The Green's function technique for spin-phonon interactions in squaric acid

1995 J. Phys.: Condens. Matter 7 1701

(http://iopscience.iop.org/0953-8984/7/8/016)

J. Phys.: Condens. Matter 7 (1995) 1701–1709. Printed in the UK

The Green's function technique for spin–phonon interactions in squaric acid

J M Wesselinowa†, A T Apostolov† and M S Marinov‡

† Department of Physics, University of Sofia, Boulevard J Bouchier 5, 1126 Sofia, Bulgaria
‡ Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Rakovski Street 92, 1000 Sofia, Bulgaria

Received 6 July 1994, in final form 10 October 1994

Abstract. A Green's function technique is used to study the effects of spin–phonon interactions in squaric acid including higher-order anharmonic terms. The renormalized energy and the damping of the spin waves and the phonons have been evaluated for the first time. The anharmonicity effects play an important role in the vicinity of T_c and above T_c.

1. Introduction

Blinc [1] and de Gennes [2] proposed the Ising model in a transverse field for the description of order–disorder ferroelectrics (FE). In the theoretical studies of the Ising model it has been shown that a first-order phase transition is possible only if the number of coupled spins is four or larger [3–5]. A first-order phase transition in certain order–disorder FE has been observed recently. The transition of $C_4H_2O_4$ near $T_c = 373$ K is just one example [6]. The squaric acid ($C_4H_2O_4$, H_2SQ) has a layered structure [7]. Each molecule is a square with oxygen ions at its four vertices linked by hydrogen bonds on equal footing. At room temperature the layers are ferroelectrically ordered and antiferroelectrically stacked. Protons move randomly along the hydrogen bonds above the transition temperature and ordered motion results at a critical temperature. The net dipole moment produced in this case lies in the plane of the square, a different situation from that of KDP [8], one of the typical order–disorder FE. So, it is clear that in a ferroelectric material of order–disorder type, the four hydrogen bonds usually appear as a group and every one is equivalent to another. This means that the four-body interaction in such structures is generally important. In fact, Deiningham and Mehring [7] have pointed out the existence of four-body interaction in the $C_4H_2O_4$ structure but neglected it in their calculations; hence, their result is still a second-order phase transition.

Recently Wang *et al* [9, 10] on the basis of the pseudospin theory have considered the four-spin interaction to study the first-order phase transition in squaric acid. The critical behaviour is investigated and characteristic temperatures are calculated. The relative polarization is discussed. Using the same model and the method of the retarded Green's function Wesselinowa and Marinov [11] have determined the relative polarization, the spin-wave energy and the damping and discussed these for different model parameters and for different temperatures. Chaudhuri *et al* [12] have investigated the temperature dependences of the dielectric properties at different fixed pressures and the phase transition of H_2SQ and its deuterated form using the four-sublattice pseudospin cluster Hamiltonian,

0953-8984/95/081701+09$19.50

together with a pseudospin–phonon interaction term. The small value of the transition entropy ΔS observed in H_2SQ [13] seems to be due to the large value of the proton–lattice interaction constant, i.e. this indicated the importance of proton–phonon and phonon–phonon interactions. Recently Serra *et al* [14] have investigated the temperature dependence of some Raman modes of KDP below the ferroelectric phase transition. Two lattice modes display an exponential dependence on T which is explained by third- and fourth-order anharmonic effets.

Matsubara *et al* [15] presented a microscopic theory to explain the improper ferroelastic phase transition in squaric acid. It was shown that the strong coupling between the lattice distortion and the proton system is important. H_2SQ belongs to the space group C_{4h}. The spontaneous strain tensor should be either $\varepsilon_1 - \varepsilon_2$ or ε_6 which have symmetry of B_g type. Then, the possible lowest-order coupling between the strain and order parameter is linear in the strain and quadratic in the order parameter. Within the molecular field approximation, they discussed the thermodynamic properties of the model system and calculated theoretically the elastic constant and dielectric susceptibility. They have left many interesting dynamical problems untouched. These include the intensity and line width of Raman scattering [16, 17], the spin–lattice relaxation time in NMR experiment and so on [18–20]. It will be an interesting theoretical problem to work out such dynamical properties on the basis of a model which can afford a good account of the static properties [9–11].

This is the aim of the present paper—to extend the treatment of our previous paper [11] including the spin–phonon interaction, i.e. the calculation of the static and dynamic properties of order–disorder FE with first-order phase transitions on the basis of the Ising model in a transverse field including four-spin and spin–phonon interactions, taking into account higher-order anharmonic phonon interaction terms.

2. Model and method

The Hamiltonian of the coupled pseudospin–phonon model is given by

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

H_s is the Hamiltonian of the pseudospin system

$$H_s = -2\Omega \sum_i S_i^x - \frac{1}{2}\sum_{i,j} J_{ij} S_i^z S_j^z - \frac{1}{4}\sum_{i,j,k,l} K_{ijkl} S_i^z S_j^z S_k^z S_l^z \tag{2}$$

where Ω is the tunnelling frequency. J_{ij} is the two-body coupling and it represents the coupling between protons in neighbouring layers as well as those in the same layer. The four-body coupling K_{ijkl} represents the interaction between the four hydrogen bonds in the C_4O_4 group.

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

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

where Q_q, P_q and ω_q are, respectively, the normal coordinate, momentum and frequency of the lattice mode with wave vector q. The vibrational normal coordinate Q_q and the momentum P_q can be expressed in terms of phonon creation and annihilation operators:

$$Q_q = (2\omega_q)^{-1/2}(a_q + a_{-q}^\dagger) \qquad P_q = \mathrm{i}(\omega_q/2)^{1/2}(a_q^\dagger - a_{-q}) \tag{4}$$

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

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

$$H_{sp} = -\sum_{q,\ p} \bar{F}(p, q) Q_{p-q} S_q^z S_{-p}^z - \frac{1}{2} \sum_{q,\ p,\ k} \bar{R}(k,\ p,\ q) Q_k Q_{-k+p-q} S_q^z S_{-p}^z \tag{5}$$

where $\bar{F}$ and $\bar{R}$ designate the amplitudes

$$\bar{F}(p, q) = \frac{1}{\sqrt{N}} \sum_h \frac{1}{h} (e_{p-q} \cdot h) J'(h) (e^{ip \cdot h} + e^{iq \cdot h})$$

$$F(p, q) = \bar{F}(p, q)/(2\omega_{p-q})^{1/2}$$

and

$$\bar{R}(k, p, q) = -\frac{1}{\sqrt{N}} \sum_h \left[(J''(h) - \frac{J'(h)}{h} \frac{(e_k \cdot h)(e_{-k+p-q} \cdot h)}{h^2} + \frac{J'(h)}{h} (e_k \cdot e_{-k+p-q}) \right] (1 - e^{ik \cdot h})(e^{ip \cdot h} + e^{iq \cdot h})$$

$$R(k, p, q) = \bar{R}(k, p, q)/(4\omega_k \omega_{-k+p-q})^{1/2}$$

for coupling phonons to the spin-wave excitations in H_s in first and second order, respectively. The summations extend over the vector $r_i - r_j = h$ connecting all possible pairs of spin sites in the crystal, and e_q is the polarization of the phonon with wave number q.

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 xz 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

$$\tilde{G}_k(t) = -i\Theta(t) \langle [B_k(t);\ B_k^\dagger] \rangle. \tag{7}$$

The operator B_k stands symbolically for the set b_k, $b_{-k}^\dagger$, a_k, $a_{-k}^\dagger$. For an approximate evaluation of this Green's function we use Tserkovnikov's method [21], which is appropriate for spin problems. After a formal integration of the equation of motion for the Green function one obtains

$$\tilde{G}_k(t) = -i\Theta(t) \langle [B_k;\ B_k^\dagger] \rangle \exp(-iE_k(t)t) \tag{8}$$

where

$$E_k(t) = \varepsilon_k - \frac{i}{t} \int_0^t dt' t' \left(\frac{\langle [j_k(t),\ j_k^\dagger(t')] \rangle}{\langle [B_k(t),\ B_k^\dagger(t')] \rangle} - \frac{\langle [j_k(t),\ B_k^\dagger(t')] \rangle \langle [B_k(t),\ j_k^\dagger(t')] \rangle}{\langle [B_k(t),\ B_k^\dagger(t')] \rangle^2} \right) \tag{9}$$

with $j_k = [B_k, H_{\rm int}]$. The time-independent term

$$\varepsilon_k = \langle [[B_k, H], B_k^\dagger] \rangle / \langle [B_k, B_k^\dagger] \rangle \tag{10}$$

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

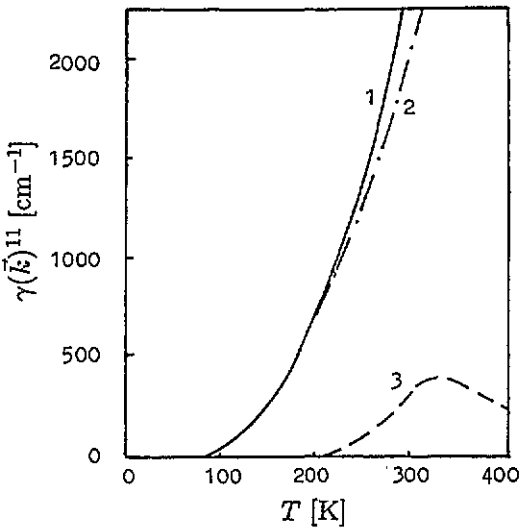

Figure 1. Temperature dependence of the spin-wave damping: 1, $\gamma(k)^{11}$; 2, $\gamma_{\rm ss}$; 3, $\gamma_{\rm sp}$.

3. The spin-wave spectrum

3.1. The generalized Hartree–Fock approximation

The energy of the coupled mode in the generalized Hartree–Fock approximation is

$$E^2(k) = 0.5[\bar{\omega}_k^2 + \varepsilon_k^2 \pm ((\bar{\omega}_k^2 - \varepsilon_k^2)^2 + 4\sigma\bar{\omega}_k \sin^2\theta J_{\rm eff}^2(k) \times (2\Omega \sin\theta + 0.5\sigma J_{\rm eff} \cos^2\theta))^{1/2}]. \tag{11}$$

The E_- mode describes an in-phase motion of the pseudospin system and the lattice, whereas in the E_+ mode the two systems move with opposite phase. In the case of $\Omega \to 0$ equation (11) shows, since $\sin\theta \sim \Omega$, that no coupling exists between the spin waves and the phonons. $\bar{\omega}_k$ is the renormalized energy of the phonons and will be discussed in the next section. ε_k is the energy of the pseudospin system:

$$\epsilon(k) = \pm\sqrt{(\epsilon_k^{11})^2 - (\epsilon_k^{12})^2} \tag{12}$$

with

$$\epsilon_k^{11} = 2\Omega \sin\theta + \frac{\sigma}{2} J_{\rm eff} \cos^2\theta - \frac{\sigma}{4} \sin^2\theta J_{\rm eff}(k) \tag{13}$$

$$\epsilon_k^{12} = -\frac{\sigma}{4} \sin^2\theta J_{\rm eff}(k). \tag{14}$$

$\sigma(T)$ is the relative polarization in the direction of the mean field which is equal to $2\langle S^{z'} \rangle$ [11]. In the generalized Hartree–Fock approximation we find the following two solutions

for the rotation angle θ:

$$\cos\theta = 0 \quad (\text{i.e.} \quad \theta = \pi/2) \qquad \text{if} \quad T \geqslant T_c \tag{15}$$

$$\sin\theta = 4\Omega/(\sigma J_{\text{eff}}) = \sigma_c/\sigma \quad \text{if} \quad T \leqslant T_c \tag{16}$$

$$J_{\text{eff}} = J_0 + \frac{1}{4}\sigma^2 K_0 \cos^2\theta + R_0 + \frac{2F_0(0.5\sigma^2\cos^2\theta F_k - B_0)\delta_{k0}}{\omega_k - 0.5\sigma^2\cos^2\theta R_k + A_k}. \tag{17}$$

From the last equation (17) it is evident that the pseudospin–phonon interaction leads to a renormalization of the spin–spin interaction constant, which is now temperature dependent. Proton–phonon interactions can thus produce a phase transition even though the direct spin–spin interaction constant would be zero. The effects of the phonon anharmonicity parameters A_k and B_k are to decrease the effective exchange coupling J_{eff} while the effects of the pseudospin–lattice coupling F_k and R_k are to increase its value. These observations for A_k and F_k are in agreement with those of Ganguli *et al* [22]. The terms containing R_k and B_k are not taken into account in this work [22].

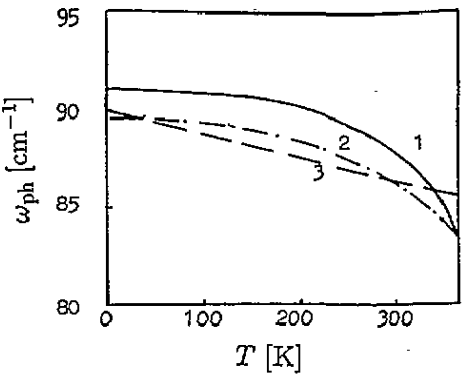

Figure 2. Temperature dependence of the phonon mode with $\omega_0 = 90$ cm^{-1}: 1, $\bar{\omega}_{ph}$; 2, $F_0 = 0$, $R_0 = 0$, i.e. without spin–phonon interaction; 3, $A_0 = 0$, $F_0 = 0$, $R_0 = 0$, i.e. without fourth-order anharmonic phonon interaction.

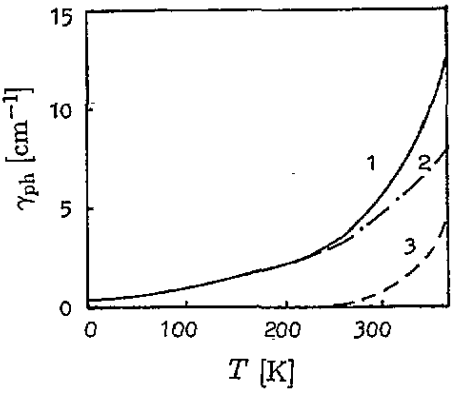

Figure 3. Temperature dependence of the phonon damping with $\omega_0 = 90$ cm^{-1}: 1, $\gamma_{ph}(k)$; 2, $F_0 = 0$, $R_0 = 0$; 3, $A_0 = 0$, $B_0 = 0$.

3.2. Spin-wave damping

In order to obtain spin-wave damping caused by the spin–phonon interaction we consider approximately the integral term in (9). In our calculations we use the approximate dynamics $b_k(t) \approx b_k \exp(-i\varepsilon_k t)$ and $a_k(t) \approx a_k \exp(-i\bar{\omega}_k t)$. We get the following expression for γ_k^{11}:

$$\gamma(k)^{11} = \gamma_{ss} + \gamma_{sp}. \tag{18}$$

γ_{ss} is the damping part which comes from the spin–spin interaction and has been discussed in our previous paper [11]:

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

$$+(\bar{J}_p + \bar{J}_{k-q})\bar{m}_{k-q}(\bar{n}_p - \bar{n}_{p+q})]\,\delta(\varepsilon_{k-q} + \varepsilon_{p+q} - \varepsilon_p - \varepsilon_k)) \tag{19}$$

with

$$V_{q,\,k-q} = \cos^2\theta\,\bar{J}_q - \frac{1}{2}\sin^2\theta\,\bar{J}_{k-q} \tag{20}$$

$$\bar{J}_q = J_q + \frac{1}{4}\sigma^2 K_q \cos^2\theta \tag{21}$$

$$\bar{n}_q = \langle b_q^\dagger b_q\rangle = \frac{\sigma}{2}\left(\frac{\varepsilon_q^{11}}{\varepsilon_q}\coth\left(\frac{\varepsilon_q}{2T}\right) - 1\right) \tag{22}$$

$$\bar{m}_q = \langle b_{-q}^\dagger b_q^\dagger\rangle = \langle b_q b_{-q}\rangle = -\frac{\varepsilon_q^{12}}{2\varepsilon_q}\coth\left(\frac{\varepsilon_q}{2T}\right). \tag{23}$$

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

γ_{sp} is the damping due to the spin–phonon interaction:

$$\gamma_{sp} = \frac{\pi\sin^2\theta\cos^2\theta}{4\sigma}F_k^2\,\delta(\bar{\omega}_k - \varepsilon_k)$$
$$+\frac{\pi(4\cos^4\theta + \sin^4\theta)}{4N}\sum_q F_{kq}^2[(\bar{N}_{k-q} - \bar{n}_q)\,\delta(\varepsilon_q + \bar{\omega}_{k-q} - \varepsilon_k)$$
$$+(1 + \bar{N}_{q-k} + \bar{n}_q)\,\delta(\varepsilon_q - \bar{\omega}_{q-k} - \varepsilon_k)] + \frac{\pi(8\cos^4\theta + \sin^4\theta)}{16N^2}\sum_{q,\,p} R_{pqk}^2$$
$$\times[\bar{N}_p(1 + \bar{N}_{p-q} + \bar{n}_{k+q}) - \bar{N}_{p-q}\bar{n}_{k+q}]\,\delta(\bar{\omega}_p - \bar{\omega}_{p-q} + \varepsilon_{k+q} - \varepsilon_k) \tag{24}$$

with

$$\bar{N}_q = \langle a_q^\dagger a_q\rangle = 1/[\exp(\bar{\omega}_q/T) - 1]. \tag{25}$$

The spin-wave damping (18) was numerically calculated using the following model parameters appropriate for squaric acid: $J_0 = 344$ cm^{-1}, $K_0/J_0 = 1.33$, $\Omega = 2.168$ cm^{-1}, $A_0 = -12$ cm^{-1}, $B_0 = 7$ cm^{-1}, $F_0 = 36$ cm^{-1}, $R_0 = -25$ cm^{-1}, $\omega_0 = 90$ cm^{-1}, $T_c = 373$ K. figure 1 shows the temperature dependence of the spin-wave damping.

At $T = 0$ equation (24) simplifies to

$$\gamma_{sp}(T = 0) = \frac{\pi\sin^2\theta\cos^2\theta}{4\sigma}F_k^2\,\delta(\bar{\omega}_k - \varepsilon_k)$$
$$+\frac{\pi(4\cos^4\theta + \sin^4\theta)}{4N}\sum_q F_{qk}^2\,\delta(\varepsilon_q - \bar{\omega}_{q-k} - \varepsilon_k). \tag{26}$$

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 where σ and $\cos\theta$ vanish we obtain

$$\gamma_{sp}(T \geqslant T_c) = \frac{\pi\sin^4\theta}{4N}\sum_q F_{qk}^2[(1 + \bar{N}_{q-k} + \bar{n}_q)\,\delta(\varepsilon_q - \bar{\omega}_{q-k} - \varepsilon_k) + (\bar{N}_{k-q} - \bar{n}_q)$$
$$\times\delta(\varepsilon_q + \bar{\omega}_{k-q} - \varepsilon_k)]$$

$$+\frac{\pi \sin^4\theta}{16N^2}\sum_{q,p} R^2_{kpq}[(\bar{N}_q(1+\bar{N}_{k+q-p}+\bar{n}_p)-\bar{N}_{k+q-p}\bar{n}_p]$$
$$\times\delta(\bar{\omega}_{k+q-p}-\bar{\omega}_q+\varepsilon_p-\varepsilon_k). \tag{27}$$

It can be seen that the anharmonic terms give a major 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 if we want to obtain correct results.

For small wave vectors k the damping due to the spin–phonon interaction is small in comparison with the damping due to the spin–spin interaction,

$$\gamma_{sp}(k) \ll \gamma_{ss}(k). \tag{28}$$

4. The phonon spectrum

4.1. The phonon energy

For the phonon energy we obtain in the generalized Hartree–Fock approximation the following expression in the ferroelectric region:

$$\bar{\omega}^2_{ph} = \omega^2_k - 2\omega_k\Big(\frac{\sigma^2\cos^2\theta}{4}R_k + \frac{\sin^2\theta}{4N}\sum_q R_{kq}\bar{n}_q$$
$$-\frac{1}{2N}\sum_q A_{kq}(2\bar{N}_q+1) - B_k\langle Q_k\rangle\delta_{k0}\Big) \tag{29}$$

with

$$\langle Q_k\rangle = \langle a_k + a^+_{-k}\rangle = \left(0.5\sigma^2\cos^2\theta F_k - \frac{1}{N}\sum_q B_{kq}(2\bar{N}_q+1)\right)$$
$$\times\left(\omega_k - 0.5\sigma^2\cos^2\theta R_k + \frac{1}{N}\sum_q A_{kq}(2\bar{N}_q+1)\right)^{-1}. \tag{30}$$

The phonon energy ω_k is renormalized due to the anharmonic phonon interaction terms. If they are not taken into account, then $\bar{\omega}_k$ is identical with the energy of the uncoupled phonon ω_k [23]. $\bar{\omega}_{ph}$ is dependent on the tunnelling frequency Ω. The anharmonicity increases the initial phonon frequency. The modification of the phonon frequency appears to be very important [22] as in the case of Rochelle salt where the disappearance of ferroelectricity [24] in presence of foreign impurities was explained [25] by considering the change of renormalized phonon frequency [26].

We have studied the temperature dependence of the phonon frequencies from (29) for one particular phonon mode with $\omega_0 = 90\ \text{cm}^{-1}$ using the same model parameters as in figure 1. The phonon mode displays a non-linear dependence on temperature when T approaches T_c (figure 2). Since it is a lattice mode this behaviour can be described to strong anharmonic effects. It can also be associated with an anomalous increase of the dielectric constant in the same temperature interval. If we take into account only the third-order interaction terms in (3) (i.e. $A_0 = 0, B_0 \neq 0$), then we obtain a linear temperature dependence close to T_c (curve 3). It is evident that there is a strong anharmonicity affecting the phonon modes near the transition point from the ferroelectric to the paraelectric phase. The temperature behaviour of the phonon mode is in very good agreement with the experimental data of Nakashima *et al* [16] and of Samuelson *et al* [17].

4.2. The phonon damping

Calculations yield the following expression for the phonon damping in the ferroelectric region:

$$\gamma_{ph}(k) = \frac{\pi\sigma \sin^2\theta\cos^2\theta}{4} F_k^2\,\delta(\varepsilon_k - \bar{\omega}_k) + \frac{\pi\cos^4\theta}{16} R_k^2\,\delta(\varepsilon_k - \bar{\omega}_k)$$
$$+\frac{\pi\sigma\sin^4\theta}{4N}\sum_q F_{qk}^2(\bar{n}_q - \bar{n}_{q-k})\,\delta(\varepsilon_{q-k} - \varepsilon_q - \bar{\omega}_k)$$
$$+\frac{\pi\sigma(16\cos^4\theta + \sin^4\theta)}{16N^2}\sum_{q,\,p} R_{kqp}^2[\bar{n}_q(1 + \bar{n}_p + \bar{N}_{p+k-q}) - \bar{n}_p\bar{N}_{p+k-q}]$$
$$\times\delta(\bar{\omega}_{k+p-q} + \varepsilon_q - \varepsilon_p - \bar{\omega}_k)$$
$$+\frac{16\pi}{N^2}\sum_{q,\,p} A_{kqp}^2[\bar{N}_p(1 + \bar{N}_q + \bar{N}_{p+k-q}) - \bar{N}_q\bar{N}_{p+k-q}]$$
$$\times\delta(\bar{\omega}_q - \bar{\omega}_p + \bar{\omega}_{p+k-q} - \bar{\omega}_k)$$
$$+\frac{9\pi}{N}\sum_q B_{kq}^2(\bar{N}_q - \bar{N}_{k-q})$$
$$\times[\delta(\bar{\omega}_q - \bar{\omega}_{k-q} - \bar{\omega}_k) - \delta(-\bar{\omega}_q + \bar{\omega}_{k-q} - \bar{\omega}_k)]. \tag{31}$$

Analogously to section 4.1 we want to discuss the phonon damping on temperature, wave vector, and anharmonicity. The temperature dependence of γ_{ph} obtained using the same model parameters as in figure 1 is shown in figure 3.

Firstly we consider the zero-temperature limit $T = 0$:

$$\gamma_{ph}(T = 0) = \left(\frac{\pi\sigma}{4}\sin^2\theta\cos^2\theta F_k^2 + \frac{\pi}{16}\cos^4\theta R_k^2\right)\delta(\epsilon_k - \bar{\omega}_k). \tag{32}$$

Provided that the δ-function can be satisfied, we get a phonon damping at $T = 0$ due to the spin–phonon coupling. The spin–phonon anharmonic terms contribute to γ_{ph} at $T = 0$ and at low temperatures. The phonon–phonon anharmonic terms do not contribute to γ_{ph} at $T = 0$ and at low temperatures. A finite value for γ_{ph} at $T = 0$ was found experimentally in KDP by Serra *et al* [14] and squaric acid by Nakashima *et al* [16] and Samuelson *et al* [17]. 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 (31)

$$\gamma_{ph}(T \geqslant T_c) = \frac{16\pi}{N^2}\sum_{q,\,p} A_{kqp}^2[\bar{N}_p(1 + \bar{N}_q + \bar{N}_{p+k-q}) - \bar{N}_q\bar{N}_{p+k-q}]$$
$$\times\delta(\bar{\omega}_q - \bar{\omega}_p + \bar{\omega}_{p+k-q} - \bar{\omega}_k)$$
$$+\frac{9\pi}{N}\sum_q B_{kq}^2(\bar{N}_q - \bar{N}_{k-q})$$
$$\times[\delta(\bar{\omega}_q - \bar{\omega}_{k-q} - \bar{\omega}_k) - \delta(-\bar{\omega}_q + \bar{\omega}_{k-q} - \bar{\omega}_k)]. \tag{33}$$

We can see that only the third- and fourth-order phonon–phonon anharmonic terms contribute to the phonon damping in the vicinity of T_c and above T_c; and so they play an important role. Above T_c γ_{ph} is nearly temperature independent.

The temperature behaviour of the phonon damping obtained is in very good agreement with the experimental data for H_2SQ [16, 17, 27].

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

$$\gamma_{ph}(k) \ll \gamma^{11}(k). \tag{34}$$

The dynamical structure factor is calculated via the imaginary part of the phonon Green's function $\langle\langle Q_k; Q_{-k}\rangle\rangle$. The intensity increases with increasing temperature, in agreement with the findings of Samuelsen *et al* [17].

5. Conclusions

We have studied the Ising model in a transverse field including four-spin interaction, which is responsible for the first-order phase transition observed in order–disorder FE, and spin–phonon interaction, taking into account higher-order anharmonic phonon interaction terms.

Using the method of the retarded Green's function we have determined the spin-wave and the phonon spectrum. We have shown the importance of the anharmonic terms in the spin–phonon interaction and in the phonon–phonon interaction. If we want to obtain correct results, they must be taken into account. As far as we know, the expressions and the discussion of the spin-wave energy, the phonon energy and the damping are given for the first time.

Acknowledgment

The financial support of this work by the Bulgarian Ministry of Science and Education under contract No F470/94 with the Research Funds Department is gratefully acknowledged.

References

[1] Blinc R 1960 *J. Phys. Chem. Solids* **13** 204
[2] de Gennes P G 1963 *Solid State Commun.* **1** 123
[3] Turban I 1982 *J. Phys. C: Solid State Phys.* **15** L65
[4] Penson K A, Jullien R and Pfeuty P 1982 *Phys. Rev.* B **26** 6334
[5] Igloi F, Kapor D V, Skrinjar M and Solyom J 1986 *J. Phys. A: Math. Phys.* **19** 1189
[6] Fischer G, Peterson J and Michel D 1987 *Z. Phys.* B **67** 387
[7] Deiningham U and Mehring M 1981 *Solid State Commun.* **39** 1257
[8] Kobayashi K K 1968 *J. Phys. Soc. Japan* **24** 497
[9] Wang C L, Qin Z K and Liu D L 1989 *Phys. Rev.* B **40** 680
[10] Wang C L, Qin Z K and Liu D L 1989 *Solid State Commun.* **71** 45
[11] Wesselinowa J M and Marinov M S 1992 *Int. J. Mod. Phys.* B **6** 1181
[12] Chaudhuri B K, Dey P K and Matsuo T 1990 *Phys. Rev.* B **41** 2479
[13] Chaudhuri B K, Ganguli S and Nath D 1981 *Phys. Rev.* B **23** 2308
[14] Serra K C, Melo F E A, Filho F M, Moreira J E and Lemos V 1992 *Phys. Status Solidi* b **170** 113
[15] Matsushita E, Yoshimitsu K and Matsubara T 1980 *Prog. Theor. Phys.* **64** 1176
[16] Nakashima S, Aziza A, Postolee M L and Balkanski M 1979 *Phys. Status Solidi* b **94** 529
[17] Samuelson J, Fjar E and Semmingsen D 1979 *J. Phys. C: Solid State Phys.* **12** 2007
[18] Petersson J and Maier H D 1980 *Ferroelectrics* **24** 157
[19] Suwelack D and Mehring M 1980 *Solid State Commun.* **33** 207
[20] Krüger J K, Maier H D, Petersson J and Unruh H G 1980 *Ferroelectrics* **25** 621
[21] Tserkovnikov Yu A 1971 *Teor. Mat. Fiz.* **7** 250
[22] Ganguli S, Nath D and Chaudhuri B K 1980 *Phys. Rev.* B **21** 2937
[23] Wesselinowa J M 1983 *Phys. Status Solidi* b **116** 71
[24] Jona F and Shirane G 1962 *Ferroelectric Crystals* (London: Pergamon)
[25] Chaudhuri B K, Atake T, Chihara H and Ganguli S 1980 *J. Phys. Soc. Japan* **49** 608
[26] Maradudin A A 1963 *Ferroelectricity* ed E F Weller (Amsterdam: Elsevier) pp 72–100
[27] Bougeard D and Novak A 1978 *Solid State Commun.* **27** 453