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Brillouin spectroscopic evidence for a relaxation mode in ferroelectric $PbHPO_4$ and $PbDPO_4$

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Brillouin spectra of ferroelectric $PbHPO_4$ ($T_c=310$ K) and its deuterated isomorph $PbDPO_4$ ($T_c=462$ K) have been measured as a function of temperature across their transition temperatures. Certain longitudinal acoustic waves are found to exhibit anomalous propagation in the vicinity of T_c. The relaxation times, τ_0, for a noninteracting dipole are evaluated from the Brillouin shifts, based on a phenomenological approach. The τ_0 values are the same in both $PbHPO_4$ and $PbDPO_4$, indicating that the ferroelectric transition is driven by an order-disorder relaxation mode. This study also reveals that the paraelectric phase symmetry is, on a macroscopic scale, centrosymmetric.

I. INTRODUCTION

Lead hydrogen phosphate (LHP) $PbHPO_4$ and its deuterium isomorph $PbDPO_4$ (LDP) have been studied extensively in recent years. Unlike the well-studied KH_2PO_4, where the H-bonded PO_4 groups are linked into a three-dimensional network, in LHP they form well-separated chains along the c axis. This structural simplicity makes LHP an excellent system for the investigation of the phase transition in hydrogen-bonded ferroelectrics. Despite the numerous investigations carried out mainly on LHP, but also on LDP, a consensus has yet to be reached on the following two aspects relating to the ferroelectric transition.

Ferroelectric LHP has monoclinic symmetry with space group Pc, and its paraelectric phase was initially assumed to be centrosymmetric[1] with space group $P2/c$. The Pc symmetry is now thought, by some, to prevail in the high-temperature phase due to an acentric heavy-atom arrangement.[2-5]

Another issue concerns the nature of the ferroelectric soft mode. Microwave measurements[6,7] for LHP reveal a heavily overdamped soft mode. Lately, however, evidence provided by hyper-Raman scattering,[8] Brillouin scattering,[9] and microwave dielectric dispersion[10] for an order-disorder relaxational mode is mounting.

This work was undertaken to address the two controversial aspects of LHP regarding the acentricity of the paraelectric phase and the nature of the transition mechanism. A recent Brillouin study[9] of LHP has shown an anomaly in a longitudinal acoustic (LA) phonon near $T_c=310$ K, indicating an order-disorder relaxation mode with relaxation time $\tau_0=4.0\times10^{-14}$ s. We have earlier reported the preliminary results of a corresponding acoustic anomaly in LDP ($T_c\approx452$ K).[11] The complete results of our Brillouin study, which covers both LA and transverse acoustic (TA) modes in LHP and LDP, are presented here.

II. EXPERIMENTAL DETAILS

Brillouin measurements were carried out on LHP and LDP specimens of respective dimensions $3.2\times2.2\times1.5$ and $3.5\times2.8\times0.6$ mm^3 with faces perpendicular to the orthogonal X, Y, and Z axes. With X and Y chosen to be parallel to the respective crystal a and b axes, Z only deviated by 7° from the c axis. The crystals examined here, which are the same ones used in earlier Raman studies,[2,12] had been stored under nitrogen atmosphere in a desiccator.

The 90°-scattering geometry was employed. $X(ZX+ZZ)Y$ and $Z(XX+XZ)Y$ spectra were excited with 100 mW of 514.5 nm radiation from a single-mode argon-ion laser. The scattered light was analyzed with a Burleigh DAS five-pass Fabry-Pérot interferometer operated with free spectral ranges of 24.91 GHz (finesse = 34) for LHP and 23.89 GHz (finesse = 38) for LDP, giving respective spectral resolutions of 0.73 and 0.63 GHz. These values of the free spectral range were chosen to observe both the TA and LA modes, in first order, within a spectral scan. The crystal temperature was varied using a Dewar, containing an ice-water mixture, equipped with a resistance-heated sample holder. An Oxford ITC4 temperature controller ensured a stability of 0.1 K. Brillouin spectra were recorded over temperature ranges that included T_c; these were 281–342 and 422–478 K for LHP and LDP, respectively.

The effects of instrumental resolution were removed, and the Brillouin shift and linewidth were obtained using

the technique of iterative Bayesian deconvolution and least-squares fitting, assuming a Lorentzian line shape for the true spectrum.[13] The Landau-Placzek ratio was computed by dividing the integrated Rayleigh intensity by twice the integral of the deconvoluted Brillouin line shape.

III. RESULTS AND DISCUSSION

The $X(ZX+ZZ)Y$ spectra of LHP and LDP contained only the LA mode. Its frequency shift and linewidth did not exhibit any anomalous temperature dependence, and we therefore did not undertake a detailed study of the crystals in this polarization.

Figures 1 and 2 show that for both LHP and LDP, the LA as well as the TA phonons appear as two bands with about equal intensity in the $Z(XX+XZ)Y$ configuration. The TA modes are not recorded as two distinct lines, but rather as a band with a shoulder which becomes more pronounced at higher temperatures. In this configuration and in the orthorhombic phase, the quasi-LA mode velocity is given by

$$v_{\mathrm{LA}}=\left[\frac{4\rho}{C_{22}+C_{33}+2C_{44}+[(C_{22}-C_{33})^2+4(C_{23}+C_{44})^2]^{1/2}}\right]^{-1/2}, \tag{1}$$

where ρ is the density and c_{ij} are the elastic constants, while the quasishear (TA) mode velocity is given by

$$v_{\mathrm{TA1}}=\left[\frac{4\rho}{C_{22}+C_{33}+2C_{44}-[(C_{22}-C_{33})^2+4(C_{23}+C_{44})^2]^{1/2}}\right]^{-1/2} \tag{2}$$

and the pure shear (TA) mode velocity by

$$v_{\mathrm{TA2}}=\left[\frac{2\rho}{C_{55}+C_{66}}\right]^{-1/2}. \tag{3}$$

Previous Brillouin measurements[9,14] have shown that it is the C_{22} component that exhibits an anomaly at T_c and thus both v_{LA} and v_{TA1} could be affected.

Good least-squares fits to the deconvoluted spectra were achieved using a Lorentzian function, as exemplified by the 468 K spectrum of LDP shown in Fig. 3.

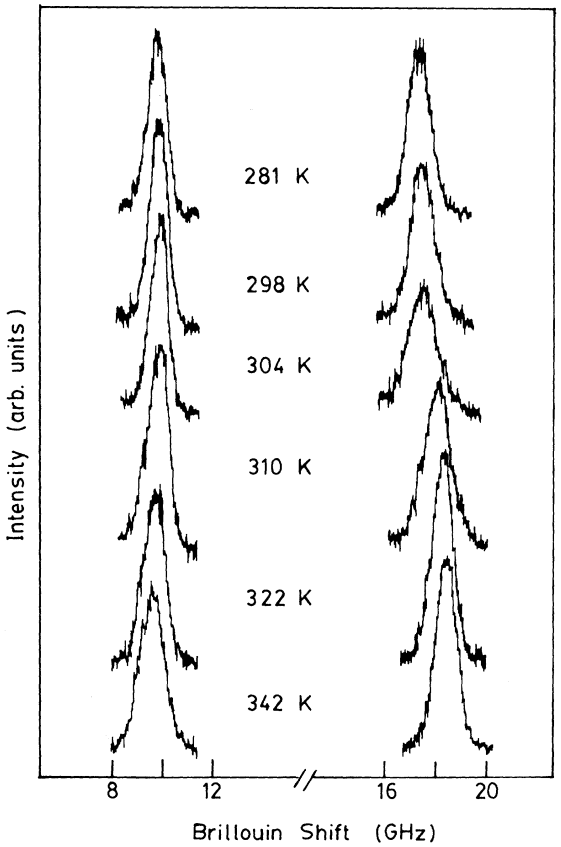

FIG. 1. Representative $Z(XX+XZ)Y$ Brillouin spectra of LHP recorded at various temperatures.

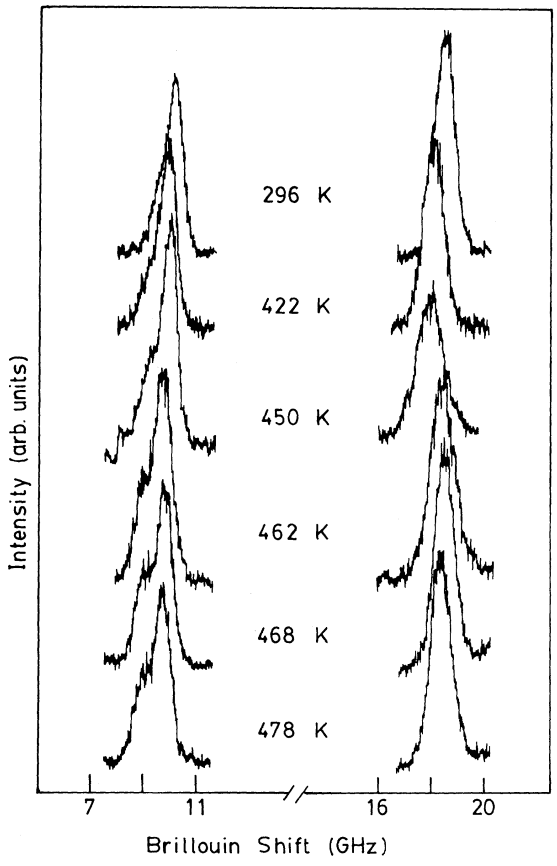

FIG. 2. Representative $Z(XX+XZ)Y$ Brillouin spectra of LDP recorded at various temperature.

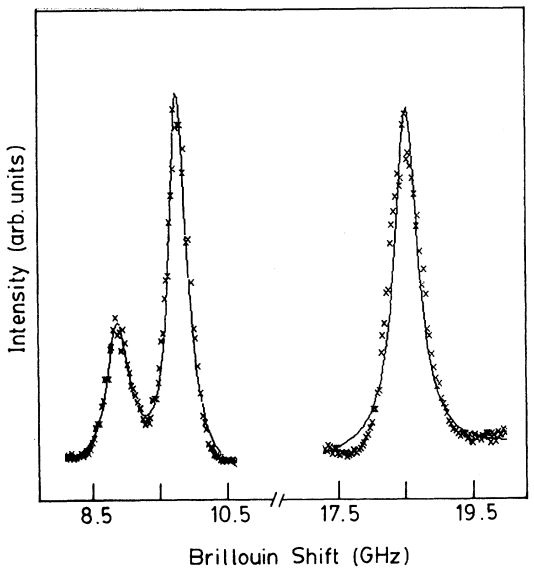

FIG. 3. Representative fits to the LA and TA bands of LDP. The crosses represent the deconvoluted $Z(XX+XZ)Y$ spectrum, measured at 468 K, while the solid curves the fitted Lorentzian line shapes.

A. LA modes

1. LHP

In the 281–342 K region, the LA-phonon frequency ranges from 18.12 to 19.08 GHz. Figure 4 shows that the anomalous temperature dependence of the LA-phonon frequency shift and linewidth occurs in the neighborhood of $T_c = 310$ K. Lu *et al.*[9] reported a similar behavior for the pure LA (C_{22}) mode of LHP. This pure LA mode is more temperature sensitive, as a frequency variation of 3 GHz was measured over the 280–333 K temperature range.[9] One reason for this difference in frequency variation is that in $Z(XX+XZ)Y$ polarization the LA mode propagates at approximately 45° to the b axis and is thus not purely longitudinal in character. The coupling of this quasi-LA mode to the fluctuating polarization,[15] via the piezoelectric coupling mechanism, is hence weaker resulting in a smaller LA velocity anomaly, as can also be seen from Eq. (1).

2. LDP

The temperature dependence of the LA-mode parameters of LDP is displayed in Fig. 5. In particular, a smaller mode frequency variation with temperature was recorded. Its frequency lies between 17.90 and 18.60 GHz in the 422–478 K temperature range. It is noteworthy in this regard that earlier Raman studies found that the $A'(B_u)$ soft mode in LDP also has a weaker frequency renormalization than that for LHP.[16,17]

The frequency and linewidth of the LA mode exhibit an anomaly in the vicinity of 462 K. Just below this temperature, the former drops steeply, while the latter broadens sharply. Also, an abrupt increase in the

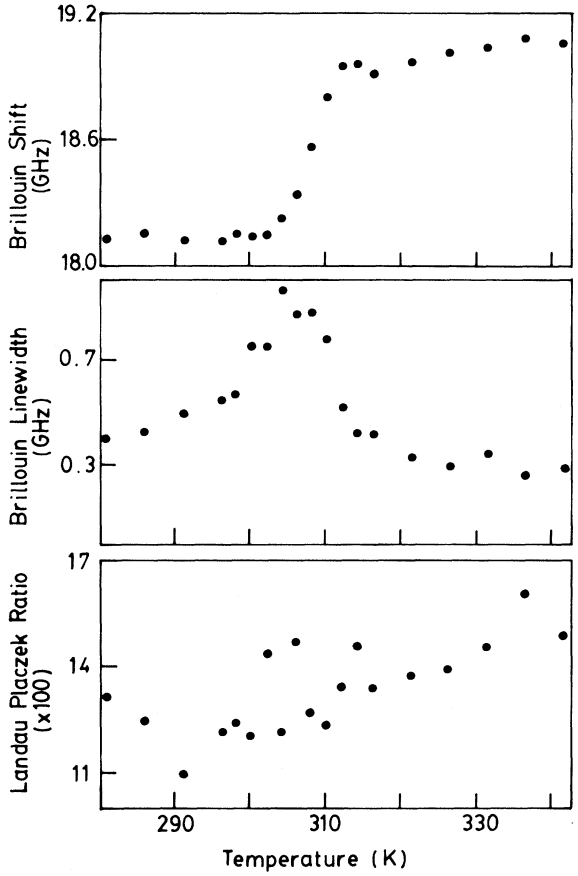

FIG. 4. Temperature dependence of the LA-mode parameters of LHP obtained with the Lorentzian function.

Landau-Placzek ratio was recorded on heating the LDP crystal above 462 K. In view of these observations, T_c for LDP was taken to be 462 K, which is higher than the value typically quoted of 452 K. Shin *et al.*[8] also reported a higher T_c of 457 K in their hyper-Raman investigation. Deuteration raises the ferroelectric transition temperature. Thus the larger T_c value obtained here is attributed to a higher deuterium content than that found in the typical "fully" deuterated specimen.

The sound velocities v for the LA mode of LHP and LDP were calculated from the formula

$$v = \frac{\lambda_0 \nu}{2n \sin(\theta/2)} , \tag{4}$$

where λ_0 is the wavelength of the laser light in vacuum, ν the LA-phonon frequency, n the refractive index, and θ the scattering angle. In the experimental configuration employed, $\theta = 90°$ and

$$n(\theta=90°) = [\tfrac{1}{2}(n_y^2+n_z^2) - \tfrac{1}{2}(n_y^2-n_z^2)^2/(n_y^2+n_z^2)]^{1/2} .$$

For the laser wavelength $\lambda_0 = 514.5$ nm used, the indices of refraction[5] are $n_x = n_y = 1.834$ and $n_z = 1.900$, giving $n(\theta=90°) = 1.866$. The velocities thus obtained for LHP are in agreement with those reported by Lavrencic, Copic, and Zgonik[14] and Lu *et al.*[9] In the temperature range

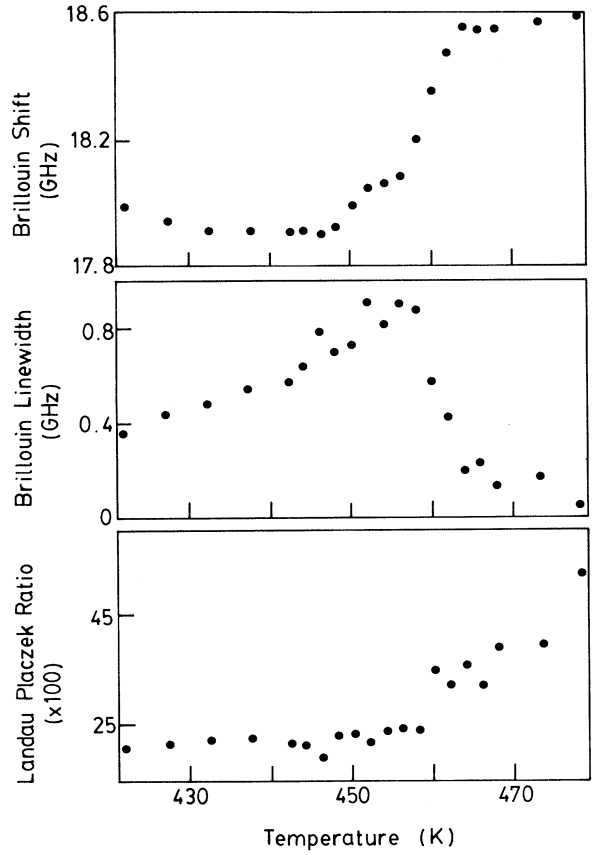

FIG. 5. Temperature dependence of the LA-mode parameters of LDP obtained with the Lorentzian function.

studied, values of v for LDP lie between 3490 and 3630 m/s.

The relaxation time $\tau(T)$ of the spontaneous polarization is assumed to obey the Curie-Weiss relation

$$\tau(T)=\tau_0 T_c/(T_c-T)\ , \tag{5}$$

where the constant τ_0 can be evaluated using the procedure, outlined in Ref. 14, which is based on Landau-Khalatnikov theory.[18]

The LA-mode velocity v is related to the elastic constant C, which is the real part of the complex elastic constant $C^*(\nu)$ at the LA-mode frequency ν, by

$$C=\rho v^2\ . \tag{6}$$

For temperatures near but below T_C, Eq. (5) requires that $1/\tau(T)$ be small and therefore less than or comparable to the LA-mode frequency ν. The complex elastic constant $C^*(\nu)$ is then given by

$$C^*(\nu)=C(T_c)-\frac{C(T_c)-C'}{1+i2\pi\nu\tau(T)}\ , \tag{7}$$

where C' and $C(T_C)$ are the respective static adiabatic elastic constant and the elastic constant at the high-frequency limit.

Thus the LA-mode velocity v can be expressed as

TABLE I. Parameters obtained from fitting Eq. (8) to the experimental LA-mode velocity.

	LHP		LDP	
	Ref. 14	This study	This study	
v_∞ (m s^{-1})	3460	3670±40	3520±40	3600±40
v_0 (m s^{-1})	3030	3520±20	3480±20	3480±20
c (m^2 s^{-2} K)	24 000	4100±500	5980±500	2600±500
B (K)	10.9	3.4±0.5	3.6±0.5	4.5±0.5
T_c (K)	310	310±2	454±2	462±2

$$v(T)=\begin{cases}\left[v_\infty^2-\dfrac{v_\infty^2-v_0^2-c(T_c-T)}{1+[B/(T_c-T)]^2}\right]^{1/2}, & T\le T_c\ ,\\ v_\infty\ , & T>T_c\ ,\end{cases} \tag{8}$$

where c, whose expression is given in Ref. 14, is a complicated function of the elastic constant and

$$v_\infty=v(T_c)\ ,\quad v_0=\rho^{-1/2}\left[C-\frac{2d^2}{\beta}\right]^{1/2}\ ,\quad B=2\pi\nu\tau_0\ ,$$

where d and β are coefficients in the expansion of the internal energy.[14]

A least-squares fit of the experimental sound velocities with Eq. (8) was then performed to extract the parameters v_∞, v_0, B, c, and T_c. Two fits over different tempera-

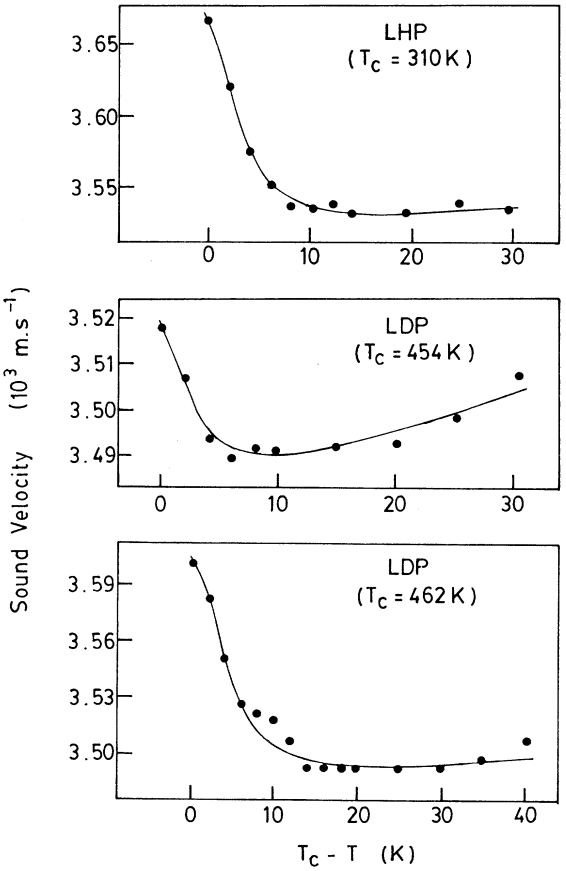

FIG. 6. Variation of LA-mode velocity with (T_c-T) for LHP and LDP. The solid lines represent the best fit of experimental data, denoted by solid circles, with Eq. (8).

TABLE II. τ_0 values, in 10^{-14} s, obtained from various experiments.

	This study	Ref. 8	Ref. 9	Ref. 14	Ref. 19	Ref. 20	Ref. 21
LHP	9.3	16[a]	4.0	30	8.1	19[a]	4.2
LDP	7.0[b]	45[a]				25[a]	
	8.4[c]						

[a]Paraelectric phase.
[b]$T_c=454$ K.
[c]$T_c=462$ K.

ture ranges, corresponding to parametric T_c values of 454 and 462 K, were carried out for the case of the LDP data. The former corresponds more closely to the accepted value of 452 K, and the latter corresponds to the T_c value inferred from our experimental results. Fits to the velocity data are shown by the solid curves in Fig. 6. The resulting parameter values, for LHP and LDP, are listed in Table I, together with those obtained by Lavrencic, Copic, and Zgonik[14] for LHP. In the case of LHP, except for parameters B and c, there is good agreement between their and our results. Any discrepancy is mainly due to the two different scattering geometries used. Lavrencic, Copic, and Zgonik observed the pure LA wave traveling along the b axis, while the quasi-LA wave examined here propagated at 45° to the b axis.

Finally, the relaxation time of a noninteracting dipole τ_0 was evaluated from the parameter B and the corresponding LA Brillouin shift. This yielded values of $(9.3\pm1.5)\times10^{-14}$ s for LHP ($T_c=310$ K) and $(7.0\pm1.1)\times10^{-14}$ s ($T_c=454$ K) and $(8.4\pm1.0)\times10^{-14}$ s ($T_c=462$ K) for LDP. A comparison of these results with those obtained from light scattering,[8,9,14,19] static dielectric,[20] and infrared[21] measurements is given in Table II. The τ_0 value obtained here for LHP lies within the minimum of 4.0×10^{-14} s and maximum of 30×10^{-14} s, derived from other Brillouin[9,14] studies. It is close to the value of 8.1×10^{-14} s found from fitting the central mode, in the Raman spectrum,[19] to a Debye relaxation function. As for LDP, the τ_0 value of 8.4×10^{-14} s ($T_c=462$ K) that best fits our data overall is lower than the 25×10^{-14} and 45×10^{-14} s determined from dielectric[20] and hyper-Raman[8] measurements, respectively. However, it should be noted that the latter two results were determined for LDP in the paraelectric phase, while in this study, τ_0 was evaluated for the ferroelectric phase.

What is more significant, however, is that, despite the large isotope shift in T_c, the τ_0 values for LHP and its deuterated isomorph are essentially the same. This clearly indicates that the ferroelectric transition is driven by an order-disorder relaxation mode and not a proton/deuteron tunneling mode. The lattice instability thus lies most likely with PO_4 tetrahedra reorientation.

B. TA modes

1. LHP

The fitted frequencies and linewidths of the two TA phonons for LHP between 281 and 342 K are plotted in Fig. 7. While the Brillouin shift of the higher-frequency phonon (the pure shear mode) remains essentially constant at ~10 GHz, that of the other (the quasi-TA mode) decreases almost linearly at 4×10^{-3} GHz/K. An anomalous linewidth broadening clearly occurs for the quasi-TA mode near 310 K, the transition temperature, and possibly also the pure shear mode. This effect could arise from the symmetry-allowed coupling between the quasi-TA mode and the pure transverse optic soft mode observed in the same scattering configuration by Lockwood and co-workers,[2,19] but it may also come from the C_{22} anomaly responsible for the LA-mode behavior [see Eqs. (1) and (2)].

2. LDP

For LDP at low temperatures, the two TA phonons, separated by ~1 GHz, appear as a single band at around 9.5 GHz (and not 12 GHz as stated in Ref. 11) and are instrumentally resolved into two bands only above 460 K. The temperature variations of their fitted frequencies and linewidths are displayed in Fig. 8. The Brillouin shifts were found to be insensitive to temperature. Unlike LHP, the TA wave for LDP does not show any anoma-

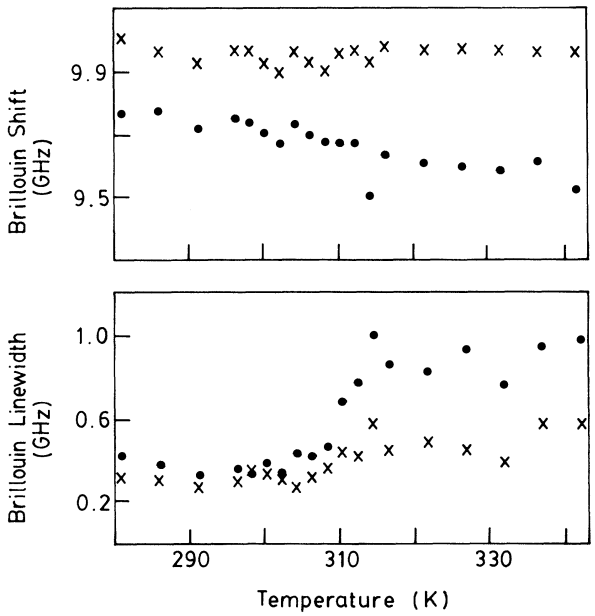

FIG. 7. Temperature dependence of the two TA-mode parameters of LHP obtained with the Lorentzian function.

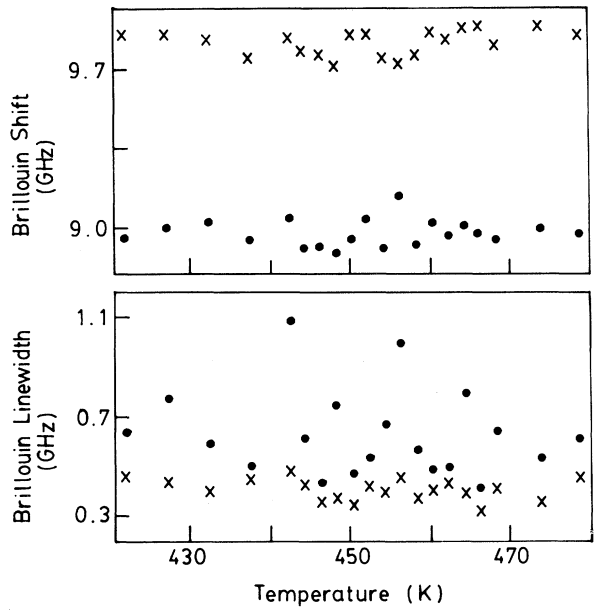

FIG. 8. Temperature dependence of the two TA-mode parameters of LDP obtained with the Lorentzian function.

lous linewidth broadening near T_c. This is because the optic soft mode in LDP scarcely lowers in frequency with increasing temperature up to T_c compared with LHP.[12] Moreover, as discussed above, the LA-mode softening is weaker in LDP than LHP. Any coupling of the TA phonon to the optic soft mode is thus expected to be very weak, as is the influence of the C_{22} anomaly.

IV. CONCLUSION

This Brillouin scattering study reveals LA-mode parameter anomalies near T_c for both LHP and its deuterated isomorph. Also, the respective relaxation time τ_0 values of 9.3×10^{-14} and 8.4×10^{-14} s for LHP and LDP, in their ferroelectric phase, are quite similar, despite the large isotope shift ($\Delta T_c \approx 150$ K) in the transition temperature.

These findings strongly suggest that the ferroelectric transition is driven by an order-disorder relaxation mode rather than a proton/deutron tunneling mode. It is very likely that the transition is associated with the reorientation and displacement of the PO_4 groups. Hence the soft mode observed by Raman spectroscopy[2,12] is a secondary effect and so is the linewidth anomaly observed here for the TA mode of LHP.

An optical second-harmonic generation study[5] has shown the existence of a short-range order of *Pc* symmetry in the paraelectric phase of LHP. This is consistent with the findings of some recent experiments that this phase has a slight acentricity due to noncentrosymmetric molecular vibrations.[22–24] No anomalous propagation of the acoustic waves of LHP and LDP was found above T_c in the present study, indicating the absence of piezoelectric coupling of these waves to any spontaneous electric polarization. Such a coupling is disallowed for symmetries with a center of inversion, for then the piezoelectric tensor would vanish. Moreover, since Brillouin scattering from long-wavelength acoustic phonons samples the *bulk* properties of a crystal, this implies that the paraelectric phase of LHP and LDP is, on a macroscopic scale, centrosymmetric; that is, it has $P2/c$ symmetry.

A temperature-dependent central mode has been found for LHP and LDP by Raman[2,19] and hyper-Raman[8] scattering. The intense Rayleigh line, however, precluded our observation of any quasielastic scattering peak in the Brillouin spectrum.

ACKNOWLEDGMENT

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