i\vec{k}\cdot\vec{R}_i}\ , \quad (18b)$$

$$-i\omega\delta\langle S^z_{i\alpha}\rangle = -\Omega_\alpha \delta\langle S^y_{i\alpha}\rangle \ , \tag{18c}$$

where the renormalized coupling constant $\tilde{J}^{\alpha\beta}_{ij}(\omega)$ is given by

$$\tilde{J}^{\alpha\beta}_{ij}(\omega) = J^{\alpha\beta}_{ij} + \sum_q \frac{|F_q|^2}{\omega_q^2 - \omega^2} e^{i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)}(1-\delta_{i,j}) . \tag{19}$$

The last result follows from a modified decoupling scheme for the mixed spin-lattice terms in the equations of motion for $d\langle S^x_{i\alpha}\rangle_t/dt$, $d\langle S^y_{i\alpha}\rangle_t/dt$, namely,

$$\tfrac{1}{2}\langle [Q_q, S^x_{i\alpha}]_+\rangle_t \sim \langle Q_q\rangle_t \langle S^x_{i\alpha}\rangle_t - \langle Q^{i\alpha}_q\rangle_t \langle S^x_{i\alpha}\rangle_t , \tag{20}$$

etc., where the first term is just the usual RPA, and $Q^{i\alpha}_q$ in the second term can be interpreted as the time-dependent projection of $Q_q(t)$ on the operator $S^z_{i\alpha}(t)$.[6] The average $\langle Q^{i\alpha}_q\rangle$ and the fluctuation $\delta\langle Q^{i\alpha}_q\rangle$ are found from the equations of motion for $\langle Q_q\rangle_t$ and $\langle P_q\rangle_t$. The only novel feature introduced by our scheme (20) is the factor $1-\delta_{i,j}$ in (19) which removes the unphysical self-interaction of the ith pseudospin.[7]

Within the same approximation as in Eq. (7) the averages $\langle S^{x,z}_{i\alpha}\rangle$ are site independent, and for $T \ll T_c$ they become

$$\langle S^x_\alpha\rangle = \tfrac{1}{2}\Omega_\alpha/H_\alpha \ , \quad \langle S^z_\alpha\rangle = \tfrac{1}{2}H_{\alpha z}/H_\alpha \ , \tag{21}$$

where by analogy with Eq. (6), $H_{\alpha z} = \sum_\beta \langle S^z_\beta\rangle C^\beta \tilde{J}^{\alpha\beta}_0$, and $\tilde{J}^{\alpha\beta}_0 = \sum_j \tilde{J}^{\alpha\beta}_{ij}(0)$.

In order to calculate the frequencies of collective modes at nonzero wave vectors q we multiply Eqs. (18) by C^α_i and average them with respect to all deuteron (or proton) configurations. Configurational averages of the type $\langle C^\alpha_i C^\beta_j \delta\langle \vec{S}_{j\beta}\rangle\rangle_{\rm av}$ are decoupled as $\sim \langle C^\alpha_i\rangle_{\rm av}\langle C^\beta_j \delta\langle \vec{S}_{j_\beta}\rangle\rangle_{\rm av}$, corresponding to the virtual crystal approximation. A better decoupling scheme based on the coherent potential approximation will be discussed in a future publication.[6]

There are again two sets of proton-deuteron collective modes with amplitudes $\delta\langle \vec{S}_{q\alpha}\rangle$, $\alpha = p$ or d, which are coupled by a term $\tilde{J}^{pd}_q(\omega)$ which is the Fourier transform of $\tilde{J}^{pd}_{ij}(\omega)$ from Eq. (18b). If this coupling were neglected, the eigenfrequencies would be given by a modified Kobayashi expression,[1,2]

$$\omega_\pm(q)^2 = \tfrac{1}{2}\{\omega_q^2 + \omega_\alpha^2 \pm [(\omega_q^2 - \omega_\alpha^2)^2 + 4\Omega_\alpha C^\alpha G_q \omega_q^2 \langle S^x_\alpha\rangle]^{1/2}\} , \tag{22}$$

where α means p or d, ω_α is the frequency of the α subsystem analogous to expressions (17),

$$\omega_\alpha^2 = (H_{\alpha z})^2 + \Omega_\alpha(\Omega_\alpha - C^\alpha \langle S^x_\alpha\rangle J^{\alpha\alpha}_q) \ , \tag{23}$$

and the coupling constant G_q follows from the Fourier transform of the second term in (19)

$$G_q = \left(N|F_q|^2 - \sum_{q'} |F_{q'}|^2\right)\Big/ \omega_0^2 \ . \tag{24}$$

We have made the assumption that the spectrum of the polar optic modes is totally flat, i.e., $\omega_q \approx \omega_0$, although $|F_q|^2$ may still be strongly q dependent. Thus G_q can be either positive or negative, depending on the actual shape of $|F_q|^2$, in sharp contrast to Kobayashi's result,[8] where $G_q > 0$ only due to the absence of the term $-\sum_{q'}|F_{q'}|^2$.

With $\tilde{J}^{pd}_q(\omega)$ restored the eigenfrequencies of the system may be obtained as the solutions of the equation

$$[\omega^2 - \omega_+^p(q)^2][\omega^2 - \omega_-^p(q)^2][\omega^2 - \omega_+^d(q)^2][\omega^2 - \omega_-^d(q)^2] - \Omega_p\Omega_d C^p C^d \tilde{J}^{pd}_q(\omega)^2 \langle p^x\rangle\langle d^x\rangle(\omega^2 - \omega_0^2)^2 = 0 \ . \tag{25}$$

Note that there are in general four coupled proton-deuteron–lattice modes, one pair for a ferroelectric motion of the proton-deuteron subsystem, and another for a ferrielectric motion. In each pair, one mode is latticelike and the other protonlike or deuteronlike.

The spectra of ω_q, ω_α, and $\omega^\alpha_\pm$ for $\alpha = p$ and $\alpha = d$ are shown schematically in Fig. 1 assuming a large maximum value of G_q ($G_q = 0$ at $q = q^*$) and $C^d \neq 0$.

From Eq. (18b) we observe that the amplitudes of the ω^p_- and ω^d_- modes will be roughly proportional to $C^p\langle p^x\rangle$ and $C^d\langle d^x\rangle$, respectively. Since $\langle d^x\rangle \propto \Omega_d$ from (21), the intensity of the deuteronlike mode is proportional to $\sim C^d\Omega_d^2$ and will be very small even in the fully deuterated crystal ($C^d = 1$) in view of $\Omega_d \ll \Omega_p$. For $\Omega_d \to 0$ the coupling between the

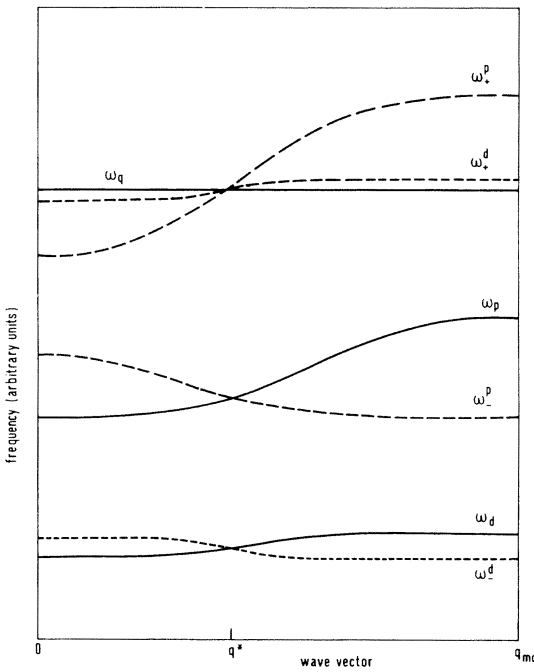

FIG. 1. Schematic spectra of coupled proton-deuteron–lattice modes. The mode ω^p_+ is ferroelectric latticelike, ω^d_- ferrielectric deuteronlike, etc.

proton-deuteron branches in Eq. (10) is negligible. Thus the eigenfrequencies are very nearly given by Eqs. (22) and (23) in analogy to the case of pure KH_2PO_4.[1,2] The observable modes with $q=0$ are the latticelike mode ω_+^p and the protonlike soft mode ω_-^p whose intensity scales as $\sim C^p\Omega_p^2$. This mode will therefore become weaker as the deuteration concentration increases and will disappear altogether in KD_2PO_4. The two branches become uncoupled in the limit $C^d \to 1$, hence $\omega_+^p = \omega_0$, while ω_-^p becomes

$$\omega_-^{p\,2} = (\tfrac{1}{2}\tilde{J}_0^{pd})^2 + \Omega_p^2 \,. \tag{26}$$

It may appear as a paradox that ω_-^p still contains Ω_p as $C^p \to 0$. Clearly, this result is only valid if there are at least a few protons left in the crystal, the point being that the last proton still tunnels with the same frequency Ω_p, which is concentration independent.

V. DISCUSSION

Let us now compare the results of the above theory with recent low-temperature experimental data of Peercy.[3,4] His results on the pressure dependence of Raman spectra of pure KH_2PO_4 and KD_2PO_4 may be summarized as follows: (a) The broad overdamped soft mode at $T > T_c$ in KH_2PO_4 becomes underdamped at high pressures. (b) The frequency of the underdamped mode decreases as $\omega^2 = A(T - T_c)$ if the pressure is smaller than a critical pressure P_c. (c) Above a critical pressure $P > P_c$ the frequency ω_- stays finite for all temperatures. (d) Below the transition temperature the soft mode becomes underdamped even at atmospheric pressure. (e) With increasing pressure below T_c the frequency of the soft mode ω_-—and of its coupled-lattice counterpart ω_+—decreases, whereas all other optic frequencies increase with pressure. This can be understood as the pressure lowers T_c, and increasing the pressure brings the system closer to the transition point. At the same time this pressure effect demonstrates the correctness of the assignment of ω_- as the soft mode below T_c. (f) The intensity of the soft mode vanishes on deuteration below T_c.

A number of important additional points has been provided by Peercy's work on mixed KH_2PO_4 systems: (i) The frequency of the underdamped soft mode below T_c *increases* with increasing deuteration, although its intensity, of course, is found to decrease. (ii) The pressure derivative of the soft-mode frequency continuously changes from negative to positive values with increasing concentration of deuterium. (iii) The frequency of the polar optic latticelike B_2 mode, which is known to couple strongly to the proton soft mode, continuously *increases* with increasing deuteration indicating that the proton-lattice coupling decreases and not increases the frequency of the latticelike mode. This can only happen if the coupling constant between the proton and the polar mode at $q=0$ is negative and not positive as assumed so far.

The theory presented in this paper explains all abovementioned results in a natural way. It is interesting to note in this connection that the coupled proton-deuteron model discussed in Sec. III already gives a correct qualitative description of the above results (a)–(f). However, a quantitative analysis of the low-temperature data on both pure and mixed systems is only possible within the framework of the coupled proton-deuteron–lattice model of Sec. IV.

To calculate the frequencies $\omega_\pm$ (we drop the superscript p from now on) as functions of the deuterium concentration C^d from (22) and (23) we use the values $\omega_0 \sim 233\ \mathrm{cm}^{-1}$ and $\Omega_p \sim 97.5\ \mathrm{cm}^{-1}$.[9,10] The remaining parameters $\tilde{J}_0^{pp}$, $\tilde{J}_0^{pd}$, and G_0 are found from the Raman spectra of pure KH_2PO_4 and from ω_- extrapolated to $C^d = 1$.[3] In particular, for $C^d = 0$ we have the relation

$$G_0 = -\tilde{J}_0^{pp}(\omega_0^2 - \omega_+^2)(\omega_0^2 - \omega_-^2)/(\Omega_p\omega_0)^2. \tag{27}$$

Since $\omega_0 > \omega_\pm$, it follows that $G_0 < 0$. We find $G_0 \cong -186\ \mathrm{cm}^{-1}$, $\tilde{J}_0^{pp} \cong 335\ \mathrm{cm}^{-1}$, and $\tilde{J}_0^{pd} \cong 254\ \mathrm{cm}^{-1}$. We realize that the effect of the proton-lattice coupling in KH_2PO_4 is to *decrease* the proton-proton interaction, a feature which cannot be explained by Kobayashi's treatment[8] of the same model.

The calculated frequencies are shown in Fig. 2.

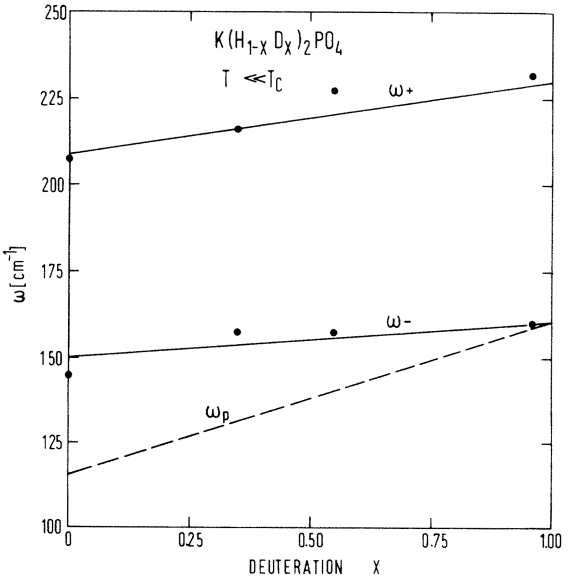

FIG. 2. Calculated concentration dependence of the frequencies of coupled proton-lattice modes in mixed $KH_2PO_4 - KD_2PO_4$. (Points: experimental data of Peercy.[4])

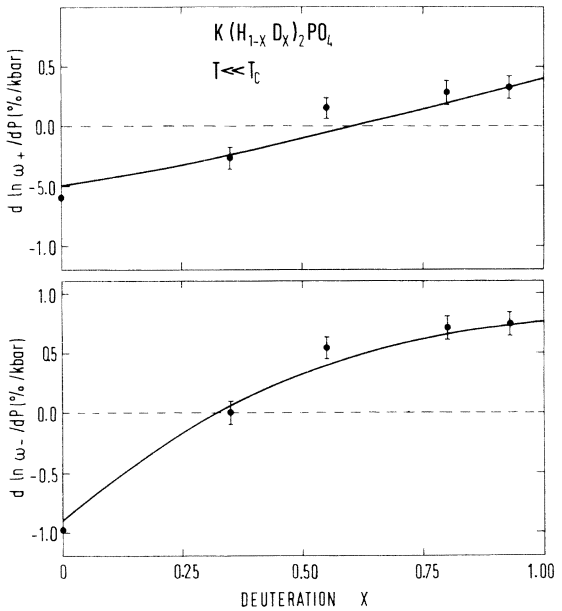

FIG. 3. Calculated pressure dependence of $\omega_{\pm}^{p}$ as function of deuteration X. (Points: experimental data of Peercy.[4])

Note the almost linear increase with deuterium concentration of $\omega_{\pm}$ and ω_p. The lattice polar mode frequency ω_0 has been determined from the limiting value of ω_+ for $C^d \to 1$ as explained earlier. Its value $\omega_0 \sim 233$ cm^{-1} is larger than believed so far.[11] The values of all other parameters should be regarded as rough estimates only in view of the small number of experimental points available.

An even more crucial test of the theory lies however in its ability to explain the peculiar behavior of the pressure derivatives of the coupled frequencies as functions of the deuterium concentration. From Eq. (22) with $\alpha = p$ we can calculate the logarithmic derivatives (always denoted by a prime on a given symbol) $\omega_{\pm}' \equiv (d\omega_{\pm}/dP)/\omega_{\pm}$ in terms of ω_0', Ω_p', $\tilde{J}_0^{pp'}$, $\tilde{J}_0^{pd'}$, and G_0'. We must assume that in general all these parameters are pressure dependent. The logarithmic derivative of the uncoupled lattice polar mode frequency ω_0' $\sim 0.4\%$ kbar^{-1} is obtained directly from the measured ω_+' at $C^d \to 1$. The positive sign and the magnitude of ω_0' are comparable to that observed for ionic crystals with large compressibility. From microscopic considerations[12] we know that $\tilde{J}_0^{pp'}$ ought to be negative, whereas $\Omega_p' > 0$ since the main effect of a hydrostatic pressure is to reduce the O-H- -O distance in the hydrogen bond. From the measured derivatives of ω_- in both limits $C^d = 0$ and $C^d \to 1$, and from Eqs (22), (23), and (26) it then follows

$$2\% \text{ kbar}^{-1} \leq \Omega_p' \leq 3.5\% \text{ kbar}^{-1}.$$

Using the value $\Omega_p' \sim 3\%$ kbar^{-1} we find $\tilde{J}_0^{pp'} \sim -0.18\%$ kbar^{-1}, $J_0^{pa'} \sim -0.55\%$ kbar, and from Eq. (27) finally $|G_0|' \sim 5.2\%$ kbar^{-1}, the last value being a rough estimate only. The pressure derivatives of $\omega_{\pm}$ for an arbitrary C^d are calculated from Eqs. (22), (23), and (21), and are plotted in Fig. 3 together with Peercy's data.[4] The agreement is reasonably good.

It should be stressed that the positive sign of ω_-' at $C^d \to 1$ is entirely due to the rather large positive derivative of Ω_p. This fact together with the above value of Ω_p, which agrees with the corresponding microscopic estimates,[12] provides a striking confirmation of the tunneling model of hydrogen-bonded ferroelectrics.[13]

In this connection the limitations of the above treatment should be as well mentioned: (i) The replacement of the true KH_2PO_4 Hamiltonian which includes four-body forces by a two-body forces Hamiltonian, i.e., by a spin-$\frac{1}{2}$ Ising model in a transverse field with one pseudospin per unit cell; (ii) the use of the random-phase approximation in the linearization of the equations of motion.

Both of these approximations have serious limitations and are expected to work quantitatively only at temperatures well below T_c, but not in the neighborhood of the transition temperature.[14,15] The point is that for temperatures near T_c four-particle correlations play a dominant role[14] and at the same time critical fluctuations may become large. For a quantitative analysis of the shape of the polarization curve or the deuterium concentration dependence of T_c a cluster approximation method like the one discussed in Refs. 5 and 15 should be used. Only at $T \ll T_c$, where our results are compared with Peercy's experiments, the above two approximations may be expected to give quantitatively correct results.

In conclusion we might reemphasize our original point, namely, that the study of mixed crystals does in fact provide a much better check on the various dynamical models of KH_2PO_4 order-disorder-type ferroelectrics than a study of isotopically pure systems, such as KH_2PO_4 or KD_2PO_4.

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