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# Variational treatment of the proton-phonon system in KDP<sup>a)</sup>

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Ferroelectric KDP is best described through an Ising Hamiltonian in a transverse field, coupled linearly to the phonon system. The soft optical mode is coupled to the order parameter, whereas the dependence of the transition temperature on deuteration follows from the coupling of the tunneling frequency to another optical branch. After unitary transformations of the Hamiltonian, in which parts of the phonon coupling are dealt with, an analytic upper bound for the free energy of the KDP system is found using Bogoliubov's inequality. This allows a choice from the class of different canonical transformations of that one leading to the lowest free energy bound. Then, in a mean field approximation, the effective coupling constant is found to be a solution of an implicit analytic function, which is solved numerically for different coupling strengths. In the ferroelectric region a strong temperature dependence of the effective coupling is found; crossing into the paraelectric region, its value changes smoothly for weak and abruptly for medium coupling strengths. These results parallel the behavior found in phonon coupled exciton systems.

## I. INTRODUCTION

KDP (KH<sub>2</sub>PO<sub>4</sub>) is one of the most extensively investigated ferroelectric substances; it is interesting not only for its physical properties but also because its good description by means of an Ising spin Hamiltonian in a transverse field makes it readily amenable to theoretical approaches (for a review see Blinc and Žekš<sup>1</sup>).

The pseudospin model originated from considering the displacements of the protons in the double-minimum potentials of their hydrogen bonds. The correlated motion of the other, heavier, ions is then introduced into the Hamiltonian by coupling the pseudospins (usually linearly) to the displacements of the heavy ions. The usual connection between the two subsystems is achieved by coupling the heavy ions to the order parameter<sup>2</sup>; while this picture describes adequately the "soft mode" character of the ferroelectric transition, it fails to explain the isotope dependence of the transition temperature<sup>3,4</sup> ( $T_{c,H} = 123$  K in KH<sub>2</sub>PO<sub>4</sub>,  $T_{c,D} = 223$  K in KD<sub>2</sub>PO<sub>4</sub>), unless one assumes a very large coupling constant.<sup>5</sup> However, by assuming the additional coupling of the pseudospin system (through the tunneling motion of the protons) to the length changes of the hydrogen bond, the isotope effect on  $T_c$  can be readily explained with moderate coupling strengths.<sup>6</sup>

These KDP Hamiltonians, with their two-level structure and their phonon-proton coupling, are akin to the Hamiltonians found in the study of the small polaron or exciton problems. Thus, departing from the perturbational approach,<sup>2</sup> recent works use canonical transformations to determine the renormalized pseudospin parameters.<sup>6-8</sup>

Recent advances in the theory of the exciton phonon coupling<sup>9-11</sup> show, however, that the complete removal of the linear coupling through a canonical transformation does not necessarily lead to a minimal free energy. The most appropriate canonical transformation is often

a complicated function of the Hamiltonian and of the temperature, to be determined through a variational procedure.

Therefore, we have felt it mandatory to reconsider the KDP problem. Thus, in Sec. II we rederive the Hamiltonian from the two-level problem, discuss its connection to the exciton Hamiltonian, and introduce the class of canonical transformations, to be considered in the variational procedure. Making use of the mean field approximation in Sec. III, we determine the Bogoliubov upper bound to the free energy of the Hamiltonian in closed form. This allows us to find in Sec. IV the optimal canonical transformation by means of its parameters, which is a solution to an implicit analytic equation. In Sec. V, we present numerical results pertaining to KDP. The conclusions of this work are then summarized in Sec. VI.

## II. HAMILTONIAN

Let us start by considering an assembly of two-level systems interacting with a phonon field. The system without the phonons will be described through the Hamiltonian

$$H_{2l} = \sum_n \sum_{\alpha=0,1} E^\alpha a_n^{\alpha+} a_n^\alpha + \frac{1}{2} \sum_{nm}' \sum_{\alpha\beta}' \sum_{\gamma\delta}' V_{nm} a_n^{\alpha+} a_n^\beta a_m^{\gamma+} a_m^\delta, \quad (1)$$

where the operators  $a_n^\alpha$  and  $a_n^{\alpha+}$  destroy and create an excitation  $\alpha$  at site  $n$ . Here  $E^\alpha$  is the energy of level  $\alpha$ , and  $V_{nm}$  represents the interaction between the sites  $m$  and  $n$ , which induces transfers between the levels, hence restricting the summation to  $m \neq n$ ,  $\alpha \neq \beta$ , and  $\gamma \neq \delta$ . Assuming, as usual, that each two-level system may be found in some state, i. e.,

$$a_n^{0+} a_n^0 + a_n^{1+} a_n^1 = 1, \quad (2)$$

the above Hamiltonian corresponds, after the transformation<sup>12</sup>

$$\begin{aligned} S_n^x &= \frac{1}{2} (a_n^{0+} a_n^0 - a_n^{1+} a_n^1), \\ S_n^y &= \frac{i}{2} (a_n^{0+} a_n^1 - a_n^{1+} a_n^0), \\ S_n^z &= \frac{1}{2} (a_n^{0+} a_n^1 + a_n^{1+} a_n^0), \end{aligned} \quad (3)$$

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to the Ising spin Hamiltonian in a transverse field:

$$H_{2I} = -2\Omega \sum_n S_n^x - \frac{1}{2} \sum_{nm}' J_{nm} S_n^z S_m^z, \quad (4)$$

where  $\Omega = (E^1 - E^0)/2$  and  $J_{nm} = -4V_{nm}$  and the constant  $N(E^0 + E^1)$  was omitted. Hamiltonian (4) was studied extensively in connection with the problems of phase transitions in ferroelectrics and Jahn-Teller systems.<sup>1,13</sup>

Hamiltonian (1) is also related to the exciton problem. Since the  $a_n, a_n^*$  obey the relation

$$a_n^{\alpha*} a_n^\beta a_n^{\gamma*} a_n^\delta = a_n^{\alpha*} a_n^\delta \delta_{\beta\gamma}, \quad (5)$$

defining  $A_n^* = a_n^{1*} a_n^0, A_n = a_n^{0*} a_n^1$ , (1) takes the form

$$H_{2I} = \sum_n (E^0 A_n A_n^* + E^1 A_n^* A_n) + \frac{1}{2} \sum_{nm}' V_{nm} (A_n^* + A_n) (A_m^* + A_m), \quad (6)$$

which corresponds to the exciton Hamiltonian,

$$H_{ex} = \sum_n E^{ex} A_n^* A_n + \frac{1}{2} \sum_{nm}' J_{nm}^{ex} A_n^* A_m, \quad (7)$$

if one neglects exciton nonconserving terms proportional to  $A_n^* A_m^*$  and  $A_n A_m$  and discards the constant  $NE^0$ .

Here, we set  $E^{ex} = E^1 - E^0, J_{nm}^{ex} = V_{nm} + V_{mn}$ .

The phonon system will be described through the Hamiltonian

$$H_{ph} = \sum_{qs} \omega_{qs} b_{qs}^* b_{qs}, \quad (8)$$

where  $b_{qs}^*$  and  $b_{qs}$  create and destroy a phonon of wave vector  $q$ , branch  $s$ , and frequency  $\omega_{qs}$ . Coupling now the localized two-level systems linearly with the phonon coordinate introduces an interaction term  $H_{int} = H_{int}^{(1)} + H_{int}^{(2)}$ ,

$$H_{int}^{(1)} = N^{-1/2} \sum_{\alpha n} \sum_{qs} \omega_{qs} G_{nqs}^\alpha a_n^{\alpha*} a_n^\alpha (b_{qs}^* + b_{-qs}), \quad (9)$$

$$H_{int}^{(2)} = N^{-1/2} \sum_{\alpha\beta} \sum_n \sum_{qs} F_{nqs}^{\alpha\beta} a_n^{\alpha*} a_n^\beta (b_{qs}^* + b_{-qs}). \quad (10)$$

In the pseudospin language, the  $H_{int}^{(1)}$  represents an  $S^x$  type,  $H_{int}^{(2)}$  an  $S^z$  type, of coupling. For KDP both coupling terms are important, the first for explaining the isotope dependence of the transition temperature,<sup>6,14</sup> and the second for the explanation of the soft-mode behavior.<sup>2,13</sup> In order for  $H_{int}^{(1)}$  and  $H_{int}^{(2)}$  to be translationally invariant,  $G_{nqs}^\alpha = e^{-iqR_n} G_{qs}^\alpha$  and  $F_{nqs}^{\alpha\beta} = e^{-iqR_n} F_{qs}^{\alpha\beta}$ . In the exciton problem the influence of the first term was studied perturbationally,<sup>15,16</sup> which was followed by an extensive variational treatment.<sup>9-11</sup> For simplicity, we will restrict our considerations in the following to  $H_{int}^{(1)}$  and to only one phonon branch; thus, we will drop the  $s$  index.

We transform now  $H$ ,

$$H = H_{2I} + H_{ph} + H_{int}^{(1)}, \quad (11)$$

through a unitary transformation given by  $\tilde{A} = e^{U_1} A e^{-U_1}$  with<sup>10,17</sup>

$$U_1 = N^{-1/2} \sum_{nq} \sum_{\alpha} X_{nq}^\alpha a_n^{\alpha*} a_n^\alpha (b_q^* - b_{-q}). \quad (12)$$

The values of  $X_{nq}^\alpha$  are not yet fixed, (except that  $X_{nq}^\alpha = e^{-iqR_n} X_q^\alpha$ ) but will be chosen to minimize the free energy; for  $X_{nq}^\alpha = G_{nq}^\alpha$  one recovers the results of Ref. 6. The transformed operators  $\tilde{a}$  and  $\tilde{b}$  are

$$\tilde{a}_n^{\alpha*} = a_n^{\alpha*} B_n^{\alpha*}$$

and

$$\tilde{b}_q^* = b_q^* - N^{-1/2} \sum_{n\alpha} X_{n-q}^\alpha a_n^{\alpha*} a_n^\alpha, \quad (13)$$

with

$$B_n^{\alpha*} = \exp\left(N^{-1/2} \sum_q X_{nq}^\alpha (b_q^* - b_{-q})\right). \quad (14)$$

We now transform the Hamiltonian according to (12) and make use of the equations (13) to express it in terms of the initial operators  $a_n^{\alpha*}$  and  $b_q^*$ , thus obtaining

$$\begin{aligned} \tilde{H} = & \sum_{n\alpha} \tilde{E}^\alpha a_n^{\alpha*} a_n^\alpha + \frac{1}{2} \sum_{nm}' \sum_{\alpha\beta} \sum_{\gamma\delta}' V_{nm} a_n^{\alpha*} a_n^\beta a_m^{\gamma*} a_m^\delta B_n^{\alpha*} B_n^\beta B_m^{\gamma*} B_m^\delta + \sum_q \omega_q b_q^* b_q \\ & - N^{-1/2} \sum_{n\alpha} \sum_q \omega_q (X_{nq}^\alpha - G_{nq}^\alpha) a_n^{\alpha*} a_n^\alpha (b_q^* + b_{-q}) + N^{-1} \sum_{nm}' \sum_{\alpha\beta} \sum_q \omega_q (X_{nq}^\alpha - 2G_{nq}^\alpha) X_{m-q}^\beta a_n^{\alpha*} a_n^\alpha a_m^{\beta*} a_m^\beta, \end{aligned} \quad (15)$$

with

$$\tilde{E}^\alpha = E^\alpha + N^{-1} \sum_q \omega_q |X_{nq}^\alpha|^2 - 2N^{-1} \sum_q \omega_q G_{nq}^\alpha X_{n-q}^\alpha.$$

In the pseudospin picture (3), the transformed Hamiltonian has the form

$$\begin{aligned} \tilde{H} = & -2\tilde{\Omega} \sum_n S_n^x - \frac{1}{8} \sum_{nm}' J_{nm} [(S_n^z - iS_n^y) B_n^{0*} B_n^1 + (S_n^z + iS_n^y) B_n^{1*} B_n^0] [(S_m^z - iS_m^y) B_m^{0*} B_m^1 + (S_m^z + iS_m^y) B_m^{1*} B_m^0] \\ & + \sum_q \omega_q b_q^* b_q + N^{-1/2} \sum_{nq} \omega_q (L_{nq} S_n^x + M_{nq}) (b_q^* + b_{-q}) + \sum_{nm} N_{nm} S_n^x S_m^x + \sum_n P S_n^z + C, \end{aligned} \quad (16)$$

where

$$\tilde{\Omega} = \Omega + \frac{N^{-1}}{2} \sum_q \omega_q (|X_{nq}^1|^2 - |X_{nq}^0|^2) - N^{-1} \sum_q \omega_q (G_{nq}^1 X_{n-q}^1 - G_{nq}^0 X_{n-q}^0), \quad (17a)$$

$$L_{nq} = G_{nq}^0 - G_{nq}^1 - X_{nq}^0 + X_{nq}^1, \tag{17b}$$

$$M_{nq} = (G_{nq}^0 + G_{nq}^1 - X_{nq}^0 - X_{nq}^1)/2, \tag{17c}$$

$$N_{nm} = N^{-1} \sum_{\alpha\beta} \sum_q \omega_q (-1)^{\alpha+\beta} (X_{nq}^\alpha - 2G_{nq}^\alpha) X_{m-q}^\alpha, \tag{17d}$$

$$P = N^{-1} \sum_{\alpha q} \omega_q (-1)^\alpha \left[ (X_{nq}^\alpha - G_{nq}^\alpha) \left( \sum_{m\beta} X_{m-q}^\beta \right) - X_{nq}^\alpha \left( \sum_{m\beta} G_{m-q}^\beta \right) \right], \tag{17e}$$

$$C = N(E_0 + E_1)/2 + \frac{N^{-1}}{2} \sum_{nq} \omega_q (|X_{nq}^0|^2 + |X_{nq}^1|^2) - N^{-1} \sum_{nq} \omega_q (G_{nq}^0 X_{n-q}^0 + G_{nq}^1 X_{n-q}^1) + \frac{N^{-1}}{4} \sum_{nm} \sum_{\alpha\beta} \sum_q \omega_q (X_{nq}^\alpha - 2G_{nq}^\alpha) X_{m-q}^\beta. \tag{17f}$$

Note that  $N_{nm}$  depends only on  $R_n - R_m$  due to the translational invariance of  $U_1$ . The Hamiltonian operator becomes simpler (and the reason for dividing it in the above way clearer) if we assume  $\omega_q = \omega_0$ , i. e., no dispersion of the optical phonon branch, and

$$X_{nq}^\alpha = X^\alpha e^{iqR_n}, \quad G_{nq}^\alpha = G^\alpha e^{iqR_n}, \tag{18}$$

where  $X^\alpha$  and  $G^\alpha$  are real valued. Then

$$\tilde{\Omega} = \Omega + \frac{\omega_0}{2} [(X^1)^2 - (X^0)^2 - 2G^1 X^1 + 2G^0 X^0], \tag{19a}$$

$$P = -N^{-1} \omega_0 \sum_{\alpha\beta} (-1)^\alpha \left[ (X^\alpha - G^\alpha) X^\beta \sum_{qm} \exp[iq(R_n - R_m)] - X^\alpha G^\beta \sum_{qm} \exp[iq(R_n - R_m)] \right] = 0, \tag{19b}$$

$$N_{nm} = N^{-1} \sum_{\alpha\beta} \omega_0 (-1)^{\alpha+\beta} (X^\alpha - 2G^\alpha) X^\beta \sum_q \exp[iq(R_n - R_m)] = \delta_{nm} \omega_0 \sum_{\alpha\beta} (-1)^{\alpha+\beta} (X^\alpha - 2G^\alpha) X^\beta, \tag{19c}$$

$$C = N(E_0 + E_1)/2 + \frac{N\omega_0}{2} [(X^1)^2 + (X^0)^2 - 2X^1 G^1 - 2X^0 G^0]. \tag{19d}$$

III. UPPER BOUND ON THE FREE ENERGY

Gibbs-Bogoliubov's theorem states that for  $H = H_0 + V$  the following inequality holds<sup>18,19</sup>:

$$-\beta^{-1} \ln \text{Tr} e^{-\beta H} \leq -\beta^{-1} \ln \text{Tr} e^{-\beta H_0} + \text{Tr}(e^{-\beta H_0} V) / \text{Tr}(e^{-\beta H_0}) \tag{20}$$

if the traces over  $e^{-\beta H_0}$  and  $e^{-\beta H}$  are finite for  $\beta > 0$ . We may now apply this inequality to our problem. We choose as unperturbed Hamiltonian

$$H_0 = -2\tilde{\Omega} \sum_n S_n^x - \tilde{J} \langle S^x \rangle \sum_n S_n^x + C + \sum_q \omega_q b_q^+ b_q; \tag{21}$$

$V$  is then given by

$$V = -\frac{1}{8} \sum_{nm} J_{nm} [(S_n^x - iS_n^y) B_n^{0+} B_n^1 + (S_n^x + iS_n^y) B_n^{1+} B_n^0] \times [(S_m^x - iS_m^y) B_m^{0+} B_m^1 + (S_m^x + iS_m^y) B_m^{1+} B_m^0] + \tilde{J} \langle S^x \rangle \sum_n S_n^x + N^{-1/2} \sum_{nq} \omega_q (L_{nq} S_n^x + M_{nq}) (b_q^+ + b_{-q}). \tag{22}$$

The last expression was simplified by assuming that the relations (18) hold.

The spin dependent part of (21) is the mean field Ising spin Hamiltonian, with  $\langle S^x \rangle$  and  $\tilde{J}$  to be determined from

$$\langle S^x \rangle = \langle S^x \rangle_0 = \text{Tr}(e^{-\beta H_0} S^x) / \text{Tr}(e^{-\beta H_0}) \tag{23}$$

and

$$\tilde{J} = \frac{1}{4} \sum_{nm} J_{nm} \langle (B_n^{0+} B_n^1 + B_n^{1+} B_n^0) (B_m^{0+} B_m^1 + B_m^{1+} B_m^0) \rangle_0. \tag{24}$$

Generally, the mean field approach is a very good approximation for three-dimensional uniaxial ferroelectrics like KDP.<sup>1,20</sup>

To evaluate  $\langle S^x \rangle$  one performs the rotation of the pseudospin system:

$$\sigma_n^x = \cos\theta S_n^x - \sin\theta S_n^z, \tag{25}$$

$$\sigma_n^z = \sin\theta S_n^x + \cos\theta S_n^z,$$

where  $\sin\theta = 2\tilde{\Omega}/\gamma$ ,  $\cos\theta = \tilde{J} \langle S^x \rangle / \gamma$ , and  $\gamma^2 = (2\tilde{\Omega})^2 + (\tilde{J} \langle S^x \rangle)^2$  were set. From

$$H_0 = -\gamma \sum_n \sigma_n^z + \sum_q \omega_q b_q^+ b_q + C \tag{26}$$

then follow  $\langle S^x \rangle$

$$\langle S^x \rangle = (\frac{1}{2} \cos\theta) \tanh(\beta\gamma/2) = (\tilde{J} \langle S^x \rangle / 2\gamma) \tanh(\beta\gamma/2), \tag{27}$$

and the mean field transition temperature

$$\tanh(\beta_c \tilde{\Omega}) = 4\tilde{\Omega} / \tilde{J}, \tag{28}$$

We now compute  $\tilde{J}$ ; for this we calculate  $\langle B_n^{\alpha+} B_n^\beta B_m^{\gamma+} B_m^\delta \rangle_0$  using Bloch's theorem:

$$\langle B_n^{\alpha+} B_n^\beta B_m^{\gamma+} B_m^\delta \rangle_0 = \left\langle \exp \left( N^{-1/2} \sum_q (X_{nq}^\alpha - X_{nq}^\beta + X_{mq}^\gamma - X_{mq}^\delta) (b_q^+ - b_{-q}) \right) \right\rangle = \exp \left[ -\frac{N^{-1}}{2} \left( \sum_q |X^\alpha - X^\beta + X^\gamma - X^\delta|^2 \right) \coth \left( \frac{\beta\omega_0}{2} \right) \right]. \tag{29}$$

Observing that  $\alpha \neq \beta$ ,  $\gamma \neq \delta$ , a term  $(X^0 - X^1)^2$  factors readily from the sum over  $q$ . Moreover,  $n \neq m$ ; thus

$$\sum_q |1 \pm \exp[iq(R_n - R_m)]|^2 = 2N$$

holds, and Eq. (29) may be further simplified:

$$\langle B_n^{\alpha+} B_n^\beta B_m^{\gamma+} B_m^\delta \rangle_0 = \exp[-(X^0 - X^1)^2 \coth(\beta\omega_0/2)] \tag{30}$$

independent of  $n - m$ . Thus, one obtains for  $\bar{J}$

$$\bar{J} = J \exp[-(X^0 - X^1)^2 \coth(\beta\omega_0/2)] \quad (31)$$

We now proceed to evaluate  $\langle V \rangle_0$ . In the sum (22) the last term vanishes, since  $\langle b_q^+ + b_{-q} \rangle_0 = 0$ . Using (30),  $\langle V \rangle_0$  is

$$\langle V \rangle_0 = N \bar{J} \langle S^z \rangle^2 - \frac{1}{2} \sum_{nm}' J_{nm} \langle S_n^z S_m^z \rangle_0 \langle B_n^{0+} B_n^1 B_m^{0+} B_m^1 \rangle_0 \quad (32)$$

Making again use of the mean field approximation, one obtains for  $\langle V \rangle_0$

$$\langle V \rangle_0 = \frac{1}{2} N \bar{J} \langle S^z \rangle^2, \quad (32')$$

and for the upper bound on the free energy, using (26),

$$-\beta^{-1} \ln \text{Tr} e^{-\beta H_0} + \langle V \rangle_0 = -\beta^{-1} N \ln \left( 2 \cosh \frac{\beta \gamma}{2} \right) - \beta^{-1} \ln q_{ph} + C + \frac{1}{2} N \bar{J} \langle S^z \rangle^2, \quad (33)$$

with

$$q_{ph} = \prod_q (1 - e^{-\beta\omega_q})^{-1} e^{-\beta\omega_q/2} = [(1 - e^{-\beta\omega_0})^{-1} e^{-\beta\omega_0/2}]^N \quad (34)$$

#### IV. DETERMINATION OF THE OPTIMAL CANONICAL TRANSFORMATION

In this section we will determine the transformation constants  $X_{nq}^\alpha$ , which minimize the free energy (33). Consider its  $X_{nq}^\alpha$  dependent part:

$$Q = -\beta^{-1} N \ln \cosh(\beta\gamma/2) + \frac{1}{8} N \bar{J} \cos^2 \theta \tanh^2(\beta\gamma/2) + C = -\beta^{-1} N \ln \cosh \left[ \frac{(2\bar{\Omega})^2 + (\bar{J}R \cos \theta)^2}{2} \beta/2 \right] + \frac{N}{2} \bar{J} R^2 \cos^2 \theta + C, \quad (35)$$

where we introduced

$$R = \frac{1}{2} \tanh \frac{1}{2} \beta\gamma \quad (36)$$

and observe that<sup>21</sup>

$$\left. \frac{\partial Q}{\partial R} \right|_{\bar{J}, \bar{\Omega}, \theta} = 0 \quad \text{and} \quad \left. \frac{\partial Q}{\partial \theta} \right|_{\bar{J}, \bar{\Omega}, R} = 0, \quad (37a)$$

and

$$\frac{\partial Q}{\partial \bar{J}} = -\frac{N}{2} R^2 \cos^2 \theta, \quad \frac{\partial Q}{\partial \bar{\Omega}} = -2NR \sin \theta. \quad (37b)$$

In the ordered phase the order parameter  $\langle S^z \rangle = R \cos \theta$  is nonzero. From (26) and (27),

$$(2\bar{\Omega})^2 + (\bar{J}R \cos \theta)^2 = \gamma^2 = (\bar{J}R)^2 \quad (38)$$

holds, which determines the limit of the ordered phase to

$$(2\bar{\Omega})^2 < (\bar{J}R)^2. \quad (39)$$

Consider first the less interesting disordered phase. From the relations

$$\frac{\partial C}{\partial X^0} = N\omega_0(X^0 - G^0), \quad \frac{\partial C}{\partial X^1} = N\omega_0(X^1 - G^1), \quad (40a)$$

$$\frac{\partial \bar{\Omega}}{\partial X^0} = \omega_0(G^0 - X^0), \quad \frac{\partial \bar{\Omega}}{\partial X^1} = \omega_0(X^1 - G^1), \quad (40b)$$

$$\frac{\partial \bar{J}}{\partial X^0} = 2\bar{J}(X^1 - X^0) \coth(\beta\omega_0/2) = -\frac{\partial \bar{J}}{\partial X^1}, \quad (40c)$$

and the corresponding  $Q$ :

$$Q^{dis} = -\beta^{-1} N \ln \cosh(\beta\bar{\Omega}) + C, \quad (41)$$

one finds that  $Q^{dis}$  is minimal for  $G^0 = X^0$  and  $G^1 = X^1$ :

$$\frac{\partial Q^{dis}}{\partial X^0} = N\omega_0(X^0 - G^0)[1 + \tanh(\beta\bar{\Omega})], \quad \frac{\partial Q^{dis}}{\partial X^1} = N\omega_0(X^1 - G^1)[1 - \tanh(\beta\bar{\Omega})], \quad (42)$$

and, for  $X^0 = G^0$ ,  $X^1 = G^1$ ,

$$\frac{\partial^2 Q^{dis}}{(\partial X^0)^2} = N\omega_0[1 + \tanh(\beta\bar{\Omega})] > 0, \quad \frac{\partial^2 Q^{dis}}{(\partial X^1)^2} = N\omega_0[1 - \tanh(\beta\bar{\Omega})] > 0, \quad (43)$$

and

$$\frac{\partial^2 Q^{dis}}{\partial X^0 \partial X^1} = 0.$$

In the ordered phase  $Q^{or}$  may be put in the form

$$\frac{\beta Q^{or}}{N} = -\ln \cosh(2\bar{J}R) + 2\bar{J}R^2 - (2\bar{J})^{-1} [\bar{\Omega} + \bar{\omega}_0(g - y)(G - X)]^2 + \bar{\omega}_0 \left[ \frac{1}{2}(X^2 + y^2) - GX - gy \right] \quad (44)$$

by defining

$$y = X^1 - X^0, \quad g = G^1 - G^0, \quad X = X^1 + X^0, \quad G = G^1 + G^0, \quad (45)$$

and

$$\bar{\omega}_0 = \beta\omega_0/2, \quad \bar{J} = \beta\bar{J}/4, \quad \bar{\Omega} = \beta\bar{\Omega} - \bar{\omega}_0 g G \quad (46)$$

thus,

$$\bar{J} = \frac{1}{4} \beta J \exp(-y^2 \coth \bar{\omega}_0), \quad (47a)$$

$$\bar{\Omega} = \beta\bar{\Omega} - \bar{\omega}_0(g - y)(G - X). \quad (47b)$$

The advantage of Form (44) is seen readily, by calculating the conditions for extremal behavior.  $\partial Q^{or}/\partial X = \partial Q^{or}/\partial y = 0$ ; it turns out that one can express them in terms of  $y$  alone. Moreover,  $\bar{\Omega}$  and  $G$  appear only in the form of  $\bar{\Omega} = \beta\bar{\Omega} - \bar{\omega}_0 g G$ , thus reducing the number of parameters of the problem:

$$\frac{\beta}{N} \frac{\partial Q^{or}}{\partial X} = \bar{\omega}_0(g - y) \bar{J}^{-1} [\bar{\Omega} + \bar{\omega}_0(g - y)(G - X)] - \bar{\omega}_0(G - X), \quad (48)$$

$$\frac{\beta}{N} \frac{\partial Q^{or}}{\partial y} = \bar{\omega}_0(G - X) \bar{J}^{-1} [\bar{\Omega} + \bar{\omega}_0(g - y)(G - X)] - \bar{\omega}_0(g - y) - y \bar{J}^{-1} \coth \bar{\omega}_0 [\bar{\Omega} + \bar{\omega}_0(g - y)(G - X)]^2 + 4R^2 \bar{J} y \coth \bar{\omega}_0, \quad (49)$$

where we used

$$\frac{\partial}{\partial y} (2\bar{J}R^2 - \ln \cosh 2\bar{J}R) = -2R^2 \frac{\partial \bar{J}}{\partial y}, \quad (50)$$

which follows by differentiating  $2R = \tanh 2R\bar{J}$  with respect to  $y$ ; the last relation being the form that Eq. (36) takes in the ordered phase. We now obtain readily an

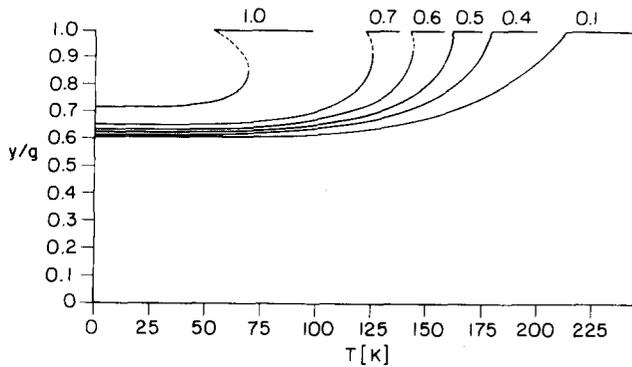


FIG. 1. Temperature dependence of the relative effective coupling strength  $y/g$  for  $g=0.1, 0.4, 0.5, 0.6, 0.7,$  and  $1$  with KDP parameters. The full lines correspond to minima in the free energy.

implicit equation for  $y$ , which corresponds to the extremal values of the free energy. Equating first  $\partial Q^{\text{or}}/\partial X$  to zero, we obtain  $X$  as a function of  $y$ :

$$X = G - \bar{\Omega}(g-y)/[\bar{J} - \bar{\omega}_0(g-y)^2]. \quad (51)$$

Setting now  $\partial Q^{\text{or}}/\partial y$  equal to zero leads to the implicit equation of  $y$ :

$$\begin{aligned} \bar{\omega}_0(g-y) \{ [\bar{J} - \bar{\omega}_0(g-y)^2] - \bar{\Omega}^2 \} \\ = \bar{J}y \coth \bar{\omega}_0 \{ 4R^2 [\bar{J} - \bar{\omega}_0(g-y)^2] - \bar{\Omega}^2 \}, \end{aligned} \quad (52)$$

where we have multiplied both sides of (49) by  $[\bar{J} - \bar{\omega}_0(g-y)^2]$ . The roots of (52) lead to the minima, maxima, and saddle points of (44). In the numerical applications of next section we found it simpler to decide by inspection for which values of  $y$   $Q^{\text{or}}$  is minimal rather than to consider the second derivatives of (44).

One should observe that the condition (39) for the ordered phase corresponds to

$$\bar{\Omega}^2 < 4R^2 [\bar{J} - \bar{\omega}_0(g-y)^2]^2, \quad (53)$$

as may be readily evaluated from (47b) and (51). *A fortiori* thus

$$\bar{\Omega}^2 < [\bar{J} - \bar{\omega}_0(g-y)^2]^2. \quad (54)$$

From (52) then follows that  $y$  has a physical meaning only if it lies between 0 and  $g$ . In the ordered phase  $y$  is smaller than  $g$ ; thus  $X^0 \neq G^0$  and  $X^1 \neq G^1$ .

We now turn to applications.

## V. NUMERICAL RESULTS

In this section we will discuss mainly Eq. (52), which expresses the dependence of  $y$  on the parameters of the problem.

Let us start by considering two extremal cases. For  $T=0$ , supposing that  $T_c$  exists and  $T_c \neq 0$ , one readily obtains

$$\coth \bar{\omega}_0 = 1 \quad \text{and} \quad R = 1/2,$$

thus,

$$y\bar{J}e^{-y^2} = 2\omega_0(g-y) \quad (55)$$

or

$$g = y [1 + (Je^{-y^2})/(2\omega_0)]. \quad (55')$$

Again, one sees that, since  $Je^{-y^2}/(2\omega_0)$  is positive,  $y$  is smaller than  $g$ . A similar behavior was found in the study of the exciton phonon coupling,<sup>8</sup> where the effective coupling constant  $x$  was found to be smaller than the coupling constant  $g$  in the Hamiltonian. In both cases, at  $T=0$ , the quotient  $y/g$  ( $x/g$  in Ref. 8) depends on the magnitude of the renormalized interaction between sites  $Je^{-y^2}$ , with respect to the frequency  $\omega_0$  of the optical mode. Larger values of  $\omega_0$  lead to a smaller departure of  $y$  from  $g$ .

Another special case occurs when  $\bar{\Omega}=0$ . This might be a good example for DKDP (deuterated KDP) since then the effective tunneling frequency is much lower than in KDP.<sup>22</sup> Then (52) takes the form

$$\bar{\omega}_0(g-y) = 4\bar{J}R^2y \coth \bar{\omega}_0 \quad (56)$$

or

$$g = y [1 + 4\bar{J}R^2 \coth(\bar{\omega}_0)/\bar{\omega}_0]. \quad (56')$$

In the case of DKDP ( $T_{c,D}=223$  K) for which  $1 < \coth \bar{\omega}_0 < 1.1$  holds in the whole ferroelectric range, the main temperature dependence of  $y/g$  is introduced by  $R$ .

Form (56') is similar to (55'). In order to have a more realistic example we now consider the case that  $\bar{\Omega}$  is nonzero. We choose the values that according to Ref. 6 correspond to KDP ( $J=620$  cm<sup>-1</sup>,  $\omega_0=470$  cm<sup>-1</sup>,  $\beta\bar{\Omega}=50$  cm<sup>-1</sup>) and vary the coupling strength  $g$ . The results are summarized in Fig. 1, where we have plotted  $y/g$  as a function of temperature.

For all coupling strengths the curve intersects the line  $y/g=1$  that corresponds to the disordered phase at the transition temperature given by Eq. (28). One verifies readily also that for  $y/g=1$  and  $T=T_c$  the free energies of the disordered and of the ordered phases are equal.

For small coupling strengths the dependence of  $y/g$  on  $T$ , as follows from (52), is given by a monotonic function of the temperature, which connects continuously the  $T=0$  value given by Eq. (55) with the  $y=g$  value at  $T=T_c$ . All values of  $y$  so obtained correspond to minima in the free energy, as may be seen by evaluating  $Q^{\text{or}}$  (44) around the extremal value ( $y_e, X_e$ ), where  $X_e$  is given by (51).

For large coupling strengths ( $g \approx 1$ ) the solution of (52) in the range  $0 < y < g$  is for some temperatures double valued. Again, one verifies directly that only the lower branch corresponds to a minimum in the free energy and that the upper branch is not an extremum. However, the minimum is very shallow around  $T_c$  and the difference in the free energies corresponding to different values of  $y$  for fixed  $T$  around  $T_c$  is small; to the marked change in  $y$  in going from the ordered ( $<g$ ) to the disordered ( $=g$ ) phase, there is no corresponding large change in  $Q$ . The free energies for the ordered (lower branch) and disordered state are exactly equal for a value of  $T$  which lies in the instability region of the upper branch. The change in  $y$  is discontinuous.

The transition from a single to a double valued behavior occurs for our choice of parameters for a value of  $g$  of about 0.6. As may be seen from Fig. 1, if we wanted, as in Ref. 6, to explain the value of  $T_{c,H} = 123$  K purely on the grounds of the  $S^*$  coupling, we would need a coupling strength of about 0.7. We thus expect the thermal hysteresis to be small. Of course the qualitative behavior of our model is incorrect in that it predicts a more abrupt change in the properties of KDP than in those of DKDP while approaching the critical temperature, whereas experimentally the transition is found to have a more distinct first-order character in DKDP than in KDP. This behavior is due to couplings to the other modes, which become important as the transition temperature is approached.

## VI. CONCLUSIONS

This work is an attempt to understand the temperature dependence of the effective phonon-proton and proton-proton coupling in the KDP system. The KDP Hamiltonian has two kinds of interaction terms: one representing the coupling between the pseudospins on different sites [see Eq. (4)], while the other describes the coupling between each pseudospin and the rest of the lattice [Eq. (9)].

For very small coupling between the protons ( $J \approx 0$ ) each pseudospin follows the lattice coupling fully. On the other hand, if the coupling constants to the lattice ( $G_q^0$  and  $G_q^1$ ) are zero, the energy is minimized by allowing the pseudospins to be in the ground state of the Ising Hamiltonian (4), so that the motion of pseudospins on different sites is correlated; it is this interaction that leads to the ordering of the system. In the case that neither  $J$  nor  $G_q^0$  and  $G_q^1$  are zero, the coupling to the lattice vibrations hinders the ordering of the pseudospin subsystem; this is evident from the lowering of the transition temperature. So that for a given set of parameters the interplay between these competing tendencies is temperature dependent. For small temperatures, where the disrupting effect of the lattice vibrations is smaller, the effective phonon-pseudospin coupling ( $X_q^0, X_q^1$ ) is smaller than at high temperatures; the equilibrium position of the pseudospins changes with temperature.

In dealing with the coupled proton-phonon system we find it helpful to use the Bogoliubov inequality for the free energy. Minimizing the obtained value, we were able to determine the coupling parameters that lead to an optimal canonical transformation. As a result, if we consider  $J \neq 0$ , starting with  $G_q^0 = G_q^1 = 0$ , and gradual-

ly increasing the values of the latter, we find that the effective phonon-pseudospin coupling is smaller than the value of this coupling for  $J=0$ . Similarly, as  $T$  increases, this effective coupling changes, as does the effective  $J$ . Thus the temperature dependence of the free energy is complicated by the intertwining of the temperature dependence of  $J$  and of the effective coupling. Figure 1 shows how, for the KDP system, the relative effective coupling ( $y = X^1 - X^0$ ) depends on the temperature for various values of the bare coupling ( $g = G^1 - G^0$ ). This clearly shows that the effective coupling is weakly dependent on  $T$  until close to the transition temperature, when it becomes strongly temperature dependent. As  $T$  approaches the phase transition temperature, the coupling to the lattice vibrations increases, until at  $T_c$ ,  $y = g$  (see Fig. 1).  $T_c$  itself, the transition temperature of the phonon-proton system, turns out to be highly dependent on the coupling of the proton system to an optical mode of the rest of the lattice, a mode that causes distortions in the length of the hydrogen bond. Invoking this type of coupling then allows a simple explanation of the isotope dependence of the transition temperature in KDP.

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