Phase transitions of $PbHPO_4$- and $PbDPO_4$-type ferroelectrics investigated with a Green's-function technique

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A Green's-function technique is used to study the effects of spin-phonon interactions in $PbHPO_4$- and $PbDPO_4$-type ferroelectrics including higher-order anharmonic terms. The renormalized energy and the damping of the spin waves and the phonons have been evaluated. The anharmonicity effects play an important role in the vicinity of T_c and above T_c. The transverse dynamic structure factor exhibits three peaks due to the coupling of the transverse soft mode and the acoustic-phonon mode. The width of the central peak is proportional to the phonon damping.

I. INTRODUCTION

Recently a central mode of H-bonded ferroelectric (FE) $PbHPO_4$ (LHP) and $PbDPO_4$ (LDP) has been found in the paraelectric phase by hyper-Raman scattering by Shin *et al.*[1,2] From the temperature and polarization dependences of the central mode it is concluded that the central mode is the soft mode in LHP. The phase transition can be considered as an order-disorder type phase transition.

Theoretical studies of the properties of LHP-type FE's have been carried out by many authors.[3–10] Chunlei *et al.*[6] have investigated the thermodynamic properties of LHP and LDP using the three-dimensional transverse Ising model including the fourth-order pseudospin interaction and obtained good agreement with the experimental data of the spontaneous polarization. The dynamic properties are not calculated in this work.[6] Wesselinowa[7] has treated the three-dimensional Ising model in a transverse field including the fourth-order interaction by means of the Green's-function technique. She calculated the spin-wave energy and the damping above and below T_c. The coupling between the transverse soft mode and the relaxing longitudinal mode produces a central mode in the dynamic structure factor. The dielectric properties of LHP near to the direction of spontaneous polarization P_s were investigated by Briskot and Happ.[11] The soft proton mode which causes the Curie-Weiss anomaly of the dielectric constant ϵ_s at T_c is of relaxation type. It can be described by a Debye formula. A very small value of the tunneling integral Ω (found theoretically in LHP with the help of the pseudospin model) supports the conclusion that tunneling plays no essential role in the dynamics of the proton system.

Chaudhuri *et al.*[8] and Banderjee *et al.*[9] used the pseudospin-lattice-coupled mode model to study the static and dynamic properties of LHP. They have not considered a term of the form $J'_{ijkl}S_i^zS_j^zS_k^zS_l^z$, but pointed out that it may be important for describing more correctly the dynamics of the phase transition in some H-bonded FE's. Another point which was mentioned is that the small value of the transition entropy ΔS observed in LHP and squaric acid crystals[10] seems to be due to the large value of the proton-lattice interaction constant; i.e., this indicates the importance of proton-phonon and phonon-phonon interactions.

Recently Serra *et al.*[12] have presented a study of the Raman spectra of potassium dihydrogen phosphate (KDP) and its temperature dependence below the transition to the ferroelectric phase. Two lattice modes display an exponential dependence with T which is explained by third- and fourth-order anharmonic effects. Silva and Roversi[13] also predicted the existence of strong anharmonicity in KDP that affects the crystalline structure of the ferroelectric phase at temperatures near $T_c = 123$ K.

The aim of the present paper is to study in detail the dynamic properties of LHP- and LDP-type FE's. To this we extend the treatment of our previous work[7] by including interactions between the spin mode and the phonons and by taking into account higher-order anharmonic terms.

II. MODEL AND METHOD

The Hamiltonian of the pseudospin-phonon model is given by

$$H = H_s + H_p + H_{sp}. \tag{1}$$

H_s is the Hamiltonian of the pseudospin system,

$$H_s = -2\Omega\sum_i S_i^x - \frac{1}{2}\sum_{i,j} J_{ij}S_i^zS_j^z - \frac{1}{4}\sum_{i,j,k,l} J'_{ijkl}S_i^zS_j^zS_k^zS_l^z, \tag{2}$$

where Ω is the tunneling frequency. S_i^z is the proton occupation difference at the two equilibrium positions of the H bound at the ith site; it measures the proton ordering. The first term in (2) is the contribution of the tunneling effect, the second term represents the dipole contribution, and the third the quadrupole contribution.

H_p contains the lattice vibrations including third- and fourth-order anharmonic phonon interactions,

$$H_p = \frac{1}{2!}\sum_{\mathbf{q}}(P_{\mathbf{q}}P_{-\mathbf{q}} + \omega_{\mathbf{q}}^2 Q_{\mathbf{q}}Q_{-\mathbf{q}}) + \frac{1}{3!}\sum_{\mathbf{q},\mathbf{q_1}} \bar{B}(\mathbf{q},\mathbf{q_1})Q_{\mathbf{q}}Q_{-\mathbf{q_1}}Q_{\mathbf{q_1}-\mathbf{q}} + \frac{1}{4!}\sum_{\mathbf{q},\mathbf{q_1},\mathbf{q_2}} \bar{A}(\mathbf{q},\mathbf{q_1},\mathbf{q_2})Q_{\mathbf{q_1}}Q_{\mathbf{q_2}}Q_{-\mathbf{q}-\mathbf{q_2}}Q_{-\mathbf{q_1}+\mathbf{q}}, \tag{3}$$

where $Q_{\mathbf{q}}$, $P_{\mathbf{q}}$, and $\omega_{\mathbf{q}}$ are, respectively, the normal coordinate, momentum, and frequency of the lattice mode with wave vector $\mathbf{q}$. The vibrational normal coordinate $Q_{\mathbf{q}}$ and the momentum $P_{\mathbf{q}}$ can be expressed in terms of phonon creation and annihilation operators,

$$Q_{\mathbf{q}} = (2\omega_{\mathbf{q}})^{-\frac{1}{2}}(a_{\mathbf{q}} + a_{-\mathbf{q}}^{\dagger}), \quad P_{\mathbf{q}} = i(\omega_{\mathbf{q}}/2)^{\frac{1}{2}}(a_{\mathbf{q}}^{\dagger} - a_{-\mathbf{q}}), \tag{4}$$

where $[a_{\mathbf{q}}; a_{\mathbf{q}'}^{\dagger}]_- = \delta_{\mathbf{q}\mathbf{q}'}$.

H_{sp} describes the interaction of the pseudospins with the phonons,

$$H_{sp} = -\sum_{\mathbf{q}} \bar{F}(\mathbf{q})Q_{\mathbf{q}}S_{-\mathbf{q}}^z - \frac{1}{2}\sum_{\mathbf{q},\mathbf{p}} \bar{R}(\mathbf{q},\mathbf{p})Q_{\mathbf{q}}Q_{-\mathbf{p}}S_{\mathbf{p}-\mathbf{q}}^z - \frac{1}{3}\sum_{\mathbf{q},\mathbf{p},\mathbf{r}} \bar{T}(\mathbf{q},\mathbf{p},\mathbf{r})Q_{\mathbf{q}}Q_{-\mathbf{p}}Q_{\mathbf{r}}S_{\mathbf{p}-\mathbf{q}-\mathbf{r}}^z, \tag{5}$$

where $F_{\mathbf{q}} = \bar{F}_{\mathbf{q}}/(2\omega_{\mathbf{q}})^{\frac{1}{2}}$, $R_{\mathbf{q}} = \bar{R}_{\mathbf{q}}/(2\omega_{\mathbf{q}})$, and $T_{\mathbf{q}} = \bar{T}_{\mathbf{q}}/(2\omega_{\mathbf{q}})^{\frac{3}{2}}$ represent the pseudospin-lattice interaction constants.

In the ferroelectric phase we have $\langle S^x\rangle \neq 0$ and $\langle S^z\rangle \neq 0$; therefore it is appropriate to choose a new coordinate system by rotating the original one used in (1) by an angle θ in the xy plane,

$$S_l^z = \frac{1}{2}[(1-2\rho_l)\cos\theta - (b_l^{\dagger} + b_l)\sin\theta],$$
$$S_l^x = \frac{1}{2}[(1-2\rho_l)\sin\theta + (b_l^{\dagger} + b_l)\cos\theta],$$
$$S_l^y = \frac{i}{2}(b_l^{\dagger} - b_l). \tag{6}$$

The rotation angle θ is determined by the requirement $\langle S^{x'}\rangle = 0$ in the new coordinate system. b_l and $b_l^{\dagger}$ are the Pauli operators in the rotated system; $\rho_l = b_l^{\dagger}b_l$. In this paper we consider only the case $S = 1/2$.

The retarded Green's function to be calculated is defined in matrix form as

$$\tilde{G}_{\mathbf{k}}(t) = -i\Theta(t)\langle[B_{\mathbf{k}}(t); B_{\mathbf{k}}^{\dagger}]\rangle. \tag{7}$$

The operator $B_{\mathbf{k}}$ stands symbolically for the set $b_{\mathbf{k}}$, $b_{-\mathbf{k}}^{\dagger}$, $a_{\mathbf{k}}$, $a_{-\mathbf{k}}^{\dagger}$. For an approximate evaluation of this Green's function we use Tserkovnikov's method,[14] which is appropriate for spin problems. After a formal integration of the equation of motion for the Green's function one obtains

$$\tilde{G}_{\mathbf{k}}(t) = -i\Theta(t)\langle[B_{\mathbf{k}}; B_{\mathbf{k}}^{\dagger}]\rangle \exp(-iE_{\mathbf{k}}(t)t), \tag{8}$$

where

$$E_{\mathbf{k}}(t) = \epsilon_{\mathbf{k}} - \frac{i}{t}\int_0^t dt't' \left(\frac{\langle[j_{\mathbf{k}}(t), j_{\mathbf{k}}^{\dagger}(t')]\rangle}{\langle[B_{\mathbf{k}}(t), B_{\mathbf{k}}^{\dagger}(t')]\rangle} - \frac{\langle[j_{\mathbf{k}}(t), B_{\mathbf{k}}^{\dagger}(t')]\rangle\langle[B_{\mathbf{k}}(t), j_{\mathbf{k}}^{\dagger}(t')]\rangle}{\langle[B_{\mathbf{k}}(t), B_{\mathbf{k}}^{\dagger}(t')]\rangle^2} \right) \tag{9}$$

with $j_{\mathbf{k}} = [B_{\mathbf{k}}, H_{\text{int}}]$. The time-independent term

$$\epsilon_{\mathbf{k}} = \langle[[B_{\mathbf{k}}, H], B_{\mathbf{k}}^{\dagger}]\rangle / \langle[B_{\mathbf{k}}, B_{\mathbf{k}}^{\dagger}]\rangle \tag{10}$$

gives the spin-wave energy in the generalized Hartree-Fock approximation. The remaining time-dependent term includes damping effects.

III. THE TRANSVERSE GREEN'S FUNCTION

We get for the transverse Green's function in the generalized Hartree-Fock approximation

$$G_{11}^{xx}(\mathbf{k}, E) = \frac{2\sigma(\epsilon_{\mathbf{k}}^{11} - \epsilon_{\mathbf{k}}^{12})}{E^2 - \epsilon_{\mathbf{k}}^2 + i\Gamma_{\mathbf{k}}^{xx}(E)}, \tag{11}$$

where

$$\Gamma_{\mathbf{k}}^{xx}(E) = 2E\gamma_{\mathbf{k}}^{11} - \frac{4i[\epsilon_{\mathbf{k}}^{13}(\epsilon_{\mathbf{k}}^{12} - \epsilon_{\mathbf{k}}^{11}) + iE\gamma_{\mathbf{k}}^{13}][\epsilon_{\mathbf{k}}^{13}\bar{\omega}_{\mathbf{k}} - i\gamma_{\mathbf{k}}^{13}(i\gamma_{\text{ph}} + E)]}{E^2 - \bar{\omega}_{\mathbf{k}}^2 - \gamma_{\text{ph}}^2 + 2i\gamma_{\text{ph}}E} \tag{12}$$

and

$$\epsilon(\mathbf{k}) = \pm\sqrt{(\epsilon_{\mathbf{k}}^{11})^2 - (\epsilon_{\mathbf{k}}^{12})^2}, \tag{13}$$

$$\epsilon_{\mathbf{k}}^{11} = 2\Omega\sin\theta + \frac{\sigma}{2}J_{\text{eff}}\cos^2\theta - \frac{\sigma}{4}\sin^2\theta\bar{J}_{\mathbf{k}}, \tag{14}$$

$$\epsilon_{\mathbf{k}}^{12} = -\frac{\sigma}{4}\sin^2\theta\bar{J}_{\mathbf{k}}, \tag{15}$$

$$\epsilon_{\mathbf{k}}^{13} = \frac{1}{2}\sigma F_{\mathbf{k}}\sin\theta, \tag{16}$$

$$\gamma_{\mathbf{k}}^{13} = \frac{\pi F_{\mathbf{k}}\sigma\sin^3\theta}{4N}\sum_{\mathbf{q}} \bar{J}_{\mathbf{q}}\bar{n}_{\mathbf{q}}\delta(\bar{\omega}_{\mathbf{k}} - \epsilon_{\mathbf{k}}). \tag{17}$$

$\sigma(T)$ is the relative polarization in the direction of the mean field which is equal to $2\langle S^{z'}\rangle$.[7,19] In the generalized Hartree-Fock approximation we find the following two solutions for the rotation angle θ:

$$(1)\quad \cos\theta = 0, \quad \text{i.e.,} \quad \theta = \pi/2, \qquad \text{if} \quad T \geq T_c, \tag{18}$$

$$(2)\quad \sin\theta = 4\Omega/(\sigma J_{\text{eff}}) = \sigma_c/\sigma, \quad \text{if} \quad T \leq T_c, \tag{19}$$

$$J_{\text{eff}} = J_0 + \frac{1}{4}\sigma^2 J_0' \cos^2\theta + \frac{(F_0 + 2T_0)2F_{\mathbf{k}}\delta_{\mathbf{k0}}}{\omega_{\mathbf{k}} - \sigma\cos\theta R_{\mathbf{k}} + 0.5A_{\mathbf{k}}}. \tag{20}$$

From Eq. (20) it is evident that the pseudospin-phonon interaction leads to a renormalization of the spin-spin interaction constant, which is now temperature dependent. The effect of the anharmonicity parameter $A_{\mathbf{k}}$ is to decrease the effective exchange coupling J_{eff} while the effects of the pseudospin-lattice coupling $F_{\mathbf{k}}, R_{\mathbf{k}}$, and $T_{\mathbf{k}}$ are to increase its value. These observations for $A_{\mathbf{k}}$ and $F_{\mathbf{k}}$ are in agreement with those of Ganguli *et al.*[15] The terms containing $R_{\mathbf{k}}$ and $T_{\mathbf{k}}$ are not taken into account in this work.[15]

$\bar{\omega}_{\mathbf{k}}$ is the renormalized energy of the acoustic phonons,

$$\bar{\omega}_{\mathbf{k}}^2 = \omega_{\mathbf{k}}^2 - 2\omega_{\mathbf{k}}\left(\frac{\sigma}{2}\cos\theta R_{\mathbf{k}} - \frac{1}{2}A_{\mathbf{k}} - B_{\mathbf{k}}\langle Q_{\mathbf{k}}\rangle\delta_{\mathbf{k0}} + \sigma T_{\mathbf{k}}\langle Q_{\mathbf{k}}\rangle\delta_{\mathbf{k0}}\right), \tag{21}$$

with

$$\langle Q_{\mathbf{k}}\rangle = \langle a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger}\rangle = \frac{\sigma\cos\theta(F_{\mathbf{k}} + T_0) - B_0}{\omega_{\mathbf{k}} - \sigma\cos\theta R_{\mathbf{k}} + A_{\mathbf{k}}}\delta_{\mathbf{k0}}. \tag{22}$$

The acoustic-phonon energy $\omega_{\mathbf{k}}$ is renormalized due to the anharmonic phonon interaction terms. If they are not taken into account, then $\bar{\omega}_{\mathbf{k}}$ is identical with the energy of the uncoupled acoustic phonon $\omega_{\mathbf{k}}$. The anharmonicity increases the initial phonon frequency. The modification of the phonon frequency appears to be very important[15] as in the case of Rochelle salt where the disappearance of ferroelectricity[16] in presence of foreign impurities was explained[17] by considering the change of renormalized phonon frequency.[18]

$\gamma_{\mathbf{k}}^{11}$ and γ_{ph} are the spin-wave damping and the phonon damping, respectively. Calculations yield the following expression for the spin-wave damping:

$$\gamma(\mathbf{k})^{11} = \gamma_{ss} + \gamma_{sp}. \tag{23}$$

γ_{ss} is the damping part caused by the spin-spin interaction and has been discussed in Ref. 19:

$$\gamma_{ss} = \frac{\pi}{2N^2}\sum_{\mathbf{p},\mathbf{q}}\{(V_{\mathbf{q},\mathbf{k}-\mathbf{q}} + V_{\mathbf{k}-\mathbf{p}-\mathbf{q},\mathbf{p}+\mathbf{q}})^2[\bar{n}_{\mathbf{p}}(1 + \bar{n}_{\mathbf{p}+\mathbf{q}} + \bar{n}_{\mathbf{k}-\mathbf{q}}) - \bar{n}_{\mathbf{p}+\mathbf{q}}\bar{n}_{\mathbf{k}-\mathbf{q}}] \times \delta\,(\epsilon_{\mathbf{k}-\mathbf{q}} + \epsilon_{\mathbf{p}+\mathbf{q}} - \epsilon_{\mathbf{p}} - \epsilon_{\mathbf{k}}) - \sin^2\theta V_{\mathbf{q},\mathbf{k}-\mathbf{q}}[(\bar{J}_{\mathbf{p}} + \bar{J}_{\mathbf{p}+\mathbf{q}})\bar{m}_{\mathbf{p}+\mathbf{q}}(\bar{n}_{\mathbf{p}} - \bar{n}_{\mathbf{k}-\mathbf{q}}) + (\bar{J}_{\mathbf{p}} + \bar{J}_{\mathbf{k}-\mathbf{q}})\bar{m}_{\mathbf{k}-\mathbf{q}}(\bar{n}_{\mathbf{p}} - \bar{n}_{\mathbf{p}+\mathbf{q}})]\delta(\epsilon_{\mathbf{k}-\mathbf{q}} + \epsilon_{\mathbf{p}+\mathbf{q}} - \epsilon_{\mathbf{p}} - \epsilon_{\mathbf{k}})\}, \tag{24}$$

with

$$V_{\mathbf{q},\mathbf{k}-\mathbf{q}} = \cos^2\theta\bar{J}_{\mathbf{q}} - \frac{1}{2}\sin^2\theta\bar{J}_{\mathbf{k}-\mathbf{q}}, \tag{25}$$

$$\bar{J}_{\mathbf{q}} = J_{\mathbf{q}} + \frac{1}{4}\sigma^2 J_{\mathbf{q}}'\cos^2\theta, \tag{26}$$

$$\bar{n}_{\mathbf{q}} = \langle b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}\rangle = \frac{\sigma}{2}\left[\frac{\epsilon_{\mathbf{q}}^{11}}{\epsilon_{\mathbf{q}}}\coth\left(\frac{\epsilon_{\mathbf{q}}}{2T}\right) - 1\right], \tag{27}$$

$$\bar{m}_{\mathbf{q}} = \langle b_{-\mathbf{q}}^{\dagger}b_{\mathbf{q}}^{\dagger}\rangle = \langle b_{\mathbf{q}}b_{-\mathbf{q}}\rangle = -\frac{\epsilon_{\mathbf{q}}^{12}}{2\epsilon_{\mathbf{q}}}\coth\left(\frac{\epsilon_{\mathbf{q}}}{2T}\right). \tag{28}$$

$\gamma_{ss}(\mathbf{k})$ takes its maximum values at $\mathbf{k} = 0$; it increases with decreasing tunneling frequency Ω.

γ_{sp} is the damping due to the spin-phonon interaction,

$$\gamma_{sp} = \frac{\pi\sin^2\theta}{4}F_{\mathbf{k}}^2\delta(\bar{\omega}_{\mathbf{k}} - \epsilon_{\mathbf{k}}) + \frac{\pi\cos^2\theta}{N}\sum_{\mathbf{q}}F_{\mathbf{q}}^2[(\bar{N}_{\mathbf{q}} - \bar{n}_{\mathbf{k}-\mathbf{q}})\delta(-\bar{\omega}_{\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}}) + (1 + \bar{N}_{\mathbf{q}} + \bar{n}_{\mathbf{k}-\mathbf{q}})\delta(\bar{\omega}_{\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}})] + \frac{\pi\cos^2\theta}{2N^2}\sum_{\mathbf{q},\mathbf{p}}R^2(\mathbf{q},\mathbf{p})[\bar{N}_{\mathbf{p}}(1 + \bar{N}_{\mathbf{q}} + \bar{n}_{\mathbf{k}+\mathbf{p}-\mathbf{q}}) - \bar{N}_{\mathbf{q}}\bar{n}_{\mathbf{k}+\mathbf{p}-\mathbf{q}}]\delta(\bar{\omega}_{\mathbf{q}} - \bar{\omega}_{\mathbf{p}} + \epsilon_{\mathbf{k}+\mathbf{p}-\mathbf{q}} - \epsilon_{\mathbf{k}}) + \frac{\pi\sin^2\theta}{8N}\sum_{\mathbf{q}}R^2(\mathbf{q},\mathbf{k}+\mathbf{q})(\bar{N}_{\mathbf{q}} - \bar{N}_{\mathbf{k}+\mathbf{q}}) \times \delta\,(\bar{\omega}_{\mathbf{k}+\mathbf{q}} - \bar{\omega}_{\mathbf{q}} - \epsilon_{\mathbf{k}}), \tag{29}$$

with

$$\bar{N}_{\mathbf{q}} = \langle a^{\dagger}_{\mathbf{q}} a_{\mathbf{q}} \rangle = 1/[\exp(\bar{\omega}_{\mathbf{q}}/T) - 1]. \tag{30}$$

At $T = 0$, Eq. (29) simplifies to

$$\gamma_{sp}(T=0) = \frac{\pi}{4}\sin^2\theta F^2_{\mathbf{k}}\delta(\bar{\omega}_{\mathbf{k}} - \epsilon_{\mathbf{k}}) + \frac{\pi\cos^2\theta}{N}\sum_{\mathbf{q}} F^2_{\mathbf{q}}\delta(\bar{\omega}_{\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}}). \tag{31}$$

At low temperatures γ_{sp} is very small. The anharmonic terms do not contribute to the spin-wave damping at $T = 0$. With increasing temperature , the damping γ_{sp} increases, and the contribution of the anharmonic term increases, too. For temperatures close to T_c and above T_c we obtain

$$\gamma_{sp}(T \geq T_c) = \frac{\pi\sin^2\theta}{4}F^2_{\mathbf{k}}\delta(\bar{\omega}_{\mathbf{k}} - \epsilon_{\mathbf{k}}) + \frac{\pi\sin^2\theta}{8N}\sum_{\mathbf{q}} R^2(\mathbf{q}, \mathbf{k}+\mathbf{q})(\bar{N}_{\mathbf{q}} - \bar{N}_{\mathbf{k}+\mathbf{q}})\delta(\bar{\omega}_{\mathbf{k}+\mathbf{q}} - \bar{\omega}_{\mathbf{q}} - \epsilon_{\mathbf{k}}). \tag{32}$$

The first term is temperature independent. Hence the anharmonic terms give the main contribution to the spin-wave damping γ_{sp} in the vicinity of T_c and above T_c, and so they must be taken into account.

For all temperatures below and above T_c and for small wave vectors $\mathbf{k}$ the damping due to the spin-phonon interaction is small in comparison with the damping due to the spin-spin interaction,

$$\gamma_{sp}(\mathbf{k}) \ll \gamma_{ss}(\mathbf{k}). \tag{33}$$

For the phonon damping we obtain the following expression in the ferroelectric region:

$$\begin{aligned}
\gamma_{\mathrm{ph}}(\mathbf{k}) = {} & \frac{\pi\sigma\sin^2\theta}{4}F^2_{\mathbf{k}}\delta(\epsilon_{\mathbf{k}} - \bar{\omega}_{\mathbf{k}}) \\
& + \frac{\pi\sigma\cos^2\theta}{N^2}\sum_{\mathbf{q},\mathbf{p}} R^2(\mathbf{k},\mathbf{q},\mathbf{p})[\bar{n}_{\mathbf{p}}(1 + \bar{N}_{\mathbf{q}} + \bar{n}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}) - \bar{N}_{\mathbf{q}}\bar{n}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}]\delta(\bar{\omega}_{\mathbf{q}} - \epsilon_{\mathbf{p}} + \epsilon_{\mathbf{p}+\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) \\
& + \frac{\pi\sigma\sin^2\theta}{4N}\sum_{\mathbf{q}} R^2(\mathbf{q},\mathbf{k})[(\bar{N}_{\mathbf{q}} - \bar{n}_{\mathbf{k}-\mathbf{q}})\delta(\bar{\omega}_{\mathbf{q}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) + (1 + \bar{N}_{\mathbf{q}} + \bar{n}_{\mathbf{k}-\mathbf{q}})\delta(\bar{\omega}_{\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}})] \\
& + \frac{16\pi}{N^2}\sum_{\mathbf{q},\mathbf{p}} A^2(\mathbf{k},\mathbf{q},\mathbf{p})[\bar{N}_{\mathbf{p}}(1 + \bar{N}_{\mathbf{q}} + \bar{N}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}) - \bar{N}_{\mathbf{q}}\bar{N}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}]\delta(\bar{\omega}_{\mathbf{q}} - \bar{\omega}_{\mathbf{p}} + \bar{\omega}_{\mathbf{p}+\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) \\
& + \frac{9\pi}{N}\sum_{\mathbf{q}} B^2(\mathbf{k},\mathbf{q})(\bar{N}_{\mathbf{q}} - \bar{N}_{\mathbf{k}-\mathbf{q}})[\delta(\bar{\omega}_{\mathbf{q}} - \bar{\omega}_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) - \delta(-\bar{\omega}_{\mathbf{q}} + \bar{\omega}_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}})].
\end{aligned} \tag{34}$$

At $T = 0$, Eq. (34) simplifies to

$$\gamma_{\mathrm{ph}}(T=0) = \frac{\pi\sigma\sin^2\theta}{4}F^2_{\mathbf{k}}\delta(\epsilon_{\mathbf{k}} - \bar{\omega}_{\mathbf{k}}). \tag{35}$$

Provided that the δ function can be satisfied, we get a phonon damping at $T = 0$ due to the spin-phonon coupling. The anharmonic terms do not contribute to γ_{ph} at $T = 0$ and at low temperatures.

With increasing temperature γ_{ph} increases, but remains finite at $T = T_c$. The phonon damping in the paraelectric region is given by the last two terms in Eq. (34):

$$\begin{aligned}
\gamma_{\mathrm{ph}}(T \geq T_c) = {} & \frac{16\pi}{N^2}\sum_{\mathbf{q},\mathbf{p}} A^2(\mathbf{k},\mathbf{q},\mathbf{p})[\bar{N}_{\mathbf{p}}(1 + \bar{N}_{\mathbf{q}} + \bar{N}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}) - \bar{N}_{\mathbf{q}}\bar{N}_{\mathbf{p}+\mathbf{k}-\mathbf{q}}]\delta(\bar{\omega}_{\mathbf{q}} - \bar{\omega}_{\mathbf{p}} + \bar{\omega}_{\mathbf{p}+\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) \\
& + \frac{9\pi}{N}\sum_{\mathbf{q}} B^2(\mathbf{k},\mathbf{q})(\bar{N}_{\mathbf{q}} - \bar{N}_{\mathbf{k}-\mathbf{q}})[\delta(\bar{\omega}_{\mathbf{q}} - \bar{\omega}_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}}) - \delta(-\bar{\omega}_{\mathbf{q}} + \bar{\omega}_{\mathbf{k}-\mathbf{q}} - \bar{\omega}_{\mathbf{k}})].
\end{aligned} \tag{36}$$

We can see that only the anharmonic terms contribute to the phonon damping in the vicinity of T_c and above T_c; and so they play an important role.

For small wave vector $\mathbf{k}$ and at temperatures above T_c γ_{ph} is small compared with the spin-wave damping γ^{11},

$$\gamma_{\mathrm{ph}}(\mathbf{k}) \ll \gamma^{11}(\mathbf{k}). \tag{37}$$

IV. THE DYNAMICAL STRUCTURE FACTOR

The 4×4 matrix, Eq. (7), can be diagonalized for different limiting cases.[20] Two limiting cases are those of real coupling, i.e., $\gamma^{13}_{\mathbf{k}} = 0$, or of imaginary coupling with $\epsilon^{13}_{\mathbf{k}} = 0$. In general, therefore, there are an infinite number of mathematically correct descriptions of a coupled-

mode spectrum. As Barker and Hopfield[20] pointed out several years earlier, any ir or Raman spectrum of two coupled modes may be fitted exactly with either a real off-diagonal matrix element or an imaginary coupling constant.

We assume at first a real coupling energy, i.e., $\gamma_{\mathbf{k}}^{13}=0$. As can be seen from Eq. (16), $\epsilon_{\mathbf{k}}^{13}$ is temperature independent and it has a finite value at T_c. For $\Omega \to 0$ $\epsilon_{\mathbf{k}}^{13}$ goes to zero. In this limit then no or a very small coupling exists between the spin waves and the phonons. This means also that the deuterated materials must have a much smaller coupling constant, which is in agreement with the experimental data. $\epsilon_{\mathbf{k}}^{13}$ is proportional to $\Omega(16)$, whereas $\gamma_{\mathbf{k}}^{13} \sim \Omega^3(17)$. For substances with smaller tunneling field, i.e., $\Omega/J_0 \ll 1$, it is valid: $\gamma_{\mathbf{k}}^{13} \ll \epsilon_{\mathbf{k}}^{13}$, so that this limiting case gives a better fit to the experimental data. Raman spectroscopic[21] and dielectric[10] results show, in contrast to the case of KDP crystal, a very low value of the tunneling integral in LHP [$\Omega = 2.168$ cm^{-1} for LHP and $\Omega = 0.273$ cm^{-1} for LDP (Ref. 6)] as well as a very small value of the soft proton mode although very large changes of T_c and the Curie-Weiss constant C occur on deuteration. So this limiting case of real coupling, i.e., $\gamma_{\mathbf{k}}^{13}=0$, must be considered in the case of LHP and LDP.

The transverse dynamic structure factor $S^{xx}(\mathbf{k},E)$ is calculated via the imaginary part of $G^{xx}(\mathbf{k},E)$ [Eq. (11)]. We obtain this in the form

$$S^{xx}(\mathbf{k},E)=\frac{4\sigma(\epsilon_{\mathbf{k}}^{11}-\epsilon_{\mathbf{k}}^{12})}{1-e^{-E/T}} \times \frac{\mathrm{Re}\Gamma_{\mathbf{k}}^{xx}(E)}{[E^2-\epsilon_{\mathbf{k}}^2-\mathrm{Im}\Gamma_{\mathbf{k}}^{xx}(E)]^2+[\mathrm{Re}\Gamma_{\mathbf{k}}^{xx}(E)]^2}, \tag{38}$$

with

$$\mathrm{Re}\Gamma_{\mathbf{k}}^{xx}(E)=E\left(\frac{8(\epsilon_{\mathbf{k}}^{13})^2\bar{\omega}_{\mathbf{k}}\gamma_{\mathrm{ph}}(\epsilon_{\mathbf{k}}^{11}-\epsilon_{\mathbf{k}}^{12})}{(E^2-\bar{\omega}_{\mathbf{k}}^2-\gamma_{\mathrm{ph}}^2)^2+4\gamma_{\mathrm{ph}}^2E^2}+2\gamma_{\mathbf{k}}^{11}\right), \tag{39}$$

$$\mathrm{Im}\Gamma_{\mathbf{k}}^{xx}(E)=\frac{4(\epsilon_{\mathbf{k}}^{13})^2\bar{\omega}_{\mathbf{k}}(\epsilon_{\mathbf{k}}^{11}-\epsilon_{\mathbf{k}}^{12})(E^2-\bar{\omega}_{\mathbf{k}}^2-\gamma_{\mathrm{ph}}^2)}{(E^2-\bar{\omega}_{\mathbf{k}}^2-\gamma_{\mathrm{ph}}^2)^2+4\gamma_{\mathrm{ph}}^2E^2}. \tag{40}$$

Equation (38) shows a three-peak structure.

In the ferroelectric region exists a central peak centered at $E=0$, the width of which is

$$\Gamma_c=\gamma_{\mathrm{ph}}\frac{\epsilon_{\mathbf{k}}^2}{\epsilon_{\mathbf{k}}^2+4(\epsilon_{\mathbf{k}}^{13})^2}, \tag{41}$$

and two soft-mode peaks of the width

$$\Gamma_s=\gamma_{\mathrm{ph}}\frac{4(\epsilon_{\mathbf{k}}^{13})^2}{\epsilon_{\mathbf{k}}^2+4(\epsilon_{\mathbf{k}}^{13})^2}+2\gamma_{\mathbf{k}}^{11}. \tag{42}$$

The soft-mode peaks are situated at

$$\omega_s=\pm\sqrt{\epsilon_{\mathbf{k}}^2+2(\epsilon_{\mathbf{k}}^{13})^2}. \tag{43}$$

At low temperatures S^{xx} exhibits only the sharp soft-mode peak. As T increases the soft-mode peak becomes lower and wider and shifts towards the origin. At higher temperatures a central peak appears additionally to the soft-mode peaks. Approaching T_c the intensity moves from the soft-mode peak to the central peak. The central peak comes out to be very narrow. The frequency of the soft mode does not reach zero at $T=T_c$, but it remains finite,

$$\omega_s(T_c)\approx\sqrt{2\epsilon_{\mathbf{k}}^{13}}. \tag{44}$$

The central peak is due to the coupling between the transverse soft mode and the acoustic-phonon mode.

Deuteration causes a reduction of the frequency of the soft ferroelectric mode and we obtain

$$\epsilon_{\mathrm{LDP}}(\mathbf{k}) \ll \epsilon_{\mathrm{LHP}}(\mathbf{k}). \tag{45}$$

The ferroelectric soft mode for LHP-type FE's is underdamped for low temperatures and overdamped near and above T_c. The spin-spin damping increases with decreasing tunneling frequency Ω,

$$\gamma_{\mathrm{LDP}}(\mathbf{k}) \gg \gamma_{\mathrm{LHP}}(\mathbf{k}). \tag{46}$$

Therefore the underdamped character of the soft mode should disappear on deuteration due to the decrease in the tunneling integral Ω,

$$\epsilon_{\mathrm{LDP}}(\mathbf{k}) \ll \gamma_{\mathrm{LDP}}(\mathbf{k}). \tag{47}$$

The ferroelectric mode in LDP is heavily overdamped, in agreement with the experimental data.[2]

In the case of deuteration, where (45) is valid, the soft-mode peaks shifts towards the origin and its intensity decreases. In LDP the peak around the soft ferroelectric mode is absent and the ferroelectric mode spectra below T_c consist only of the central peak around $E=0$. The height of the central peak increases as $T \to T_c$.

Above T_c the ferroelectric mode in LHP and LDP is overdamped. S^{xx} is represented by a peak centered at $E=0$. For $T \to T_c$ this central peak becomes higher and narrower. This is in agreement with the experimental results of Shin *et al.*[1] The peak in the deuterated case is much smaller than in the undeuterated case; then the width of the central peak (41) is proportional to the phonon damping: $\Gamma_c \sim \gamma_{\mathrm{ph}} \sim \Omega^2$. As a consequence deuteration ($\Omega \approx 0$) may decrease the width of the central peak, in agreement with Shin *et al.*[2]

We have shown that the anharmonic terms in γ_{ph} (34) play an important role in the vicinity of T_c and above T_c. It is evident that they give the main contribution to the central peak in LHP and LDP.

The numerical calculations are in preparation and will be published elsewhere.

V. CONCLUSIONS

In the generalized Hartree-Fock approximation we get the renormalized energy of the spin waves and the

phonons. The phonon energy is renormalized due to the anharmonicity effects. Deuteration causes a reduction of the frequency of the soft ferroelectric mode, $\epsilon_{\mathrm{LDP}}(\mathbf{k}) \ll \epsilon_{\mathrm{LHP}}(\mathbf{k})$, and an increase in the spin-spin damping, $\gamma_{\mathrm{LDP}}(\mathbf{k}) \gg \gamma_{\mathrm{LHP}}(\mathbf{k})$. As a consequence the underdamped character of the soft mode disappears on deuteration due to the decrease in the tunneling integral Ω, $\epsilon_{\mathrm{LDP}}(\mathbf{k}) \ll \gamma_{\mathrm{LDP}}(\mathbf{k})$. The ferroelectric mode in LDP is heavily overdamped.

The coupling constant $\epsilon_{\mathbf{k}}^{13}$ is temperature independent. It has a finite value at T_c. For $\Omega \to 0$, $\epsilon_{\mathbf{k}}^{13}$ goes to zero. In this limit no or very small coupling exists between the spin waves and the phonons. This means that the deuterated materials must have a much smaller coupling constant which is in agreement with the experimental data.

The dynamical structure factor $S^{xx}(\mathbf{k}, E)$ exhibits three peaks: a central peak centered at $E = 0$ and two soft-mode peaks situated at $\omega_s = \pm\sqrt{\epsilon_{\mathbf{k}}^2 + 2(\epsilon_{\mathbf{k}}^{13})^2}$. In LDP the peak around the soft ferroelectric mode is absent and the ferroelectric mode spectra below T_c consist only of the central peak around $E = 0$.

Above T_c the ferroelectric mode in LHP and LDP is overdamped. S^{xx} is represented by a peak centered at $E = 0$. The peak intensity of the central mode increases and its half width becomes narrower as the temperature decreases toward T_c, in agreement with the experimental data.[1] The peak in the deuterated case is much smaller than in the undeuterated case, in agreement wit Shin *et al.*[2]

The central peak is due to the coupling between the transverse soft mode and the acoustic-phonon-mode. The width of the central peak is proportional to the phonon-mode damping. We have shown that the anharmonic terms play an important role in the vicinity of T_c and above T_c. It is evident that they give the main contribution to the intensity and the half width of the central peak and must be taken into account if we want to obtain correct results.

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