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Green's-function theory of phase transitions in hydrogen-bonded ferroelectric crystals with pseudo-spin-lattice coupled mode model

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In this paper the recent Green's-function theory of Ramkrishnan and Tanaka for studying ferroelectric phase transitions in potassium dihydrogen phosphate (KDP)-type crystals using pseudo-spin-lattice coupled mode (PLCM) model has been extended to include the effect of phonon anharmonicity and to compare the calculated results with the recent experimental data. The renormalized proton-phonon energy spectrum, Curie-Weiss constant (C), Curie temperature (T_C), and the logarithmic behavior of specific heat (C_v) calculated from the internal energy have been studied with this extended PLCM model. Our theory in particular is able to explain, along with other physical properties, the large shift of the Curie temperature in all the KDP-type crystals on deuteration compared to the small change of the Curie-Weiss constant. The latter has not been possible using the cluster satistical treatment taking into account the excited Slater-Takagi (ST) energy levels. It is also observed that, except for the specific heat, the calculated quantities (such as electrical susceptibility and Curie-Weiss constant) depend on the tunneling energy explicitly. A very good agreement between our theoretical results and those of recent experimental data indicates the suitability of the Green-function technique and the Tyablikov-type decoupling scheme for studying phase transitions in the KDP family. We have also shown that our present theory leads to a pseudo-Jahn-Teller-like mechanism in the KDP system and shows close resemblance between the topologies of the order disorder and displacive type of phase transition. It therefore indicates the possibility of a unified theory of phase transition in ferroelectric crystals. Finally the Blinc-de Gennes parameters calculated for different KDP salts have also been compared with the experimental results available.

I. INTRODUCTION

After the pioneering work of Slater[1] and Takagi[2] (hereafter referred to as ST), many attempts have been made to study the phase transitions in (potassium dihydrogen phosphate) KDP (KH_2PO_4)-type crystals using a modified ST model such as the transverse Ising model[3] (or pseudospin model) with defining Hamiltonian

$$H_P=-2\Omega\sum_i S_i^x-\tfrac{1}{2}\sum_{ij}J_{ij}S_i^zS_j^z\ , \qquad (1)$$

where Ω is the tunneling frequency, $S^\alpha(\alpha=x,y,z)$ is the αth component of the pseudo-spin variable $\vec{S}$, and i and j run over proton configurations. J_{ij} represent the exchange interactions between the pseudospins. Except for the Raman spectroscopic data, the model (1) has been found to explain much of the ferroelectric behavior of KDP and its isomorphs, particularly the isotope effect, which was not possible with the original (nontunneling) ST model. Though the ST model has another drawback in that it does not take into account the shifts of the ions K^+, O^{2-}, and P^{5+} from their equilibrium positions[4] at the transition point, the model (1) and any other suitable microscopic model must contain the ST energy parameters ($U=J_{12}=J_{34}=-2\omega+2\epsilon$, $V=J_{24}=J_{23}=J_{14}=J_{13}=2\omega-\epsilon$, and $\omega_1=4\omega=2\epsilon$).[3,5] The separations between the two highest excited levels and the lower levels are so large[5-8] that we may put $\omega_1=\infty$ and $\omega>>\epsilon=k_BT_C\ln2$, but since the lowest of these levels in most of the KDP series has an energy lower than or of the order of k_BT_C, they must play an important role in any physical description of the KDP dynamics. It has also been observed that for the more realistic model of Silsbee *et al.*[6] (SUS) including the ST short-range four-particle interaction forces, long-range two-body forces, and tunneling term, the static properties of such a system investigated with the help of a cluster expansion gives qualitative agreement[7,9] between the calculated and the experimental dielectric properties. Vaks *et al.*[9] (VZS) used the model of Blinc and Svetina[7] (BS) and explained most of the physical properties of the KDP system but failed to explain the differences between the Curie and the Curie-Weiss temperatures.

Further extension of the pseudospin model (1) was made by Kobayashi,[10] who allowed for only one proton per unit cell [thereby interpreting i and j of Eq. (1) as Bravais-lattice sites] but considered the interaction of the proton mode with the optic vibrations of the $K-PO_4$ system, writing

$$H=H_p+H_{pl}\ , \qquad (2)$$

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where

$$H_{pl}=\frac{1}{2}\sum_{\vec{q}}(P_{\vec{q}}P_{-\vec{q}}+\omega_{\vec{q}}^{2}Q_{\vec{q}}Q_{-\vec{q}})+\sum_{i\vec{q}}V_{i\vec{q}}S_i^zQ_{\vec{q}} \ .$$

[In Eqs. (2) and (3a), shown below, i and j run over the Bravais-lattice sites.] $Q_{\vec{q}}$ and $P_{\vec{q}}$ are, respectively, the normal coordinates and the conjugate momenta, $\omega_{\vec{q}}^2$ is the bare harmonic frequency, and $V_{i\vec{q}}$ represents the linear pseudospin phonon-coupling constant. This model (2) explains very well the Raman spectroscopic data,[11–15] along with other characteristic features of ferroelectric phase transitions in the KDP family but neglects some details of intracell proton dynamics. With this model one can not explain simultaneously the large shifts of the Curie temperatures (T_C) corresponding to the small shifts of the Curie-Weiss constants (C) on deuteration of the KDP samples. The model used by VZS and others[16] also suffers from this drawback. It might be concluded from their[10,16,17] calculated results that the isotope effect on T_C is contributed mainly from the decrease in proton-tunneling energy, while the isotope effect on C results from the proton-lattice coupling term. Using a Kobayashi-type model, Houston and Bolton[16] (HB) showed that the Curie constant and specific heat should contain the tunneling factor. But the Green-function theory of Pak[17] showed, on the other hand, that the electrical susceptibility (χ) and specific heat (C_v) do not contain the tunneling frequency explicitly. Pak's theory, using Kobayashi's model, is also unable to explain the above-mentioned large shift of T_C compared to C on deuteration.

In the present paper we have taken into account the higher-order anharmonic phonon-interaction terms in addition to Kobayashi's model (2) which have not been considered either by BS or VZS in their calculations. With this extended model we have succeeded in finding the exact isotope dependences of C, C_v, and χ. From our more elaborate calculations we may also conclude that the approximation made by Pak[10] to calculate χ and C are not appropriate for the KDP-type crystals. Though our method of using Green's functions is parallel to that of Pak, the expressions for all the Green functions (as well as the energy spectrum) obtained by us, are not the same as those derived by Pak since our expressions are modified by the contribution from the anharmonic interaction term. However, the relative success of the two approaches (one using the cluster-statistical treatment by SUS, BS, and VZS and the other approach considering the higher-order interaction terms treated in this paper) indicates the validity of both approaches. But we should emphasize the basic difference between the cluster theories (which account for fundamental intracell proton correlations, but neglect all dispersion phenomena) and lowest-order Kobayashi theories like the present one, which neglect intracell proton correlations to some extent but do include wave-vector dispersion.

Finally, for the sake of completeness, we should mention the recent Green's-function theory of Ramkrishnan and Tanaka[18] (RT). They showed the superiority of the Green-function method for the KDP system over the usual mean-field and linearized Bloch equations-of-motion methods. RT did not consider the anharmonic term in their Hamiltonian and also did not calculate the model parameters from exact fitting of the various experimental results.

In Sec. II the Green-function method has been discussed and the thermal averages of the pseudospin operators are calculated with pure tunneling model H_p in Eq. (3a) for comparison with the results of other authors. In Sec. III expressions for correlation functions, internal energy, electrical susceptibility, Curie constant, and specific heat have been derived with the use of the total Hamiltonian (3a). In Sec IV we present some of the theoretical results calculated for different members of the KDP family. Blinc-de Gennes (BG) parameters which are very important for the interpretations of the various physical properties, and the anharmonicity parameters have also been calculated for all the KDP salts and compared with the recent experimental results available. Finally, Sec. V ends with a conclusion.

II. GREEN'S-FUNCTION METHOD AND THE SOLUTION

The total Hamiltonian in the pseudo-spin-lattice coupled mode model containing quartic anharmonic term as discussed in Sec. I can be written[19,20]

$$H=H_p+H_{pl}+H_A \ , \tag{3a}$$

where

$$H_A=\sum_{q_1,q_2,q_3,q_4}A(q_1,q_2,q_3,q_4)Q_{q_1}Q_{q_2}Q_{q_3}Q_{q_4} \tag{3b}$$

represents the fourth-order anharmonicity constant. Following the procedure of Silverman,[21] the third-order anharmonicity is considered from the renormalization of A. The Green functions[22] for our calculations can be represented in the form (in units of $\hbar=1$)

$$G_{ij}^{mn}(t-t')=\langle\langle S_i^m(t)|S_j^n(t')\rangle\rangle \tag{4}$$

and the Fourier transform of Eq. (4) has the form

$$E\langle\langle S_i^m|S_j^n\rangle\rangle_E=(2\pi)^{-1}\langle[S_i^m,S_j^n]\rangle+\langle\langle[S_i^m,H]|S_j^n\rangle\rangle_E \ , \tag{5}$$

where $m,n=x,y$, or z. For different values of m and n, we get, using Eqs. (1) and (5), nine coupled equations of motion which can be written

$$\hat{G}\hat{M}=\hat{N} \ , \tag{6a}$$

where $\hat{G}$ is a (9×9) matrix given by

$$\hat{G}=m'\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\;,\quad m'=\begin{pmatrix}E&-ia&0\\ia&E&-ib\\0&ib&E\end{pmatrix}\;. \tag{6b}$$

$\hat{M}$ and $\hat{N}$ are the column matrices of the form

$$\hat{M}=(2\pi)^{-1}\begin{pmatrix}G^{xx}(E)\\G^{yx}(E)\\G^{zx}(E)\\G^{xy}(E)\\G^{yy}(E)\\G^{zy}(E)\\G^{xz}(E)\\G^{yz}(E)\\G^{zz}(E)\end{pmatrix}\;;\quad \hat{N}=\begin{pmatrix}0\\-\langle S^z\rangle\\\langle S^y\rangle\\\langle S^z\rangle\\0\\-\langle S^x\rangle\\-\langle S^y\rangle\\\langle S^x\rangle\\0\end{pmatrix}\;.$$

$$a=J_0'\langle S^z\rangle,\quad b=2\Omega\;,$$

$$J_0'=\frac{1}{2}\sum_j J_{ij},\quad \langle S_i^z\rangle\equiv\langle S_j^z\rangle=\langle S^z\rangle\;.$$

In the above calculations we used the Tyablikov decoupling[23] scheme to linearize the complex Green's functions as

$$\langle\langle S_i^x S_j^y | S_i^z\rangle\rangle=\langle S_i^x\rangle\langle\langle S_j^y|S_i^z\rangle\rangle \tag{7}$$

and so on. The energy spectrum is obtained from the solution of

$$|m'|=0\;, \tag{8}$$

which gives

$$E_1=0$$

and

$$E_{2,3}=\pm(a^2+b^2)^{1/2}\;. \tag{9}$$

The correlation functions like $\langle S_j^n S_i^m\rangle$, which are related to the Green functions $\langle\langle S_i^m|S_j^n\rangle\rangle$, can be otained from the spectral theorem using

$$\langle S^nS^m\rangle=i\lim_{\epsilon\to 0+}\int_{-\infty}^{+\infty}\frac{\langle\langle S^mS^n\rangle\rangle_{E+i\epsilon}-\langle\langle S^mS^n\rangle\rangle_{E-i\epsilon}}{\exp\beta E-1}\exp[-iE(t-t')]\,dE\;. \tag{10}$$

We now assume the physical condition that the correlation functions are finite and use the identity

$$\langle S^xS^x\rangle+\langle S^yS^y\rangle+\langle S^zS^z\rangle=S^2=S(S+1) \tag{11}$$

and then we get the relation

$$\frac{\langle S^x\rangle}{b}=\frac{\langle S^z\rangle}{a}=\frac{S(S+1)}{F}\tanh\frac{\beta F}{2}\;, \tag{12}$$

where $F^2=(a^2+b^2)$, $\beta=1/k_BT$ (T is the absolute temperature and k_B is the Boltzmann's constant). From Eq. (12) we get the expressions for the thermal averages $\langle S^x\rangle$ and $\langle S^z\rangle$. We define the thermal averages as

$$\sigma_x=\langle S^x\rangle/S(S+1)\;, \tag{13a}$$

$$\sigma_z=\langle S^z\rangle/S(S+1)\;. \tag{13b}$$

The factor $S(S+1)$ appears for the use of quantum condition that the eigenvalue of S^2 is $S(S+1)$ in Eq. (11). If we use the classical rule that $S^2=1$, our expressions for $\langle S^x\rangle$ and $\langle S^z\rangle$ become identical to those obtained from mean-field approximation[24] and those obtained by other authors.[18,25] It is evident from the above calculations that $E_{2,3}$ do not show any softening. However, it can be easily shown that the pure pseudospin tunneling model can show microscopic behavior of mode softening[26] if we use the following decoupling:

$$\langle\langle AB|C\rangle\rangle=\langle A\rangle\langle\langle B|C\rangle\rangle+\langle B\rangle\langle\langle A|C\rangle\rangle \tag{14}$$

and define the spin-wave transformation

$$S_i^m(\vec{q})=\sum_i S_i^m\exp i\vec{q}\cdot\vec{R}_i\;, \tag{15}$$

where R_i denotes the Bravais-lattice site of the i th bond. Since this point has also been discussed by (RT),[18] we shall focus our attention on the dynamic properties of the KDP system with the total Hamiltonian (3).

III. DYNAMIC PROPERTIES

To study the dynamic properties, we require the Green functions like

$$G_{\vec{q}}^{QQ}(t-t')=\langle\langle Q_{\vec{q}}(t)|Q_{-\vec{q}}(t')\rangle\rangle\;.$$

The required equations of motion using the decoupling procedure shown in Eq. (14) can be written in the matrix form

$$\begin{pmatrix}\omega&-iJ_0\langle S^z\rangle&0&-i\bar{V}_{\vec{q}}\langle S^y\rangle&0\\iJ_0\langle S^z\rangle&\omega&iJ_{\vec{q}}\langle S^x\rangle-2i\Omega&i\bar{V}_{\vec{q}}\langle S^x\rangle&0\\0&2i\Omega&\omega&0&0\\0&0&0&\omega&-i\\0&0&i\bar{V}_{\vec{q}}&i(\omega_{\vec{q}}^2+\bar{A})&\omega\end{pmatrix}\begin{pmatrix}\langle\langle S_i^x|Q_{-q}\rangle\rangle\\\langle\langle S_i^y|Q_{-q}\rangle\rangle\\\langle\langle S_i^z|Q_{-q}\rangle\rangle\\\langle\langle Q_q|Q_{-q}\rangle\rangle\\\langle\langle P_q|Q_{-q}\rangle\rangle\end{pmatrix}=\begin{pmatrix}0\\0\\0\\0\\-i/2\pi\end{pmatrix}\;, \tag{16a}$$

where

$$J_{\vec{q}}=\sum_{ij} J_{ij} \exp i\, \vec{q} \cdot (\vec{R}_i-\vec{R}_j); \quad \bar{V}_{\vec{q}}=\sum_{\vec{q}} V_{\vec{q}} \ , \tag{16b}$$

$$\bar{A}(\vec{q},T)=\frac{6}{\omega_{\vec{q}}{}'} \sum A_{q_1q_2q_3q_4}(\vec{q}, -\vec{q}, \vec{q}', -\vec{q}')[2n_{\vec{q}}(T)+1] \ . \tag{16c}$$

$n_{\vec{q}}(T)$ is the phonon number operator. The secular determinant Δ giving the spin-phonon spectrum has the form

$$\Delta=\omega[\omega^2-\omega_1^2(\vec{q})][\omega^2-\omega_2^2(\vec{q})] \ , \tag{16d}$$

where

$$\omega_{1,2}^2(\vec{q})=\tfrac{1}{2}(L_{\vec{q}}^2+\omega_{\vec{q}}^2+\bar{A}(\vec{q},T) \pm \{[L_{\vec{q}}^2-\omega_{\vec{q}}^2-\bar{A}(\vec{q},T)]^2+16\Omega \bar{V}_{\vec{q}}^2 \langle S^x\rangle\}^{1/2}) \tag{17a}$$

$$L_{\vec{q}}^2=4\Omega^2+J_0^2\langle S^z\rangle^2-2\Omega J_{\vec{q}}\langle S^x\rangle \ . \tag{17b}$$

This expression (17a), identical to that derived by Kobayashi[10] and Pak,[17] is found to be modified by the anharmonicity parameter. Equation (17a) gives the transition temperature T_C when $\omega_2 \to 0$ (as shown in Sec. III B).

Again using the spectral theorem (10) the different correlation functions can be represented as

$$\langle Q_{-\vec{q}}S_{\vec{q}}^x\rangle=\frac{J_0\langle S^x\rangle\langle S^z\rangle \bar{V}_{\vec{q}}}{2(\omega_1^2-\omega_2^2)}\left[\frac{1}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{1}{\omega_2}\coth\frac{\beta\omega_2}{2}\right] , \tag{18a}$$

$$\langle Q_{-\vec{q}}S_{\vec{q}}^x\rangle=0 \ , \tag{18b}$$

$$\langle Q_{-\vec{q}}S_{\vec{q}}^z\rangle=\frac{-2\Omega \bar{V}_q\langle S^x\rangle}{2(\omega_1^2-\omega_2^2)}\left[\frac{1}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{1}{\omega_2}\coth\frac{\beta\omega_2}{2}\right] , \tag{18c}$$

$$\begin{aligned}\langle P_{-\vec{q}}P_{\vec{q}}\rangle=&\frac{\omega_q^2+\bar{A}^2(\vec{q},T)}{2(\omega_1^2-\omega_2^2)}\left[\frac{\omega_1^2-L_{\vec{q}}^2}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{\omega_2^2-L_{\vec{q}}^2}{\omega_2}\coth\frac{\beta\omega_2}{2}\right]\\ &+\frac{2\Omega \bar{V}_{\vec{q}}^2\langle S^x\rangle}{2(\omega_1^2-\omega_2^2)}\left[\frac{1}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{1}{\omega_2}\coth\frac{\beta\omega_2}{2}\right] ,\end{aligned} \tag{18d}$$

$$\langle Q_{-\vec{q}}Q_{\vec{q}}\rangle=\frac{1}{2(\omega_1^2-\omega_2^2)}\left[\frac{\omega_1^2-L_{\vec{q}}^2}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{\omega_2^2-L_{\vec{q}}^2}{\omega_2}\coth\frac{\beta\omega_2}{2}\right] , \tag{18e}$$

$$\langle S_{-\vec{q}}^zS_{\vec{q}}^z\rangle=\frac{2\Omega\langle S^x\rangle}{2(\omega_1^2-\omega_2^2)}\left[\frac{\omega_1^2-\omega_q^2-\bar{A}(\vec{q},T)}{\omega_1}\coth\frac{\beta\omega_1}{2}-\frac{\omega_2^2-\omega_q^2-\bar{A}(\vec{q},T)}{\omega_2}\coth\frac{\beta\omega_2}{2}\right] , \tag{18f}$$

$$\langle Q_{-\vec{q}}P_{\vec{q}}\rangle=\tfrac{1}{2} \ . \tag{18g}$$

These correlation functions have been used to calculate the internal energy and hence the specific heat.

A. Electrical susceptibility and internal energy

Using the Kubo[27] formula, the expression for the dynamic susceptibility is

$$\chi_{\vec{q}}=\frac{1}{2k_BT}\left[\frac{L_q^2-\omega_1^2}{(\omega_1^2-\omega_2^2)(\omega^2-\omega_1^2)}\omega_1\coth\frac{\beta\omega_1}{2}-\frac{L_q^2-\omega_2^2}{(\omega_1^2-\omega_2^2)(\omega^2-\omega_2^2)}\omega_2\coth\frac{\beta\omega_2}{2}+\frac{\omega(L_q^2-\omega^2)}{(\omega^2-\omega_1^2)(\omega^2-\omega_2^2)}\right] . \tag{19}$$

Equation (19) reduces to the form derived by Silverman[21] and also by Pak[17] when $\omega_{1,2} << 1$ and the anharmonicity parameter $\bar{A}(\vec{q},T)=0$. From Eq. (19) we find that the anharmonic contribution is directly involved in the expressions for the static and the dynamic susceptibilities. The expression for the static susceptibility can be obtained from Eq. (19), putting $\vec{q}=0$. The internal energy calculated from the correlation functions (18) has the mathematical form

$$U_{\vec{q}} = \langle H(\vec{q}) \rangle$$

$$= -2\Omega \langle S^x \rangle - \frac{\langle S^x \rangle J_q \tau_q}{2(\omega_1^2 - \omega_2^2)} \left(\frac{\omega_1^2 - \gamma_q}{\omega_1} \coth \frac{\beta\omega_1}{2} - \frac{\omega_2^2 - \gamma_q}{\omega_2} \coth \frac{\beta\omega_2}{2} \right) , \tag{20}$$

where

$$\tau_q = \left(1 - \frac{2\omega_q^2 + 3\bar{A}(\vec{q},T)}{2\Omega J_{\vec{q}} \langle S^x \rangle} \right) ,$$

$$\gamma_{\vec{q}} = (\tau_q)^{-1} \left[\omega_{\vec{q}}^2 \left(1 - \frac{2L_q^2}{2\Omega J_{\vec{q}} \langle S^x \rangle} \right) + \bar{A}(\vec{q},T) \left(1 - \frac{3L_q^2}{2\Omega J_{\vec{q}} \langle S^x \rangle} \right) + \frac{3\bar{V}_q^2}{J_{\vec{q}}} \right] . \tag{21}$$

The first part of Eq. (20) shows no singularity. The anomalous contribution to the specific heat comes from the second part of Eq. (20) which is more complicated than that derived by Pak[17] due to the presence of the contribution from the anharmonic term of the Hamiltonian (3a). Equation (20) reduces to that derived by Pak if one neglects the higher-order anharmonic term from Eq. (3a). Again neglecting the contribution of ω_1 in the parentheses of Eq. (20) and putting $\bar{A} = 0$ we can obtain the expression derived by HB.[16] Equations (19) and (20) represent the most exact expressions for dynamic susceptibility and internal energy where contributions of ω_1 and ω_2 along with that of the higher-order anharmonic interaction have been taken into consideration. From Eq. (20) it is evident that for small ω_1 and ω_2 the internal energy is independent of the tunneling term Ω which was also shown by HB.

B. Curie temperature

The Curie temperature T_C is calculated from Eq. (17a) using the lattice instability condition; i.e., $\omega_2 \to 0$ as $T \to T_C$. This condition gives

$$\frac{\Omega}{K_B T_C} = \operatorname{arc\,tanh} \eta , \tag{22a}$$

where

$$\eta = 4\Omega / J^*_{q=0} , \tag{22b}$$

$$J^*_{q=0} = J'_0 + \bar{V}_0^2 / [\omega_0^2 + \bar{A}(q=0,\ T=T_C)] , \tag{22c}$$

$$= J'_0 + \bar{G}^* , \tag{22d}$$

$$\bar{G}^* = \bar{V}_0^2 / [\omega_0^2 + \bar{A}(q=0,\ T=T_C)] , \tag{22e}$$

$\bar{G}^*$ reduces to G^* of Kobayashi[10] and Peercy and Samara[15,28] in the absence of the anharmonicity parameter $\bar{A}(0,T_C)$ and then the right-hand side of Eq. (22a) becomes temperature independent as in the case of T_0 (the transition temperature derived from MFA) given by

$$\frac{\Omega}{K_B T_0} = \operatorname{arc\,tanh}(4\Omega / J'_0) . \tag{23}$$

Equation (23) can also be calculated from Eq. (13b), in which case $\langle S^z \rangle \to 0$ as $T \to T_0$. From Eqs. (22b)–(22e) it is evident that the effect of the anharmonicity parameter is to decrease the effective exchange coupling J^* while the effect of the proton-lattice coupling is to increase its value. The latter finding is in agreement with those of Peercy and Samara[14,15] and Blinc and Zĕkš.[25] The ratio of J'_0 and $\bar{G}^*$ is also found to be greater than unity and lies between 1 and 3, which is in agreement with the results obtained from Raman studies[14,15] in case of KH_2PO_4 and RbH_2PO_4.

C. Curie-Weiss constant

To calculate the static susceptibility and hence the Curie-Weiss constant, we use the formula

$$\chi = -\frac{n\mu^2}{v_0} G^{QQ}_{\vec{q}}(\omega) \Big|_{\substack{\omega=0,\\ q=0}} , \tag{24a}$$

which gives

$$\chi = \frac{n\mu^2}{v_0} \left(\omega_0^2 + \bar{A}(0,T) - \frac{2\bar{V}_0^2 \tanh \Omega/k_B T}{4\Omega - J_0 \tanh \Omega/k_B T} \right)^{-1} , \tag{24b}$$

where n is the number of pseudospin variables, v_0 is the volume of the unit cell, and μ is the effective dipole moment. Expanding $1/\chi$ around T_C, we get the Curie-Weiss behavior

$$\chi = \frac{n\mu^2}{v_0} \left[\left(\frac{\partial \bar{A}}{\partial T} \right)_{T=T_C} + \frac{8\Omega^2 \bar{V}_0^2 (1 - \tanh^2 \Omega / k_B T_C)}{k_B T_C^2 (4\Omega - J_0 \tanh \Omega / k_B T_C)^2} \right]^{-1}$$

$$\times (T - T_C)^{-1} , \tag{25a}$$

$$= C/(T - T_C) , \tag{25b}$$

where C is the Curie-Weiss constant, expressed by the relation

$$C=\frac{n\mu^2}{v_0}\left(k_B\bar{A}_0'(0,T_C)+\frac{8\bar{V}_0^2\,\Omega^2(1-\tanh^2\Omega/k_BT_C)}{k_BT_C^2(4\Omega-J_0\tanh\Omega/k_BT_C)^2}\right)^{-1} . \tag{25c}$$

In Eq. (25c) we have put $\bar{A}\,(0,T)\simeq k_BT\bar{A}_0'$. The static dielectric constant can be calculated using the usual relation viz.

$$\epsilon=1+4\pi\chi\ . \tag{26}$$

It is observed from Eqs. (24a) and (25c) that both the susceptibility and the Curie constant depend on the tunneling frequency explicitly. Our result contradicts with that of Pak,[17] who, however, did not consider the anharmonic term and also did not calculate the susceptibility from the Green function $G_q^{QQ}(\omega)$. The expression for C consists of two parts, as shown in Eq. (25c). The first part arises from the anharmonic contribution and the second part comes from the proton-lattice interaction part and depends on the tunneling frequency. This result definitely indicates the importance of tunneling frequency and also the anharmonic interaction term in the Hamiltonian (3a). In case of the deuterated system when the tunneling is very small, contribution to the Curie-Weiss constant comes mainly from the anharmonic part. But in the pure system the effect of tunneling is found to be more important. If we neglect the anharmonic contribution from Eq. (25c), we cannot fit the expression for the transition temperature, susceptibility, and Curie-Weiss constant with a single set of BG parameters (see Sec. IV for details).

D. Specific heat

Assuming ω_1 and ω_2 are small around T_C, we have from Eq. (20) the expression for the internal energy

$$\bar{U}=-\frac{1}{2}\sum_{\vec{q}}\frac{J_q^*(B+3)}{1-J_{\vec{q}}^*/k_BT}+\frac{1}{2}\sum_{\vec{q}}\frac{k_BT(B+2)}{1-J_{\vec{q}}^*/k_BT}+\frac{1}{2}\sum_{\vec{q}}\frac{B\bar{V}_q^2/[\omega_q^2+\bar{A}(\vec{q},T)]}{1-J_{\vec{q}}^*/k_BT}\ , \tag{27a}$$

where

$$B=\bar{A}(\vec{q},T)/[\omega_{\vec{q}}^2+\bar{A}(\vec{q},T)]\ , \tag{27b}$$

$$J_{\vec{q}}^*=J_{\vec{q}}+\bar{V}_{\vec{q}}^2/[\omega_{\vec{q}}^2+\bar{A}(\vec{q},T)]^2\ . \tag{27c}$$

The specific heat C_v can be calculated by differentiating $\bar{U}$ with respect to T. It is interesting to note that, in the absence of $\bar{A}(\vec{q},T)$, Eq. (27a) reduces to a simple form

$$\bar{U}=-\frac{3}{2}\sum_{\vec{q}}\frac{J_q^*}{1-J_q^*/k_BT}+\sum_{\vec{q}}\frac{k_BT}{1-J_{\vec{q}}^*/k_BT}\ . \tag{28}$$

The first term of Eq. (28) is identical to the expression derived by Pak and HB. For the sake of simplicity, we retain in Eq. (27a) only the first term to show the logarithmic dependence of C_v around T_C. Further, assuming B to be constant around T_C, and following the procedure of HB, it can be easily shown that

$$C_v\simeq\frac{d\bar{U}}{dT}\simeq(B+3)(T_C/\bar{V}_0)^2\ln|T-T_C|\ . \tag{29}$$

Thus we may write

$$C_v\simeq a'\ln(T-T_C)\ . \tag{30}$$

Equation (30) is of the same form first derived by Grindlay[29] for KDP crystal. It is also observed from Eq. (29) that C_v, unlike C, χ, and T_C, does not depend on the tunneling frequency explicitly, as was pointed out by HB. Thus it might be concluded that the KDP-type hydrogen-bonded ferroelectric crystals undergoing order–disorder-like transitions should have limiting behavior shown by Eq. (29) and thereby indicating long-range electrostatic dipolar interactions. It is interesting to note that RPA-like decoupling of the complex Green's functions can exhibit this logarithmic character in the specific heat. It should also be mentioned at this point that our results calculated from the Tyablikov[23]-type-decoupling approximation can be used everywhere except in the millidegree range around T_C. It has already been pointed out[25,30] that for KDP-type crystals where the critical region is supposed to be very narrow, relatively rough approximations like MFA and RPA can be used. Tyablikov-type decoupling used in this paper has also been found[31] to explain very well the dynamics of transverse susceptibility in KDP-type hydrogen-bonded ferroelectric crystals.

IV. RESULTS AND DISCUSSION

To calculate the anharmonicity parameter $(k_B\bar{A}_0')$ which is involved in the expressions for χ, T_C, C, and also in C_v for different KDP-type crystals, we used the experimental data of the pseudo-spin parameters obtained by Peercy and Samara (PS)[14,15] and Fairall and Reese (FR).[32] Unfortunately, except for KH_2PO_4 and RbH_2PO_4, experimental values of Ω, $\bar{V}_{0A}$, J_{0A}, and J_{0A}^* (where $A=H$ or D; H denotes undeuterated and D denotes deuterated) are not available. The calculated values of Ω and J_0^* obtained from the best fitting of T_C, C, and spontaneous polarization (P_s) are found to be very close to those of PS as shown in Tables I and II, respectively, for the H and D systems. In the case of mixed KDP-DKDP system, we have shown[19] earlier that the Raman spectroscopic data of PS agree very well with our theoretically calculated values. The fitting was done by varying the ratios J_H^*/J_D^* and Ω_H/Ω_D such that the relation[28]

$$P_{0D}^2 / P_{0H}^2 = (J_{0D}^* / J_{0H}^*)^{1/2} \approx 1.44 \ , \qquad (31)$$

is satisfied. From our fitting we find Ω (for DKDP) $\simeq 0.5$ cm^{-1} instead of zero as calculated by others.[32] Again, since the second part of Eq. (25c) is very small for the deuterated system we may neglect this part and calculate $\bar{A}_0'$ comparing the experimental values of C_D (for the deuterated system) using the experimental values of μ and v_0 from the results of Cook[33] and VZS. The calculated values of $\bar{A}_0'$ are shown in Table I. The experimental data of PS for KDP and RDP (RbH_2PO_4) showed that $J_0' / J_0^* \approx 0.75$. Assuming same value of this ratio for other members of KDP family for which experimental data are not available, we again calculate $\bar{A}_0'$, knowing $\bar{V}_0$ (the MFA value of FR), and these values are also shown in Table I for comparison with the values of $\bar{A}_0'$ calculated by earlier method. These two sets of parameters are found to be of the same order of magnitude, indicating the validity of the mean-field data. Putting $J_0' / J_0^* \approx 0.75$ (as discussed above) and using the first set of values of A_0', we calculate $\bar{V}_0$ from Eq. (25c), knowing the experimental data (from the table given by VZS) for comparison with the mean-field data of FR and are shown in Table I. Very good agreement between the two sets of data of $\bar{V}_0$ again indicates the validity of the relation (31). Another test of the validity of the calculated BG parameters obtained, for example, for KDP crystal comes from the agreement between the calculated and experimentally observed[34–38] values of the Landau parameters[34] A_1 and B_1 related to the free energy (F) as

$$F = \tfrac{1}{2} A_1 \sigma_s^2 + \tfrac{1}{4} B_1 \sigma_s^4 + \tfrac{1}{6} C_1 \sigma_s^6 \ , \qquad (32)$$

(σ_s is the order parameter which is the spontaneous polarization in this case). Using the pseudospin model we have shown earlier[35] that the expressions

TABLE I. Pseudo-spin model (BG) parameters for undeuterated KDP system.[a]

Crystals	KH_2PO_4	RbH_2PO_4	KH_2AsO_4	RbH_2AsO_4	CsH_2AsO_4
J_{0H}^* cm^{-1}	440.90 450.00[b]	483.60 473.00[b]	281.80 . . .	321.50 . . .	415.10 . . .
J_{0H}' cm^{-1}	334.80 344.00[b]	362.70 357.00[b]	211.35 . . .	241.12 . . .	311.33 . . .
Ω_H cm^{-1}	82.00 86.00[b]	78.40 78.40[b]	28.80 16.10[c]	30.80 22.70[c]	28.50 20.20[c]
T_{cH} K	122.89 122.70[f] 122.90[f] 121.70[f]	146.09 144.00[f] 146.80[f] 147.10[f]	96.35 96.15[f] 96.30[f] 95.80[f]	109.91 110.90[f] 109.10[f]	145.53 144.50[f] 143.30[f] 145.50[f]
C_H K	254.87 254.77[f] 238.73[f]	238.90 238.73[f] 286.48[f] 302.39[f]	183.22 183.12[f] 214.85[f]	247.00 246.69[f] 205.31[f] 222.81[f]	254.80 254.77[f] 268.97[f]
$\bar{V}_0/k_B T_c$	0.299 0.160[c]	0.252 0.135[c]	0.314 0.205[c]	0.178 0.185[c]	0.132 0.154[c]
$\bar{A}_0' k_B \times 10^{17}$ (erg/K)	9.763[d] 13.160[e]	10.133[d] 13.020[e]	9.528[d] 15.490[e]	9.844[d] 9.948[e]	9.391[d] 8.908[e]
n	4	4	4	4	4

[a] Parameters outside the brackets correspond to our calculated values.
[b] Values taken from Refs. 14, 15, and 28.
[c] Values taken from the table of Ref. 32.
[d] Calculated values neglecting the second part of Eq. (25c).
[e] Calculated from Eq. (25c) using the values of $\bar{V}_0/k_B T_{cH}$ from Ref. 32.
[f] Values taken from Ref. 9.

for A_1 and B_1 can be written[36]

$$A_1=\frac{J_0c_0}{k_BT_C}(T-T_C)\,\mathrm{sech}^2\frac{2\Omega}{k_BT_C}=A_{01}(T-T_C)\quad ,(33)$$

$$B_1=\frac{\alpha'}{8\overline{\Omega}^2}\tanh^2\alpha'+\frac{1}{8\overline{\Omega}^3}\tanh\alpha'-\frac{\alpha'}{8\overline{\Omega}^2}\quad ,\qquad (34)$$

where

$$A_{01}=\frac{J_0c_0}{k_BT_C}\,\mathrm{sech}^2\,\frac{2\Omega}{k_BT_C}\quad ,$$

$$\alpha'=\frac{\beta J_0}{2N\mu^2};\quad \overline{\Omega}=\frac{4\Omega N\mu}{J_0}\quad ;$$

and

$$c_0=\frac{J_0n}{N\mu^2}\quad .$$

Using the required values of the BG parameters (viz., J_0 and Ω) for KDP from Table I, we have calculated the values of A_{01} and B_1 which are shown in Table III along with other experimental values[37] for comparison. We have not, however, shown in Table III the value C_1, since C_1 comes out to be one order of magnitude smaller than the experimentally observed value.[37–39] This might be due to some error in the expression for C_1 arising from the approximation made to calculate C_1 and/or due to the inadequacy of the pure pseudospin model used to calculate the energy spectrum.[35] The values of A_{01} and B_1, however, agree very well with those of experimental results[37–39] shown in Table III.

Thus it is evident that using the Green-function method and taking into account higher-order anharmonic term in the pseudospin-lattice-coupled Hamiltonian, a single set of pseudo-spin-model parameters (BG), being different for different salts, can be used to explain all the behaviors of ferroelectric phase transitions in KDP-type crystals. Further, the large shift of the Curie point and the correspondingly small change of the Curie-Weiss constant due to deuteration which was not explained by other theoretical work on these salts can also be simultaneously explained with the above-mentioned single set of parameters given in Tables I and II, respectively, for H and D systems. This is not at all possible if we neglect the anharmonic term from the pseudo-spin-lattice-coupled Hamiltonian similar to the earlier calculations with Kobayashi model. Experimental determination of the anharmonicity parameter is therefore highly important for the actual comparison of the experimental and the theoretical values of C, ϵ, C_v and the other parameters of phase transitions in KDP system. Another interesting point which we note from our calculations is that, if we calculate the frequency ω_0 from Eq. (22a) using the parameters from Tables I and II, we get a negative value of ω_0^2. This means that the initial phonon frequencies are imaginary, and this mode cannot be stabilized by zero-point anharmonicities alone. It is the thermal fluctuations which then renormalize ω_0 and make it real at finite temperatures. This case is similar to $BaTiO_3$ undergoing a displacive type of phase transition and may be explained[40] considering a pseudo-Jahn-Teller (PJT) mechanism. Bersuker[41] already proposed a PJT effect in hydrogen-bonded KDP-type crystals. This indicates a close similarity between the topologies of order-disorder and displacive types of phase transitions.

TABLE II. Pseudospin model (BG) parameters for deuterated KDP-type crystals.[a]

Crystals	J_D^* cm^{-1}	J'_{0D} cm^{-1}	Ω_D cm^{-1}	T_{cD} K	C_D K
KD_2PO_4	626.00	472.63	0.486	229.89	373.70
RbD_2PO_4	644.60	486.68	0.652	249.87	335.11
KD_2AsO_4	400.10	302.10	0.450	163.45	357.88
RbD_2AsO_4	460.60	347.76	0.459	176.56	318.47
CsD_2AsO_4	600.10	453.01	0.585	223.10	303.50

[a]Experimental values of J_{0D}^* and J'_{0D} are available only for KD_2PO_4 and RbD_2PO_4 (Refs. 15 and 28), and they are found to be very close to our calculated values shown in this table. The values of T_{cD} and C_D shown in this table are also very close to those shown in Ref. 9 by VZS.

TABLE III. Comparison of the calculated and other experimental values of the Landau parameters in KH_2PO_4.

$A_{01}\times10^3$ (esu)	(5.33)[a]	(4.30 ±0.2)[b]	(4.00 ±0.2)[b]
$B_1\times10^{11}$ (esu)	(2.951)[a]	(2.35 ±0.4)[b]	(1.48 ±0.2)[b]

[a]Present theory.

[b]Reference 39; our calculated data are also very close to the experimental data of Okada and Sugie (Ref. 37).

V. CONCLUSION

This paper extends the coupled proton-lattice mode model of Kobayashi type to include the effects of higher-order anharmonic terms on the physical properties of KDP-type crystals. These calculations represent the first attempt to include directly the anharmonicity in the PLCM Hamiltonian for studying the static and the dynamic properties of KDP system. Using the simple decoupling procedure of Tyablikov,[23] it has been shown that the Green-function theory can successfully explain the most salient features of ferroelectric transitions in KDP series along with logarithmic dependence of specific heat, exact isotope dependence of the Curie-Weiss constant, electrical susceptibility, etc. Our results also leads to pseudo-Jahn-Teller-like mechanism even in KDP-type crystals. It is also justified from other theoretical work that the PJT Hamiltonian takes the form[42] of a pseudo-spin model, viz.,

$$H_{\mathrm{JT}} = -S^x - 2V_0Q_0S^z \ .$$

This finding also supports the results and conclusions of earlier workers[42–44] that the order-disorder and the displacive type of ferroelectric phase transitions might be described with a single model[44] and that there is no basic difference between these two types of transitions. This finally leads to the possibility of a unified theory of ferroelectric phase transitions.[44]

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