On the theory of the central peak in hydrogen-bonded $PbHPO_4$-type ferroelectrics

1990 J. Phys.: Condens. Matter 2 7645

(http://iopscience.iop.org/0953-8984/2/37/009)

J. Phys.: Condens. Matter **2** (1990) 7645–7652. Printed in the UK

On the theory of the central peak in hydrogen-bonded $PbHPO_4$-type ferroelectrics

J M Wesselinowa
Department of Physics, University of Sofia, Boulevard Anton Ivanov 5, 1126 Sofia, Bulgaria

Received 7 July 1989, in final form 9 January 1990

Abstract. The three-dimensional Ising model in a transverse field including the fourth-order interaction is treated by means of the Green function technique to calculate the excitation spectrum 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 temperature dependence of the dynamic structure factor for zero wavevector is calculated numerically taking parameters appropriate to LHP and LDP.

1. Introduction

Lead hydrogen phosphate $PbHPO_4$ (LHP) and its isomorphs form another very interesting group of H-bonded ferroelectrics (FEs) similar to the vastly studied KH_2PO_4 (KDP) family. Both $PbHPO_4$ and its deuterated variety $PbDPO_4$ (LDP) undergo second-order phase transitions at 310 K and 452 K, respectively [1]. Raman spectroscopic and dielectric results show, in contrast with the case of KDP crystals, a very low value of the tunnelling integral as well as a very small value of the soft proton mode although very large changes in the transition temperature T_c and the Curie–Weiss constant C occur on deuteration. The direction of proton ordering, i.e. H-bond direction projected onto the a–c plane is parallel to the direction of spontaneous polarisation; there is no spontaneous polarisation along the b axis because the c glide plane is perpendicular to the b axis. The temperature dependence of proton ordering is in close agreement with that of spontaneous polarisation [2]. This indicates that spontaneous polarisation is the result of the formation of dipoles due to proton ordering. The heavy-atom displacements are almost perpendicular to the direction of spontaneous polarisation, and the temperature dependence of the heavy-atom displacements does not agree with that of spontaneous polarisation.

In view of the above-mentioned differences in the physical properties as well as in the configuration of the H bonds compared with that of the KDP-type FEs, it appears to be very interesting to study the static and dynamic properties of both LHP and LDP FEs to elucidate the mechanism of the phase transition in these and other similar crystals. The properties of the phase transition in H-bonded order–disorder FEs are usually investigated through a study of the motion of protons. The Ising model in a transverse field describes well the soft mode in a KDP-type FEs and the large damping effects observed in these materials. Although in LHP and LDP crystals the PO_4 groups are bound

0953-8984/90/377645 + 08 $03.50

to one another by H bonds in the form of a one-dimensional chain along the c axis, the inter-chain interaction as well as the intra-chain interaction should be considered in the Hamiltonian. The experimental data show that the major contribution to the spontaneous polarisation is proton ordering; so the effect of the lattice vibration can be omitted in our model, but it is necessary to consider higher-order interactions between the pseudo-spins.

Theoretical studies of the properties of LHP and LDP-type FEs have been carried out by several groups of workers [3–10]. LHP as well as CsH_2PO_4 have been considered as a quasi-one-dimensional FEs [3–6] because the PO_4^{3-} ions are one-dimensionally linked into chains along the c axis by the H bonds. The Ising-type model (without considering the tunnelling term) used by Carvalho and Salinas [3] is definitely an oversimplified model for LHP because of the special feature of the H bonds in this crystal. The quantum tunnelling effect was taken into consideration by Blinc *et al* [4], Zinenko [5] and Plascak and Salinas [6]. Blinc *et al* [7] tried to explain the anomalous properties of LHP crystals by considering an additional coupling term $B_{ij}S_i^xS_j^x$ along with the pure tunnelling Hamiltonian. This modification also appears to be inadequate for the LHP crystal to explain the isotope dependence of T_c and C. Chaudhuri *et al* [8] used the pseudo-spin lattice-coupled mode model to study the static and dynamic properties of LHP and LDP. Levstik *et al* [9] have measured the static dielectric constant of the H-bonded FE LHP and the results have been analysed by the quasi-one-dimensional Ising model. They have concluded that tunnelling should be taken into account in LHP as well as in LDP and that the quasi-one-dimensional Ising model does not represent a good description of LHP and LDP.

The one-dimensional characteristic in the phase transition causes the deviation from the Curie–Weiss law in the dielectric constant as is observed in CsH_2PO_4. Slight deviation from the Curie–Weiss law has been reported for LHP [9, 11]. However, very recently, studies of Shin *et al* [12] and Deguchi and Nakamura [13] suggest that the deviation of the dielectric constant from the Curie–Weiss law is very small, i.e. that the one-dimensional nature in the phase transition is not large. At present, it seems that there is no definite evidence for the one-dimensional nature of the phase transition of LHP.

Chunlei *et al* [10] have investigated the thermodynamic properties of LHP and LDP using the three-dimensional transverse Ising model including the fourth-order pseudo-spin interaction and obtained good agreement with the experimental data of the spontaneous polarisation. The dynamic properties are not calculated in [10].

The dynamic dielectric properties of LHP have been studied by several researchers. Happ *et al* [14] measured the complex dielectric constant and concluded that the soft mode is a heavily damped mode with a frequency-dependent damping function, while Kroupa *et al* [15], Deguchi and Nakamura [13] and Shin *et al* [12] reported that the soft mode is a relaxation mode.

Recently a central mode of the H-bonded FE $PbHPO_4$ is found in the para-electric phase by hyper-Raman scattering by Shin *et al* [12]. From the temperature and polarisation dependences of the central mode it is concluded that the central mode is the soft mode of LHP. The temperature dependences of the intensity and the half-width of this central mode follow the Curie–Weiss law. The phase transition can be considered as an order–disorder-type phase transition.

The main aim of this paper is to calculate the dynamic structure factor of the three-dimensional transverse Ising model with fourth-order interaction. Our results are compared qualitatively with the experimental results on the LHP-type FEs.

2. Model and method

The Hamiltonian of the Ising model in a transverse field that we use to describe the phase transition properties of LHP and LDP is

$$H = -\Omega \sum_i S_i^x - \tfrac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \tfrac{1}{4} \sum_{i,j,k,l} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z \tag{1}$$

where Ω represents the tunnelling effect. S_i^z is the proton occupation difference at the two equilibrium positions of the H bond at the ith site; it measures the proton ordering. The first term in (1) is the contribution of the tunnelling effect, the second term represents the dipole contribution, and the third the quadrupoles contribution.

In the ordered phase we have the mean values $\langle S^x \rangle \neq 0$ and $\langle S^z \rangle \neq 0$, and it is appropriate to choose a new coordinate system rotating the original one used in (1) by the angle ϑ in the x–y plane:

$$\begin{aligned} S_l^z &= \tfrac{1}{2}[(1 - 2\rho_l)\cos\vartheta - (b_l^+ + b_l)\sin\vartheta] \\ S_l^x &= \tfrac{1}{2}[(1 - 2\rho_l)\sin\vartheta + (b_l^+ + b_l)\cos\vartheta] \\ S_l^y &= (\mathrm{i}/2)(b_l^+ - b_l). \end{aligned} \tag{2}$$

The rotation angle ϑ is determined by the requirement $\langle S^{x'} \rangle = 0$ in the new coordinate system. b_1 and b_l^+ are the Pauli operators in the rotated system; $\rho_l = b_l^+ b_l$. We are concerned with the case $S = \frac{1}{2}$ throughout the paper.

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

$$\begin{aligned} \mathbf{G}_k(t) &= -\mathrm{i}\theta(t)\langle [B_k(t), B_k^+] \rangle \\ &= \begin{pmatrix} \langle\langle b_k(t); b_k^+ \rangle\rangle & \langle\langle b_k(t); b_{-k} \rangle\rangle & \langle\langle b_k(t); \rho_{-k} \rangle\rangle \\ \langle\langle b_{-k}^+(t); b_k^+ \rangle\rangle & \langle\langle b_{-k}^+(t); b_{-k} \rangle\rangle & \langle\langle b_{-k}^+(t); \rho_{-k} \rangle\rangle \\ \langle\langle \rho_k(t); b_k^+ \rangle\rangle & \langle\langle \rho_k(t); b_{-k} \rangle\rangle & \langle\langle \rho_k(t); \rho_{-k} \rangle\rangle \end{pmatrix}. \end{aligned} \tag{3}$$

The operator B_k stands symbolically for the set b_k, b_{-k}^+, ρ_k. For the approximate calculation of the Green function (3) we use a method proposed by Tserkovnikov [16], which is appropriate for spin problems. After a formal integration of the equation of motion for the Green function one obtains

$$\mathbf{G}_k(t) = -\mathrm{i}\theta(t)\langle [B_k, B_k^+] \rangle \exp[-\mathrm{i}E_k(t)t]$$

where

$$\begin{aligned} E_k(t) = \varepsilon_k - \frac{\mathrm{i}}{t} \int_0^t \mathrm{d}t'\, t' \Bigg(& \frac{\langle [j_k(t), j_k^+(t')] \rangle}{\langle [B_k(t), B_k^+(t')] \rangle} \\ & - \frac{\langle [j_k(t), B_k^+(t')] \rangle \langle [B_k(t), j_k^+(t')] \rangle}{\langle [B_k(t), B_k^+(t')] \rangle^2} \Bigg) \end{aligned} \tag{4}$$

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

$$\varepsilon_k = \langle [[B_k, H], B_k^+] \rangle / \langle [B_k, B_k^+] \rangle \tag{5}$$

gives the spin-wave energy in the generalised Hartree–Fock approximation (GHFA). The time-dependent term includes damping effects.

3. Static properties

In the GHFA we have followed two solutions for the rotation angle ϑ:

$$\begin{array}{lll} \cos\vartheta = 0 & \text{i.e. } \vartheta = \pi/2 & \text{if } T \geqslant T_c \\ \sin\vartheta = 4\Omega/\sigma\bar{J}_0 & \bar{J}_0 = J_0 + \frac{1}{4}\sigma^2 J_0' \cos^2\vartheta & \text{if } T \leqslant T_c. \end{array} \tag{6}$$

The spin-wave energy in the GHFA is

$$\left.\begin{array}{l} \varepsilon_{1/2}(\boldsymbol{k}) = \pm\frac{1}{2}\sigma\bar{J}_0\sqrt{1-\sin^2\vartheta\,\gamma_k} \\ \varepsilon_3(\boldsymbol{k}) = 0 \end{array}\right\} \quad \text{if } T \leqslant T_c \tag{7}$$

and

$$\left.\begin{array}{l} \varepsilon_{1/2}(\boldsymbol{k}) = \pm 2\Omega\sqrt{1-\gamma_k/\sin\vartheta} \\ \varepsilon_3(\boldsymbol{k}) = 0 \end{array}\right\} \quad \text{if } T \geqslant T_c \tag{8}$$

with the notation $\gamma_k = \bar{J}_k/\bar{J}_0$ and $\varepsilon_{1/2}(\boldsymbol{k}) = \pm\sqrt{(\varepsilon_k^{11})^2 - (\varepsilon_k^{12})^2}$. ε_3 is the solution of the system of integral equations for ε_k^{11}, ε_k^{12}, ε_k^{21}, ε_k^{22} and ε_k^{33} putting the correlation functions $\langle\rho; b\rangle$, $\langle\rho; b^+\rangle$, $\langle b^+; \rho\rangle$ and $\langle b; \rho\rangle$ equal to zero.

The energies $\varepsilon_{1/2}(\boldsymbol{k})$ belong to the transverse excitations, i.e. to the spin waves which are soft modes. For $\boldsymbol{k} = 0$ the spin-wave energy tends to zero, if $T \to T_c$. In LHP this FE soft mode has been found experimentally by Ohno and Lockwood [17] using Raman scattering. $\varepsilon_1(\boldsymbol{k})$ from (7) increases with increase in J_0' and decreases with increase in Ω.

In both temperature regions, there is a solution with $\varepsilon_3 = 0$. It corresponds to the longitudinal mode, i.e. a relaxation of the spin components parallel to the mean field.

$\sigma(T)$ is the relative polarisation in the direction of the mean field and is equal to $2\langle S^{z\prime}\rangle$:

$$\sigma = \left[\frac{\sigma\bar{J}_0}{2N}\sum_k \frac{1 - 0.5\sin^2\vartheta\,\gamma_k}{\varepsilon_k}\coth\left(\frac{\varepsilon_k}{2T}\right)\right]^{-1} \tag{9}$$

where $\varepsilon_k = \varepsilon_1(\boldsymbol{k})$. The relative polarisation $\sigma(T)$ was numerically calculated for different T-, Ω- and J_0'-values. $\sigma(T)$ according to equation (9) shows a steeper slope near T_c in comparison with the MFA. This steeper slope is found in experiments on LHP-type FEs, too [1, 18]. $\sigma(T)$ increases with increase in J_0' and decreases with increase in Ω. The greater the Ω, the smaller is the effect of J_0', in agreement with [10]. In other words, it is important to consider the fourth-order interaction in the case of small Ω, i.e. the case of LHP and LDP crystals. In other ways, the spontaneous polarisation in LHP and LDP crystals results from the formation of dipoles due to proton ordering described by the pseudo-spin model, but in KDP-type crystals the spontaneous polarisation is due to the contribution of the heavy-atom displacements along the FE axis, and the proton ordering is only a side effect. In view of the above points, the model proposed in [10] is more suitable for explaining the phase transition in LHP-type crystals.

The phase transition temperature T_c increases with increase in J_0' and decreases with increase in Ω.

3. Dynamic properties

In order to obtain damping effects, we consider approximately the integral term in equation (4). In our calculations we use the approximate dynamics $b_k(t) \simeq b_k \exp(-i\varepsilon_k t)$

and the approximate commutation relation $[b_k, b_{k'}^+] \simeq \sigma\delta_{kk'}$. The first assumption takes the GHFA as a starting approximation, while the second is equivalent to a certain decoupling of higher-order correlation functions. $\varepsilon_k = \varepsilon_1(\boldsymbol{k})$ is the spin-wave energy from equation (7) or (8).

Taking into account damping effects we obtain for the spin-wave energy in the simplest approximation

$$\varepsilon_{1/2}(\boldsymbol{k}) = -\mathrm{i}\gamma_k^{11} \pm \sqrt{\varepsilon_k^2 - (\gamma_k^{12})^2} \tag{10}$$

$$\varepsilon_3(\boldsymbol{k}) = -\mathrm{i}\gamma_k^{33}. \tag{11}$$

Calculations yield the following expressions for γ_k^{11}, γ_k^{12} and γ_k^{33}:

$$\begin{aligned}\gamma_k^{11} = \frac{\pi}{2N^2}\sum_{q,p}\{&(V_{q,k-q} + V_{k-p-q,p+q})^2[\bar{n}_p(\sigma + \bar{n}_{p+q} + \bar{n}_{k-q}) \\ &- \bar{n}_{p+q}\bar{n}_{k-q}]\delta(\varepsilon_{k-q} + \varepsilon_{p+q} - \varepsilon_p - \varepsilon_k) \\ &- \sin^2\vartheta\, V_{q,k-q}[(\bar{J}_p + \bar{J}_{p+q})\bar{m}_{p+q}(\bar{n}_p - \bar{n}_{k-q}) \\ &+ (\bar{J}_p + \bar{J}_{k-q})\bar{m}_{k-q}(\bar{n}_p - \bar{n}_{p+q})]\delta(\varepsilon_{k-q} + \varepsilon_{p+q} - \varepsilon_p - \varepsilon_k)\}\end{aligned} \tag{12}$$

$$\begin{aligned}\gamma_k^{12} = \frac{\sin^2\vartheta}{2N^2}\pi\sum_{q,p}\bar{J}_{k-q}\{&(V_{k-p,p} + V_{q,k-q})[\bar{n}_p\bar{n}_{k-q} \\ &- \bar{n}_{p+q}(\sigma + \bar{n}_p + \bar{n}_{k-q})]\delta(\varepsilon_p + \varepsilon_{k-q} - \varepsilon_{p+q} - \varepsilon_k) \\ &- 0.5\sin^2\vartheta\,[(\bar{J}_{p+q} + \bar{J}_p)(\bar{n}_{p+q} - \bar{n}_{k-q})\bar{m}_p \\ &+ (\bar{J}_{k-q} + \bar{J}_{p+q})(\bar{n}_{p+q} - \bar{n}_p)\bar{m}_{k-q}]\delta(\varepsilon_{p+q} - \varepsilon_p - \varepsilon_{k-q} + \varepsilon_k)\}\end{aligned} \tag{13}$$

$$\begin{aligned}\gamma_k^{33} = \frac{\pi\sin^4\vartheta}{16N}\sum_q\Big\{&(\bar{J}_q + \bar{J}_{k-q})^2(\sigma + \bar{n}_q + \bar{n}_{k-q})\delta(\varepsilon_q + \varepsilon_{k-q} \\ &- \varepsilon_k) + (\bar{J}_q - \bar{J}_{k-q})^2(\bar{n}_q - \bar{n}_{k-q})[\delta(\varepsilon_{k-q} - \varepsilon_q - \varepsilon_k) \\ &- \delta(\varepsilon_q - \varepsilon_{k-q} - \varepsilon_k)]\} + \frac{\pi}{8}\sin^2\vartheta\cos^2\vartheta\frac{1}{N^2} \\ &\times\sum_{q,p}(\bar{J}_{k-q} + \bar{J}_{q-p})^2\{[\bar{n}_p(\sigma + \bar{n}_{p+k-q} + \bar{n}_q) \\ &- \bar{n}_{p+k-q}\bar{n}_q]\delta(\varepsilon_q + \varepsilon_{p+k-q} - \varepsilon_p - \varepsilon_k) + [\bar{n}_{p+k-q}(\sigma \\ &+ \bar{n}_p + \bar{n}_q) - \bar{n}_p\bar{n}_q]\delta(\varepsilon_p + \varepsilon_q - \varepsilon_{p+k-q} - \varepsilon_k) \\ &+ [\bar{n}_q(\sigma + \bar{n}_{p+k-q} + \bar{n}_p) - \bar{n}_p\bar{n}_{p+k-q}]\delta(\varepsilon_p + \varepsilon_{p+k-q} - \varepsilon_q - \varepsilon_k)\Big\}\end{aligned} \tag{14}$$

where

$$\bar{n}_q \equiv \langle b_k^+ b_k\rangle = (\sigma/2)[\bar{J}_0/2\varepsilon_q)(1 - 0.5\sin^2\vartheta\,\gamma_q)\coth(\varepsilon_q/2T) - 1]$$

$$\bar{m}_q \equiv \langle b_k b_{-k}\rangle = \langle b_{-k}^+ b_k^+\rangle = (\sigma^2/8\varepsilon_q)\sin^2\vartheta\,\bar{J}_q\coth(\varepsilon_q/2T)$$

$V_{q,k-q} = \cos^2\vartheta \bar{J}_q - 0.5\sin^2\vartheta \bar{J}_{k-q}$.

We get for the transverse Green function

$$G^{xx}(\boldsymbol{k}, E) = 2\sigma(\varepsilon_{11} - \varepsilon_{12})/(E^2 - \varepsilon_k^2 + iE\Gamma_k) \tag{15}$$

with the frequency-dependent

$$\Gamma_k(E) = 2\gamma_{11} + i\varepsilon_{13}^2/(E + i\gamma_{33}). \tag{16}$$

The central mode and the renormalisation of the soft mode is due to $\Gamma_k(E)$. The transverse Green function (15) is calculated taking into account the mixed matrix elements ε_{13}, ε_{23}, ε_{31}, ε_{32}. For ε_{13} we obtain

$$\begin{aligned}\varepsilon_{13}(\boldsymbol{k}) &= \frac{1}{2N}\sin^2\vartheta \sum_q \bar{J}_{k-q}(\langle b_q \rho_{-q}\rangle - \langle b_q^+ \rho_q\rangle) - \frac{\cos^2\vartheta}{N}\sum_q \bar{J}_q \langle b_q \rho_{-q}\rangle \\ &= \frac{1}{2N}\sin^2\vartheta \sum_q \bar{J}_{k-q}\varepsilon_{13}(\boldsymbol{q})\frac{\coth(\omega_q/2T)}{\omega_q} \\ &\quad + \frac{\cos^2\vartheta}{2N}\sum_q \bar{J}_q \varepsilon_{13}(\boldsymbol{q})\left[\frac{1}{\omega_q}\coth\left(\frac{\omega_q}{2T}\right) + \frac{\varepsilon_{11} + \varepsilon_{12}}{\omega_q^2}\right]\end{aligned} \tag{17}$$

with the renormalised soft mode

$$\omega_q = (\varepsilon_q^2 + \varepsilon_{13}^2)^{1/2}. \tag{18}$$

For $T \simeq T_c$, where $\cos\vartheta \simeq 0$ and $\coth(\omega_q/2T) \simeq 2T/\omega_q$, $\varepsilon_{13} \propto T$. ε_{13} increases with $T \to T_c$.

The transverse dynamic structure factor $S^{xx}(\boldsymbol{k}, E)$ is calculated via the imaginary part of G^{xx} (15). We obtain this in the form

$$\begin{aligned}S^{xx}(\boldsymbol{k}, E) &= \{2\sigma(\varepsilon_{11} - \varepsilon_{12})E/[1 - \exp(-E/T)]\} \\ &\quad \times (\{[2\gamma_{11}E^2 + \gamma_{33}(2\gamma_{11}\gamma_{33} + \varepsilon_{13}^2)]/(E^2 + \gamma_{33}^2)\} \\ &\quad /[[E^2 - \varepsilon_k^2 - E^2\varepsilon_{13}^2/(E^2 + \gamma_{33}^2)]^2 \\ &\quad + E^2\{2\gamma_{11}E^2 + \gamma_{33}(2\gamma_{11}\gamma_{33} + \varepsilon_{13}^2)]/(E^2 + \gamma_{33}^2)\}^2]).\end{aligned} \tag{19}$$

The peaks of S^{xx} are determined by the zeros of the denominator. The transverse dynamic structure factor exhibits three peaks: two soft-mode peaks and a very narrow central peak, which is caused by the coupling between the transverse soft mode and the longitudinal diffusive mode.

4. Numerical results

The temperature dependence of the damping and of the transverse dynamic factor $S^{xx}(\boldsymbol{k}, E)$ have been computed numerically for $\boldsymbol{k} = 0$ taking appropriate parameters: for LHP, $\Omega = 2.168\ \text{cm}^{-1}$, $J_0 = 862.08\ \text{cm}^{-1}$, $J_0' = 448\ \text{cm}^{-1}$ and $T_c = 310$ K; for LDP, $\Omega = 0.273\ \text{cm}^{-1}$, $J_0 = 1256.56\ \text{cm}^{-1}$, $J_0' = 1049.36\ \text{cm}^{-1}$ and $T_c = 452$ K [10].

γ_{11} and γ_{33} increase with increase in T. We obtain $\gamma_{11} \gg \gamma_{33}$. γ_{11} and γ_{33} decrease with increase in J_0'. γ_{11} increases whereas γ_{33} decreases with decrease in Ω.

For 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, and a central

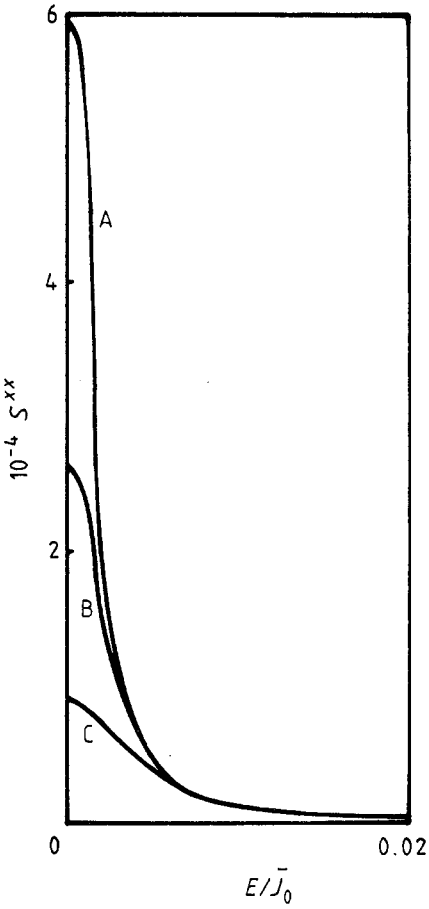

Figure 1. Transverse dynamic structure factor S^{xx} as a function of $E/\bar{J}_0$ for LHP ($\Omega = 2.168\ cm^{-1}$, $J_0 = 862.08\ cm^{-1}$, $J_0' = 448\ cm^{-1}$, $k = 0$) for different temperatures $T > T_c$: curve A, $T/T_c = 1.016$; curve B, $T/T_c = 1.032$; curve C, $T/T_c = 1.048$.

peak appears in addition to the soft-mode peaks. The greater the fourth-order interaction constant J_0' the smaller is the damping, and the narrower is the central peak for LHP and LDP. Approaching T_c, the intensity moves from the soft-mode peak to the central peak. The central peak becomes very narrow. The frequency of the soft-mode does not reach zero at $T = T_c$, but it remains finite:

$$\omega_s(T_c) = \varepsilon_{13}. \tag{20}$$

In the case of deuteration where

$$\varepsilon_{LDP}(\boldsymbol{k}) \ll \varepsilon_{LHP}(\boldsymbol{k}) \tag{21}$$

is valid, the soft mode peak shifts towards the origin and its intensity decreases. In LDP the peak around the soft FE mode is absent and the FE mode spectra below T_c consist of only the central peak at around $E = 0$. The height of the central peak increases as $T \to T_c$.

In the disordered phase ($T \geqslant T_c$) we have $\cos\vartheta = 0$. As a consequence, the expressions for γ_k^{11}, γ_k^{12} and γ_k^{33} are simpler than for the ordered phase. Because of the factor $\cos^2\vartheta$ the second term in $\bar{J}_0$, namely $\frac{1}{4}\sigma^2 J_0' \cos^2\vartheta$, goes to zero above T_c and $\bar{J}_0 \equiv J_0$ for $T \geqslant T_c$. This means that the influence of the last term in the Hamiltonian (1)

decreases as $T \rightarrow T_c$ for $T \leqslant T_c$ and it does not contribute to the static and dynamic properties above T_c.

Above T_c the FE mode in LHP and LDP is overdamped, i.e. $\gamma_{11} \gg \omega_s$, in agreement with the work of Happ *et al* [14]. The dynamic structure factor S^{xx} is represented by a very narrow peak centred at $E = 0$, given by

$$S_c^{xx} = \{2\sigma(\varepsilon_{11} - \varepsilon_{12})E/[1 - \exp(-E/T)]\}(\varepsilon_{13}^2/\omega_s^2)[\gamma'_{33}/(E^2 + \gamma'^2_{33})] \quad (22)$$

where $\gamma'_{33} = \gamma_{33}\varepsilon_k^2/\omega_s^2$, and a broader component at $E = \varepsilon_{13}$ ($\simeq 0$), given by

$$S_s^{xx} = \{2\sigma(\varepsilon_{11} - \varepsilon_{12})E/[1 - \exp(-E/T)]\}(\varepsilon_k^2/\omega_s^2)\{(\omega_s^2/2\gamma_{11})/[E^2 + (\omega_s^2/2\gamma_{11})^2]\} \quad (23)$$

with $2\gamma_{33}\gamma_{11} \ll \omega_s^2$.

So S^{xx} represented above T_c for LHP (figure 1) by a peak centred at $E = 0$. For $T \rightarrow T_c$ the central peak becomes higher and narrower, in agreement with the experimental data [12]. The peak in the deuterated case is much smaller than in the undeuterated case.

5. Conclusions

The central peak in the three-dimensional Ising model is due to the coupling between the transverse soft mode and the longitudinal relaxing mode. We emphasise that this peak is without coupling to other degrees of freedom and, in particular, without coupling to other phonon branches (as for example in the KDP-type FEs [19, 20]) or heat diffusion modes. The experimental evidence of the central peak for a LHP-type FEs may be explained with the help of the three-dimensional Ising model only as long as additional experimental information does not require the consideration of other phonon branches.

References

[1] Negran T J, Glass A M, Brickenkamp C S, Rosenstein R D, Osterheld R K and Susott R 1974 *Ferroelectrics* **6** 179
[2] Lockwood D J, Ohno N, Nelmes R J and Arend H 1985 *J. Phys. C: Solid State Phys.* **18** L559
[3] Carvalho A V and Salinas S R 1978 *J. Phys. Soc. Japan* **44** 238
[4] Blinc R, Arend H and Kanduser A 1976 *Phys. Status Solidi* b **74** 425
[5] Zinenko V I 1979 *Fiz. Tverd. Tela* **21** 1819
[6] Plascak J A and Salinas S R 1982 *Phys. Status Solidi* b **113** 367
[7] Blinc R, Zeks B, Sampaio J F, Pires A S T and Sa Barreto F C 1979 *Phys. Rev.* B **20** 1991
[8] Chaudhuri B K, Ganguli S and Nath D 1981 *Phys. Rev.* B **23** 2308
[9] Levstik A, Filipic C, Zeks B, Blinc R and Arend H 1986 *J. Phys. C: Solid State Phys.* **19** L25
[10] Chunlei W, Zikai Q and Jingbo Z 1988 *Ferroelectrics* **77** 21
[11] Nakatani N 1987 *J. Phys. Soc. Japan* **56** 2542
[12] Shin S, Ishigame M, Deguchi K and Nakamura E 1988 *Solid State Commun.* **65** 749
[13] Deguchi K and Nakamura E 1988 *J. Phys. Soc. Japan* **57** 413
[14] Happ H, Langhardt D and Voss G 1986 *J. Phys. C: Solid State Phys.* **19** 2575
[15] Kroupa J, Petzelt J, Kozlov G V and Volkov A A 1978 *Ferroelectrics* **21** 387
[16] Tserkovnikov Yu A 1971 *Teor. Math. Fiz.* **7** 250
[17] Ohno N and Lockwood D J 1987 *Ferroelectrics* **72** 1
[18] Smutny F and Fousek J 1978 *Ferroelectrics* **21** 385
[19] Wesselinowa J M 1983 *Phys. Status Solidi* b **116** 71
[20] Wesselinowa J M 1987 *Phys. Status Solidi* b **139** 329