LETTER TO THE EDITOR

Relaxation time for hydrogen-bonded PbHPO$_4$-type ferroelectrics

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Abstract. A Green function technique is developed to study the relaxation time of PbHPO$_4$-type ferroelectrics using the transverse Ising model including the fourth-order interaction of pseudospins. The inverse relaxation time is numerically calculated taking parameters for PbHPO$_4$ and PbDPO$_4$. The temperature dependence of $1/\tau$ is in very good agreement with the experimental data.

Recently, a central mode of the H-bonded ferroelectric (FE) PbHPO$_4$ (LHP) has been found in the paraelectric phase by hyper-Raman scattering by Shin *et al* [1]. From the temperature and polarization dependences of the c-mode it is concluded that the central mode is the soft mode of LHP. The phase transition can be considered as the order–disorder type phase transition. Shin *et al* [1] obtained the transverse relaxation time, $1/\tau$, using the half width of the central peak. By using the dynamic dielectric measurements, Deguchi and Nakamura [2] evaluated the relaxation times in the vicinity of T_c, which are slightly higher than the results in [1].

The dynamic dielectric properties of LHP have been studied by several researchers. Happ *et al* [3] 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* [4], Deguchi and Nakamura [2], and Shin *et al* [1] reported that the soft mode is a relaxation mode.

Chunlei *et al* [5] have investigated the thermodynamic properties of LHP and PbDPO$_4$ (LDP) using the three-dimensional transverse Ising model, including the fourth-order interaction of pseudospins [6, 7], and obtained good agreement with the experimental data for the spontaneous polarization. Wesselinowa [8] has shown that the coupling between the transverse soft mode and the relaxing longitudinal mode produces a central mode in the dynamic structure factor in LHP and LDP.

The aim of the present letter is to calculate the relaxation time of LHP-type FEs.

The Hamiltonian of the pseudospin system is given by

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

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, and it measures the proton ordering. The first term in (1) is the contribution due to the tunnelling effect, the second

term represents the contribution due to dipoles, and the third the contribution due to quadrupoles.

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

In order for the retarded Green function to be calculated, it is defined in matrix form as

$$\vec{G}_k(t) = -i\theta(t)\langle [B_k(t), B_k^+] \rangle. \tag{2}$$

The operator B_k stands for the set b_k, b_{-k}^+, ρ_k, where b and b^+ are Pauli operators and $\rho = b^+b$. Using the same method as in [8] we get for the transverse Green function

$$G^{xx}(k, E) = 2\sigma(\varepsilon_{11} - \varepsilon_{12})/(E^2 - \varepsilon_k^2 + 2iE\gamma_{11} - E\varepsilon_{13}^2/(E + i\gamma_{33})) \tag{3}$$

where

$$\varepsilon_k^2 = \varepsilon_{11}^2 - \varepsilon_{12}^2$$

$$\varepsilon_{11} = 2\Omega\sin\vartheta + \tfrac{1}{2}\sigma\bar{J}_0\cos^2\vartheta - \tfrac{1}{4}\sin^2\vartheta\bar{J}_k\sigma \qquad \varepsilon_{12} = -\tfrac{1}{4}\sin^2\vartheta\bar{J}_k\sigma$$

$$\varepsilon_{13}(k) = \frac{1}{2N}\sin^2\vartheta \sum_q \bar{J}_{k-q}\varepsilon_{13}(q)(\coth(\omega_q/2T)/\omega_q)$$

$$+ \frac{1}{2N}\cos^2\vartheta \sum_q \bar{J}_q\varepsilon_{13}(q)\left[\frac{1}{\omega_q}\coth(\omega_q/2T) + (\varepsilon_{11} + \varepsilon_{12})/\omega_q^2\right]$$

$$\gamma_k^{11} = \frac{\pi}{2N^2}\sum_{q,p}\{(V_{q,k-q} + V_{k-p-q,p+q})^2[\bar{n}_p(\sigma + \bar{n}_{p+q} + \bar{n}_{k-q}) - \bar{n}_{p+q}\bar{n}_{k-q}]$$

$$\times \delta(\varepsilon_{k-q} + \varepsilon_{p+q} - \varepsilon_p - \varepsilon_k) - \sin^2\vartheta V_{q,k-q}[(\bar{J}_p + \bar{J}_{p+q})\bar{m}_{p+q}(\bar{n}_p - \bar{n}_{k-q})$$

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

$$\gamma_k^{33} = \frac{\pi\sin^4\vartheta}{16N}\sum_q \{(\bar{J}_q + \bar{J}_{k-q})^2(\sigma + n_q + \bar{n}_{k-q})\delta(\varepsilon_q + \varepsilon_{k-q} - \varepsilon_k)$$

$$+ (\bar{J}_q - \bar{J}_{k-q})^2(\bar{n}_q - \bar{n}_{k-q})[\delta(\varepsilon_{k-q} - \varepsilon_q - \varepsilon_k) - \delta(\varepsilon_q - \varepsilon_{k-q} - \varepsilon_k)]\}$$

$$+ \frac{\pi\sin^2\vartheta\cos^2\vartheta}{8N^2}\sum_{q,p}(\bar{J}_{k-q} + \bar{J}_{q-p})^2\{[\bar{n}_p(\sigma + \bar{n}_{p+k-q} + \bar{n}_q) - \bar{n}_{p+k-q}\bar{n}_q]$$

$$\times \delta(\varepsilon_q + \varepsilon_{p+k-q} - \varepsilon_p - \varepsilon_k) + [\bar{n}_{p+k-q}(\sigma + \bar{n}_p + \bar{n}_q) - \bar{n}_p\bar{n}_q]$$

$$\times \delta(\varepsilon_p + \varepsilon_q - \varepsilon_{p+k-q} - \varepsilon_k) + [\bar{n}_q(\sigma + \bar{n}_{p+k-q} + \bar{n}_p) - \bar{n}_p\bar{n}_{p+k-q}]$$

$$\times \delta(\varepsilon_p + \varepsilon_{p+k-q} - \varepsilon_q - \varepsilon_k)\}$$

where $V_{q,k-q} = \cos^2\vartheta\bar{J}_q - 0.5\sin^2\vartheta\bar{J}_{k-q}$, $\sin\vartheta = 4\Omega/\sigma(J_0 + \tfrac{1}{4}\sigma^2 J_0'\cos^2\vartheta) = 4\Omega/\sigma\bar{J}_0$, if $T \leqslant T_c$, $\sigma(T)$—the relative polarization and $\bar{n}_q \equiv \langle b_q^+ b_q \rangle$, $\bar{m}_q \equiv \langle b_q b_{-q} \rangle$—the correlation functions are calculated in [8].

The coupling of the transverse soft mode and the longitudinal relaxing mode renormalizes the spin wave energy ε_k to ω_k

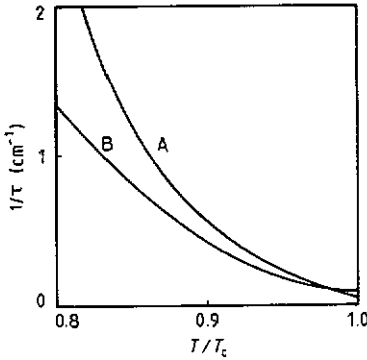$$\omega_k = \pm(\varepsilon_k^2 + \varepsilon_{13}^2)^{1/2}. \tag{4}$$

Figure 1. Temperature dependence of the inverse relaxation time $1/\tau$ below T_c for LHP (A) and LDP (B).

The transverse spin wave energy ω_k decreases very strongly for $T \to T_c$ ($\varepsilon_k \to 0$) but remains finite at T_c, namely

$$\omega_k(T = T_c) = \varepsilon_{13}(k). \tag{5}$$

The transverse dynamic structure factor $S^{xx}(k, E)$ is calculated via the imaginary part of $G^{xx}(k, E)$ (equation (3)). The inverse relaxation time $1/\tau = \omega_k^2/2\gamma_{11}$ was numerically calculated taking the following model parameters. For LHP: $\Omega = 2.168\ \mathrm{cm}^{-1}$, $J_0 = 862.08\ \mathrm{cm}^{-1}$, $J_0' = 448\ \mathrm{cm}^{-1}$ and $T_c = 310\ \mathrm{K}$. For LDP: $\Omega = 0.273\ \mathrm{cm}^{-1}$, $J_0 = 1256.56\ \mathrm{cm}^{-1}$, $J_0' = 1049.36\ \mathrm{cm}^{-1}$ and $T_c = 452\ \mathrm{K}$ [5]. Figure 1 illustrates the temperature dependence of $1/\tau$ for $k = 0$ in the ferroelectric phase. $1/\tau$ decreases with $T \to T_c$ in both regions below and above T_c. The same behaviour has been found experimentally [1, 2]. It can be seen that $1/\tau$ has a finite value at $T = T_c$ and that

$$1/\tau\ (\mathrm{LHP}) > 1/\tau\ (\mathrm{LDP}) \qquad \text{for } T \lesssim T_c. \tag{6}$$

At temperatures very close to T_c we obtain

$$1/\tau\ (\mathrm{LDP}) > 1/\tau\ (\mathrm{LHP}) \qquad \text{for } T \approx T_c \tag{7}$$

in accordance with Deguchi and Nakamura [2].

It may be concluded that in order to obtain correct results for LHP- and LDP-type FEs, the coupling between the transverse soft mode and the longitudinal relaxing mode must be properly taken into account.

References

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