Pramāṇa, Vol. 11, No. 2, August 1978, pp. 119–134, © printed in India.

Propagation of longitudinal ultrasonic waves in RbH_2PO_4 near its ferroelectric phase transition temperature

G P SINGH and B K BASU
Tata Institute of Fundamental Research, Bombay 400 005

MS received 27 February 1978; revised 19 May 1978

Abstract. Ferroelectric phase transition in RbH_2PO_4 has been investigated using propagation of longitudinal acoustic waves along the polar axis near the transition temperature. The velocity of this mode is continuous across the transition temperature. Velocity data in the ferroelectric phase are analyzed in terms of coupled soft mode-acoustic mode model of Pytte to obtain the temperature dependence of the soft mode frequency. The attenuation data in the ferroelectric phase show power law dependence. It follows scaling behaviour of the type predicted by Kawasaki from the mode-mode coupling theory and the dynamical scaling.

Keywords. Ferroelectricity; phase transition; ultrasonic attenuation and velocity change; soft mode; RbH_2PO_4.

1. Introduction

It is well known that the study of the propagation behaviour of ultrasonic waves near a phase transition gives valuable information about both the static and dynamic aspects of phase transition. The low frequency ultrasonic velocity yields information about the static aspects, while the absorption data give information about the dynamic aspects. There have been several experiments on the propagation of ultrasonic waves near the ferroelectric phase transition temperature in KDP type ferroelectrics. Garland and Novotony (1969) have studied the propagation of X_y mode (i.e., ultrasonic waves propagating along the [100] direction and polarized along [010] direction) in the paraelectric phase of KH_2PO_4. This mode couples to the order parameter for the phase transition via a linear interaction (i.e., piezoelectric interaction). The acoustic wave for this mode is scattered by domain walls and, therefore, measurements in the ferroelectric phase can be performed only in the presence of a polarizing electric field. Litov and Uehling (1970) carried out measurements in both the paraelectric and ferroelectric phases of KD_2PO_4 for the X_y mode. Litov and Garland (1970) performed the measurements in KH_2PO_4 in both the paraelectric and ferroelectric phases by applying an electric field. In these studies it was found that the elastic data in both the crystals follow the elastic Curie-Weiss law and the magnitudes of the elastic Curie constants are nearly the same in both the crystals. The ultrasonic attenuation data were found to conform to a relaxation type behaviour with a single relaxation time. The relaxation time at constant stress τ_x was found to follow a temperature dependence of the type predicted by Landau-Khalatnikov

(1954) theory viz. $\tau_x \propto |T_c - T|^{-1}$. However, it was found that the relaxation time τ_x for KH_2PO_4 was about an order of magnitude smaller than that in KD_2PO_4 in the paraelectric phase. The magnitudes of τ_x are the same in the ferroelectric phase in the two materials. It is apparent from these investigations that even though the static behaviour of these crystals are quite similar, there is considerable difference in the dynamic behaviour.

Harnik and Shimshoni (1969) and Shimshoni and Harnik (1970) studied the propagation of the longitudinal mode along the polar axis in KH_2PO_4 and KD_2PO_4. This mode is not scattered by domain walls and the measurements can be made in the ferroelectric phase without the application of a polarizing field. Assuming a linear interaction of this mode with the order parameter, the authors obtained the values of the polarization relaxation time for the ferroelectric phase. The values obtained for KD_2PO_4 from this mode are nearly the same as the values obtained by Litov and Uehling (1970) from the X_y mode. But in KH_2PO_4, the values of the polarization relaxation time obtained by these authors are about two orders of magnitude smaller than the ones obtained from the X_y mode propagation. Also the longitudinal mode velocity behaviour apparently does not follow the static dielectric behaviour in the same way as the X_y mode velocity data do (Litov and Garland 1970). So far, there have been no explanation for these discrepancies. It appears to us that an understanding of the ultrasonic behaviour is likely to emerge by examining the behaviour of other members of the family. We present here the propagation behaviour of longitudinal ultrasonic wave along the polar axis of RbH_2PO_4 near the phase transition temperature. We show that the assumption of piezoelectric coupling between the longitudinal acoustic mode and the order parameter is only approximate. By using correct form of coupling we find that the velocity data for this mode follow the static dielectric behaviour much in the same way as the velocity behaviour of the X_y mode. For the ultrasonic absorption we find that the interaction of the ultrasonic waves with the order parameter fluctuations must be considered. Studies on RbH_2PO_4 are particularly useful because phase transition in this material is close to second order.

Another motivation for the measurement of the velocity of the longitudinal mode in the ferroelectric phase was that the present study forms part of a programme to understand the equilibrium behaviour of the KDP type ferroelectrics in terms of microscopic pseudospin model and the phenomenological soft mode model. In another publication (Singh and Singh 1978) we show that the velocity behaviour observed here can be explained in terms of a modification of the pseudospin model proposed by us earlier (Singh and Basu 1976 a, b). We also interpret here our data in terms of coupled soft mode-acoustic mode model proposed by Pytte (1970) to obtain the temperature dependence of the soft mode frequency in the ferroelectric phase. This is important, because although the existence of a soft mode was demonstrated by Raman scattering experiments at high pressures (Peercy 1973), it has not been possible to obtain the temperature dependence of the soft mode frequency near the transition temperature in the ferroelectric phase because of overdamping of the soft mode and the central peak effects.

Anomaly of the elastic constants in RbH_2PO_4 has been studied by Mnatsakanyan *et al* (1966), Pierre *et al* (1971) and Mischenko *et al* (1972). These measurements in RbH_2PO_4 were not accurate enough near the transition temperature. No measurements of ultrasonic attenuation in this material exist to our knowledge. A preliminary report of the present investigation has been published elsewhere (Singh and Basu 1978).

In section 2 we describe the experimental techniques, and present our data in section 3. Section 4 is devoted to theoretical considerations, and in section 5 we analyse the data. The conclusions are discussed in section 6.

2. Experimental techniques

The sample holder and the cryostat assembly for the ultrasonic measurements are shown in figure 1. The sample holder was a heavy cylindrical block of copper (approximately 1·1 kg) which was supported coaxially inside another copper cylinder. The whole assembly was immersed in liquid nitrogen contained in a glass dewar. The temperature was controlled by varying current through a heater wound on the sample holder by means of a proportional temperature controller. The temperature sensor, both for measurement and control, was a platinum resistance thermometer made from thermometric grade platinum wire using Barber's design (Barber 1950). The temperature was measured by the four probe technique using Leeds and Northrup K-5 potentiometer. The absolute accuracy of temperature measurement was 0·1° K, the temperature resolution was 2·5 m° K and the stability was better than 3 m° K.

The sample holder was carefully checked for temperature gradients. It was so

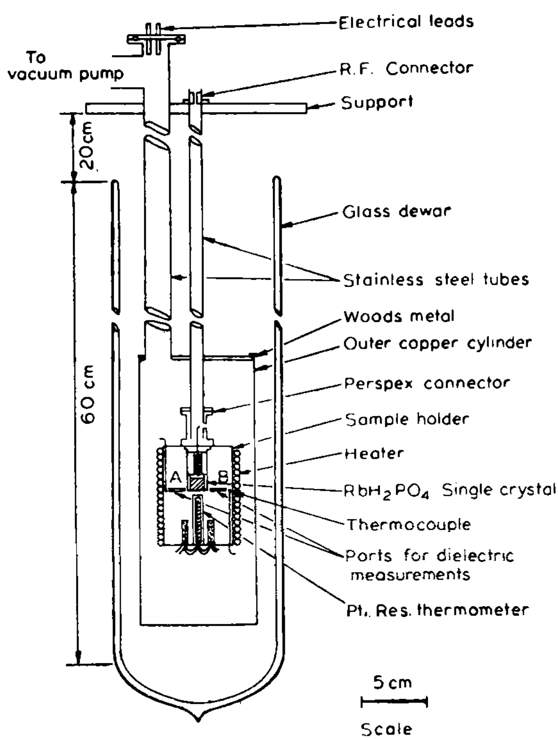

Figure 1. The cryostat.

designed that it could house two crystals about 3 cm apart (see figure 1) on which dielectric measurements could be simultaneously performed. Two Z-cut KDP crystals, cut from the same parent crystal, were placed in these ports in the sample holder and the dielectric measurements were carried out. The transition temperature indicated by the two crystals were within ± 5 m° K of each other, proving thereby negligible temperature gradients. All electrical leads to the thermometer and the samples were anchored to the sample holder using stycast 2850 GT.

Two RbH_2PO_4 samples were used in our experiments. One of these (sample 1) was grown in our laboratory using standard techniques, the other (sample 2) was bought from Quantum Technology Inc., Canada. The crystals were oriented to better than 1° from the Z-axis, and the opposite faces were polished parallel to better than 1 part in 10^4.

The ultrasonic measurements were performed using standard pulse-echo techniques. For longitudinal mode measurements an X-cut quartz transducer of fundamental frequency 8 MHz was bonded to the Z-face of the crystal, using Apiezon-N low temperature grease. Good echo patterns were obtained throughout the temperature region 125° K to 300° K. The bond material did not show any anomalous behaviour in this temperature range. The measurements were made by keeping the temperature stable for a time sufficient for the sample to reach equilibrium (approximatey 2 h). Both attenuation and velocity measurements were done in the same run.

3. Experimental results

3.1. *Velocity data*

Velocity measurements were done at 8 MHz using the calibrated delay of Tektronix 545 A oscilloscope. The accuracy of the velocity measurement was 1 % and resolution 0·1 %. As the attenuation at 8 MHz was small, the velocity could be measured very close to the transition temperature.

Figure 2 shows the velocity V_{33} of RbH_2PO_4 near the transition temperature. The velocity of sound in sample 2 was somewhat lower than that in sample 1, but both showed similar temperature dependences. The elastic constant $C_{33}=\rho V^2_{33}$ ($\rho=$ density of $RbH_2PO_4=2{\cdot}866$ gm/cm³), measured at 22° C, was $5{\cdot}21\times10^{11}$ dyne/cm² for sample 1 and $4{\cdot}94\times10^{11}$ dyne/cm² for sample 2. The reason for this difference is not clear. C_{33} for RbH_2PO_4 measured by Mnatsakanyan *et al* (1966) at 25° C is $5{\cdot}31\times10^{11}$ dyne/cm². The temperature corresponding to the velocity minimum was taken to be the transition temperature. The transition temperature of sample 2 was 1·7° K lower than that of sample 1.

The velocity very close to the transition temperature is shown in detail in the inset of figure 2. The velocity V_{33} is continuous across the transition temperature, indicating that the transition in RbH_2PO_4 is closer to second order than those in KH_2PO_4 or KD_2PO_4, where finite discontinuities were observed in the velocity at T_c. In the ferroelectric phase the velocity data follow a relation of the type (figure 3),

$$(C^0_{33}-C_{33})^{-1}=B(T-(T_c+T_0)). \quad (1)$$

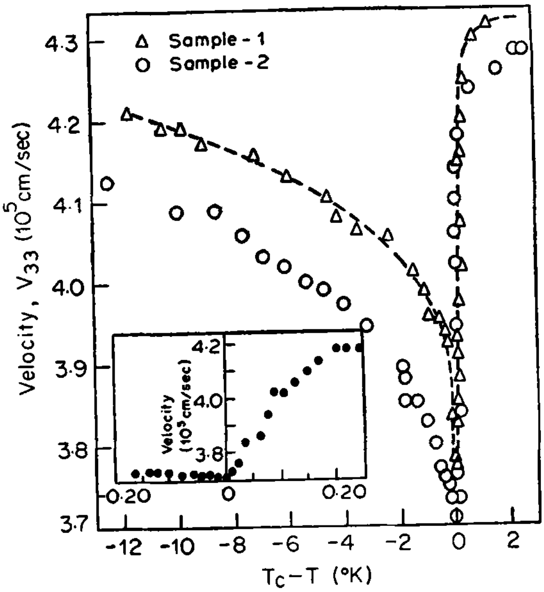

Figure 2. Temperature dependence of the velocity V_{33} of RbH_2PO_4. The inset shows the data close to the transition temperature.

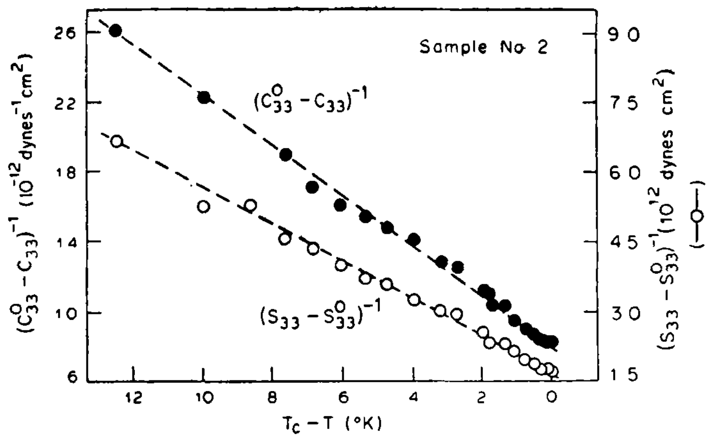

Figure 3. Temperature dependence of $(C^0_{33}-C_{33})^{-1}$ and $(S_{33}-S^0_{33})^{-1}$ for RbH_2PO_4 (ferroelectric phase).

Here $C^0_{33}=\rho V^0_{33}{}^2$, V^0_{33} is a linear extrapolation of V_{33} from temperatures much higher than the transition temperature. The values of B and T_0 for the two samples were as follows:

Sample 1: $B = -1{\cdot}31 \times 10^{-12}$ dyne/cm^2, $T_0 = 6{\cdot}2°$ K,

Sample 2: $B = -1{\cdot}45 \times 10^{-12}$ dyne/cm^2, $T_0 = 5{\cdot}5°$ K.

The velocity anomaly in the paraelectric phase is much sharper than that in the ferroelectric phase. As is seen in the inset the velocity rises to its normal value within about 0·3° K of the transition temperature. In the paraelectric phase, close to T_c, it was found that the sample does not achieve thermal equilibrium even though the temperature of sample holder was kept constant for several hours. The echo patterns were non exponential and, therefore, no reliable data could be obtained in this phase. This behaviour is perhaps connected with the low thermal conductivity of KDP type ferroelectrics in the paraelectric phase (Suemene 1967). For $T > T_c + 1°K$, the elastic constant C_{33} varies as $C_{33}(T) = (5{\cdot}21 + (295 - T) \times 1{\cdot}99 \times 10^{-3}) \times 10^{11}$ dyne/cm^2 for sample 1 and $C_{33}(T) = (4{\cdot}94 + (295 - T) \times 1{\cdot}91 \times 10^{-3}) \times 10^{11}$ dyne/cm^2 for sample 2.

3.2. *Attenuation data*

The attenuation measurements were carried out at 8, 24, 40, 56, and 72 MHz in the ferroelectric phase. The attenuation at 130°K was subtracted as the background attenuation. Below this temperature there was no attenuation change for any of the frequencies. Background attenuation in the ferroelectric phase was less than that in the paraelectric phase. Because of large attenuation close to T_c, the attenuation was measured by measuring the height of the first echo. The attenuation was reproducible better than $\pm$ 15%.

Figure 4 is a log-log plot of the attenuation α against $(T_c - T)$. The prominent features of the attenuation are the power law dependences and a crossover behaviour near the transition temperature. For $\omega^{3/2}(T_c - T)^{-1} < 1{\cdot}3 \times 10^{14}$ °K^{-1} sec.$^{-3/2}$, where ω is the angular frequency of the ultrasonic wave, a least square fit to the entire data yields a power law $\alpha \propto \omega^{1{\cdot}71\pm0{\cdot}12} \times (T_c - T)^{-0{\cdot}69\pm0{\cdot}10}$. For $\omega^{3/2}(T_c - T)^{-1} > 1{\cdot}3 \times 10^{14}$ °K^{-1} sec$^{-3/2}$ the attenuation follows a power law $\alpha \propto \omega^{1{\cdot}0}(T_c - T)^{-0{\cdot}16}$. The linear frequency dependence of attenuation at T_c is shown in figure 5.

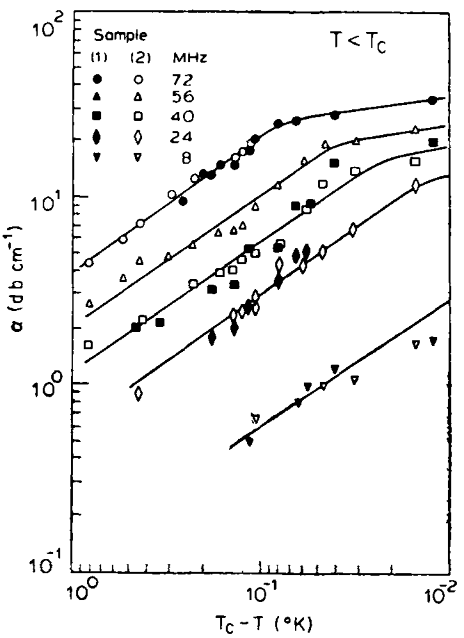

Figure 4. Temperature dependence of the ultrasonic absorption in RbH_2PO_4.

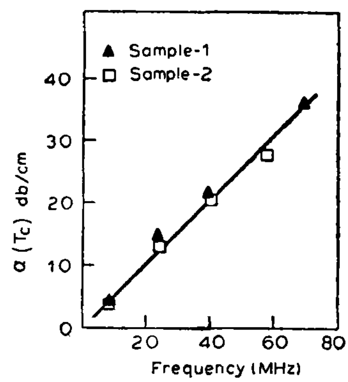

Figure 5. Frequency dependence of attenuation at the transition temperature.

Our attenuation data in RbH_2PO_4 differ from the corresponding data in KH_2PO_4 reported by Harnik and Shimshoni (1969) in several respects: (1) The maximum attenuation in RbH_2PO_4 is about 5 to 6 times higher than that in KH_2PO_4 (2) Cross-over behaviour was not reported in KDP (3) Harnik and Shimshoni (1969) did not observe any attenuation above the transition temperature. In RbH_2PO_4 limited attenuation data at 8 MHz for $T > T_c$ do point out to the existence of an attenuation anomaly above the transition temperature.

4. Theoretical considerations

In order to understand the anomaly of the acoustic waves near phase transition, it is important to consider the coupling of the acoustic wave with the order parameter. RbH_2PO_4 has a tetragonal structure (point group $\bar{4}2$ m) in the paraelectric phase. In this phase only one acoustic mode X_y is coupled by piezoelectric interaction to the polarization along the Z-axis, the order parameter for the transition. The acoustic longitudinal mode (ALM) propagating along the Z-axis is coupled to the order parameter by electrostrictive interaction. This implies, in the language of lattice dynamics, that the LA mode is coupled to the optical soft mode (OSM) by an interaction which is bilinear in the OSM coordinate and linear in ALM coordinate. In the ferroelectric phase, RbH_2PO_4 has orthorhombic structure (point group *mm*). Because of the lowering of symmetry and the appearance of spontaneous polarization the electrostrictive interaction now acquires an effective piezoelectric coupling part, the piezoelectric coupling coefficient being proportional to the spontaneous polarization. (This is also known as quadratic piezoelectric effect, see Jona and Shirane 1962).

The kind of interaction of the soft mode with the acoustic mode, mentioned above, has been considered by Pytte (1970). His results were derived for the phase transition in $SrTiO_3$ type of systems. But the results are valid for any soft mode phase transition. A summary of Pytte's results is also given by Fleury (1971). We reiterate some of these for the sake of clarity of our presentation.

We can write a simple schematic Hamiltonian for the coupled OSM and ALM as follows:

$$H = H_{\text{OSM}} + H_{\text{ALM}} + H_{\text{coup}}. \tag{2}$$

Here,

$$H_{\text{OSM}} = a\,\eta_1^2 + \xi_1^2/2m_1, \tag{2a}$$

$$H_{\text{ALM}} = b\,\eta^2 + \xi^2/2m, \tag{2b}$$

and

$$H_{\text{coup}} = d\,\eta_1\eta_1\eta. \tag{2c}$$

H_{OSM} (H_{ALM}) is the Hamiltonian for the OSM (ALM). η_1, m_1, ξ_1 (η, m, ξ) are respectively the normal coordinate, effective mass and the momentum conjugate to the normal coordinate for the OSM (ALM). H_{coup} describes the interaction between the two modes, and d is the strength of interaction. The normal coordinate η_1 of OSM can be written as,

$$\eta_1 = \langle \eta_1 \rangle + \delta\eta_1. \tag{3}$$

Heie $\langle\ \rangle$ indicates thermal average, and $\delta\eta_1$ is the fluctuation from the equilibrium value. It may be noted that $\langle \eta_1 \rangle$ is proportional to the spontaneous polarization. We can now write the coupling Hamiltonian,

$$H_{coup} = d\langle \eta_1 \rangle^2 \eta + 2d\langle \eta_1 \rangle\, \delta\eta_1 \eta + d\delta\eta_1 \delta\eta_1 \eta. \tag{4}$$

The first term on rhs produces only static strain in the system and no anomalous acoustic behaviour. In the paraelectric phase the second term is zero, since $\langle \eta_1 \rangle = 0$. Hence only the third term, which represents the interaction of the acoustic wave with the order parameter fluctuations, is responsible for the acoustic anomaly in this phase. In the ferroelectric phase $\langle \eta_1 \rangle \neq 0$ and hence, both the second and the third terms contribute to attenuation and velocity changes. The second term represents the effective linear interaction of the soft mode and the acoustic mode, with the interaction coefficient equal to $2d\langle \eta_1 \rangle$. This term is commonly known as resonant interaction. For $T < T_c$, as one approaches the transition temperature $\langle \eta_1 \rangle$ decreases, whereas the order parameter fluctuations and the correlations between them increase. The third term, therefore, is the dominant term close to T_c. Away from the transition temperature the second term dominates. We give below the predictions of acoustic anomaly due to resonant interaction and polarization fluctuations in the ferroelectric phase.

(i) *Resonant interaction*

Pytte's (1970) results for the attenuation and velocity changes due to resonant interaction are,

$$V^2 = V_0^2 \left(1 - \frac{d^2 \langle \eta_1 \rangle^2}{\omega_1^2(T)} \cdot \frac{1}{1 + \omega^2 \tau_1^2}\right), \tag{5}$$

$$\alpha = \frac{d^2 \langle \eta_1 \rangle^2}{V\, \omega_1^2(T)} \cdot \frac{\omega^2 \tau_1}{1 + \omega^2 \tau_1^2}. \tag{6}$$

Here, V_0 is the velocity of the uncoupled acoustic mode, V the normalized velocity, $\omega_1(T)$ the angular frequency of the soft mode, and τ_1 the relaxation time describing the damping of the soft mode,

$$\tau_1 = \frac{2\Gamma_1}{\omega_1^2(T)}, \tag{7}$$

where Γ_1 is the width of the soft mode. At ultrasonic frequencies we expect $\omega\tau_1 \ll 1$ and we can write,

$$V^2 = V_0^2\left(1 - \frac{d^2\langle\eta_1\rangle^2}{\omega_1^2(T)}\right), \tag{8}$$

$$a = \frac{d^2\langle\eta_1\rangle^2}{V\,\omega_1^2(T)} \cdot \omega^2\tau_1. \tag{9}$$

We see from eq. (8) that at ultrasonic frequencies (MHz region) the damping of the soft mode does not affect the velocity behaviour.

(ii) *Polarization fluctuation*

As mentioned earlier, the interaction of sound wave with the order parameter fluctuation should affect the observed behaviour close to the transition temperature. It may be mentioned here that the electrostrictive interaction is formally the same as the magnetostrictive interaction, which is responsible for the acoustic anomaly in magnetic phase transitions. In these systems, because of the short range nature of forces, the effects of order parameter fluctuations are dominant over a larger temperature region. There are several treatments available for the fluctuation term. The evaluation of acoustic anomaly due to fluctuations involves the evaluation of four spin correlation (Rehwald 1973). Inoue (1969) has also treated a similar interaction. Because of the nature of approximations employed, all these treatments overestimate the effect of fluctuations. Kawasaki (1971) has avoided this by the use of mode-mode coupling theory (Lüthi *et al* 1970). We state the results obtained by Kawasaki and compare them with our experimental results.

According to Kawasaki, the attenuation due to fluctuation is given by an expression of the form,

$$a_{\text{fluc}} \propto \omega\ \epsilon^{2W+3\nu'-2}\ \mathcal{F}\ (\omega/\Omega_{q=\kappa}). \tag{10}$$

Here W is a small positive number $\ll 1$, ν' the exponent for inverse correlation length, $\epsilon = |(T-T_c)/T_c|$, κ the inverse correlation length, Ω_q the characteristic angular frequency of fluctuation with wave vector q, and $\mathcal{F}(x)$ is a function of x. The characteristic frequency Ω_q given above can be expressed as,

$$\Omega_q = q^z\, G\,(q/\kappa), \tag{11}$$

where $G(y)$ is a function of y, the exponent z gives the wave vector dependence of Ω_q. Since $\kappa = \kappa_0\ \epsilon^{\nu'}$ we can write,

$$\Omega_{q=\kappa} = \kappa_0^{\,z}\ \epsilon^{z\nu'}\ G\,(1). \tag{12}$$

The function $\mathcal{F}(x)$ in eq. (10) is a complicated function of the argument. Kawasaki (1971) evaluated this function approximately for various regions of sound frequency and temperature and predicted the attenuation and velocity behaviours. For low sound frequency such that $\omega \ll \Omega_\kappa$ or at large values of ϵ, the attenuation and velocity anomaly behave as,

$$\alpha_{\text{fluc}} \propto \omega^2 \, \epsilon^{2W+3\nu'-2-z\nu'}, \tag{13}$$

and,

$$\triangle V = 0. \tag{14}$$

Here $\triangle V$ is the change in velocity. For intermediate temperature and frequency region the predictions are,

$$\alpha_{\text{fluc}} \propto \omega \, \epsilon^{2W+3\nu'-2} \, [b_0(\omega/\Omega_\kappa) - b_1(\omega/\Omega_\kappa)^{3/2}] \tag{15}$$

$$\triangle V/V = V \, \epsilon^{2W+3\nu'-2} \, (\omega/\Omega_\kappa)^{3/2}. \tag{16}$$

In eq. (16) b_0 and b_1 are constants. For high frequencies, $\omega \gg \Omega_\kappa$ or for small ϵ we have

$$\alpha_{\text{fluc}} \propto \omega \epsilon^0, \tag{17}$$

$$\triangle V/V \propto \omega^0 \epsilon^0. \tag{18}$$

The predictions in eqs (17) and (18) are transparent. The other predictions will be clear after we evaluate the exponents from the experimental results.

5. Data analysis

5.1. *Velocity data*

As explained in section 4, acoustic anomaly in the paraelectric phase should arise because of the interaction of the sound wave with the order parameter fluctuations. Further, the effect of fluctuations is believed to be symmetric about the transition temperature (Williams and Rudnick 1970; Pytte 1970; Tozaki and Ikushima 1977). In the paraelectric phase the entire velocity change occurs within 0·3°K of the transition temperature. Hence we expect that the order parameter fluctuations will affect the velocity behaviour only to within 0·3°K of the phase transition temperature in the ferroelectric phase. Putting a safer limit, the velocity behaviour for $T_c - T > 1$°K should be adequately described by the resonant interaction.

We rewrite eq. (8) as

$$\left(C_{33}^0 - C_{33}\right)^{-1} = \frac{\omega_1^2(T)\, S_{33}^0}{d^2 \langle \eta_1 \rangle^2}. \tag{19}$$

Here $S_{33}^0 = 1/C_{33}^0$. Thus using the temperature dependence of $\langle \eta_1 \rangle$ [$\langle \eta_1 \rangle$ is proportional to spontaneous polarization] and the elastic constant data for the longitudinal mode, we can determine the temperature dependence of the soft mode frequency. We determine below the temperature dependence of the soft mode frequency from the shear wave (X_y mode) data and show that the same result is obtained from the longitudinal wave data within a constant factor. This will be done for KDPr of which both the shear mode and the longitudinal data are available. For KH_2PO_4, Harnik and Shimshoni (1969) observed that,

$$\left(C^0_{33} - C_{33}\right)^{-1} = -9{\cdot}61 \times 10^{-12}\,[T-(T_c+1{\cdot}5)\,], \tag{20}$$

valid for $0{\cdot}005°K<T_c-T<1{\cdot}5°K$. The soft mode frequency from the longitudinal wave data is then from eqs (19) and (20).

$$\omega_1^2(T) = hP_s^2(T)\,[T-(T_c+1{\cdot}5)\,],\ T<T_c. \tag{21}$$

Here h is a constant. The acoustic shear mode (X_y) in KH_2PO_4 is coupled to the soft mode by piezoelectric interaction. One can show that for this mode (Fleury 1971),

$$\omega_1^2(T) = j\left(C^P_{66} - C^E_{66}\right)^{-1}, \tag{22}$$

where j is a constant, C^P_{66} $\left(C^E_{66}\right)$ is the elastic constant for the X_y mode at constant polarization (constant electric field). A comparison of $\omega_1^2(T)$ obtained from eqs (21) and (22) is given in figure 6. The points are the values of $\left(C^P_{66} - C^E_{66}\right)^{-1}$ from the data of Brody and Cummins (1968). The dashed curve is plotted from the rhs of eq. (21). For $P_s(T)$, we have used the data of Benepe and Reese (1971), which gives $P_s(T) \propto (T_c-T)^{0{\cdot}168}$. Since the constants j and h are unknown, the scale is so adjusted as to make the value of $\omega_1^2(T)$ given by eq. (21) equal to the value of $\left(C^P_{66} - C^E_{66}\right)$ at $T_c-T=4{\cdot}9°K$. We have assumed here that eq. (20) holds good up to $T_c-T=4{\cdot}9°K$ in the ferroelectric phase, though experimental data are available up to $T_c-T=1{\cdot}5°K$. The agreement between the two is indeed satisfactory. This shows that both the longitudinal and shear wave behaviour can be understood on the basis of dielectric behaviour, which is determined by $\omega_1^2(T)$.

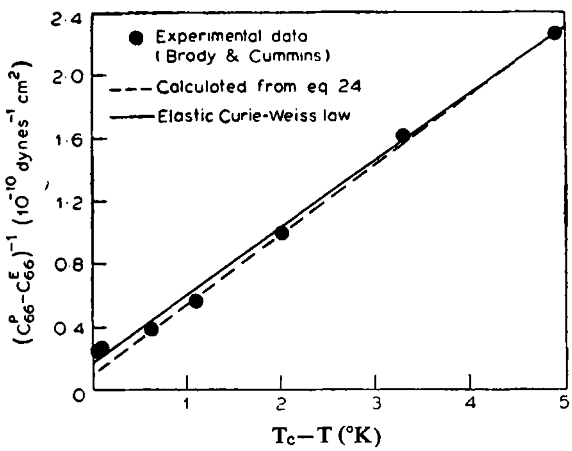

Figure 6. Comparison of the shear and longitudinal elastic constant anomaly in KH_2PO_4.

For RbH_2PO_4, using eqs (1) and (19), the soft mode frequency is,

$$\omega_1^2(T) = D\, P_s^2(T)\, [T - (T_c + T_0)]. \tag{23}$$

Here D is a constant and $T_0 \simeq 6°K$. Beck and Granicher (1950) and Chabin and Gilleta (1977) both give $P_s(T) \propto (T_c - T)^{0\cdot 16}$. Putting numerical values we find that the expression on the rhs of eq. (23) can also be fitted to give a relation of the type,

$$\omega_1^2(T) = D' [T - (T_c + 1°K)], \tag{24}$$

for $T < T_c - 1°K$. In eq. (24) D' is a constant. Thus the elastic constant data for the longitudinal mode give us the frequency of the soft mode within a constant factor. The factor can be determined from the measurement of the electrostrictive coefficient Q_{33}.

Finally, from eq. (19) one can write,

$$\left(S_{33} - S^0_{33}\right)^{-1} = C^0_{33}\left(\frac{\omega_1^2(T)}{d^2 \langle \eta_1 \rangle^2} - 1\right). \tag{25}$$

Here $S_{33} = 1/C_{33}$. Using eqs (1) and (19) we find.

$$\left(S_{33} - S^0_{33}\right)^{-1} = C\,[T - (T_c + T_1)]. \tag{26}$$

Here $C = B\, C^0_{33}$, and $T_1 = T_0 + S^0_{33} / B$. Such relations were shown to hold good for elastic constant data on KDP and DKDP by Harnik and Shimshoni (1969), and Shimshoni and Harnik (1970). They hold good for our data as well (figure 3). The point we want to emphasize here is that it is the resonant interaction and not the linear interaction (direct piezoelectric interaction) which governs the longitudinal velocity data in the ferroelectric phase.

For $T_c - T < 1°K$, the velocity anomaly should be caused by a combination of resonant interaction and fluctuation. Within the accuracy of the present data, it has not been possible to separate the two contributions.

5.2. *Attenuation data*

Our attenuation data for the longitudinal mode in the ferroelectric phase show several interesting features. First of all, the attenuation shows deviation from square frequency dependence in the temperature range of our measurements. This seems to indicate critical scattering. This view is confirmed by other findings given below. The temperature region for critical scattering in these materials is believed to be much smaller than the one observed here. The reason for this is not clear.

Another interesting feature of the attenuation data is the crossover behaviour. Often, an apparent crossover behaviour in the ultrasonic absorption is observed in magnetic phase transitions (Lüthi *et al* 1970) and also structural phase transition (Berre and Fossheim 1971) due to crystal imperfections, etc. This appears to be unlikely in the present case because of the following reasons. (1) In the present case two samples of different origin show very similar behaviour. (2) The crossover temperature is frequency dependent in RbH_2PO_4. This should be compared with the impurity ' roll off ' in magnetic and structural phase transitions where the crossover temperature is frequency-independent. (3) Dielectric measurements performed on a crystal which was cut from sample 1 showed a perfectly sharp transition. We believe, therefore, that the crossover is of dynamic origin.

In the temperature range of interest the observed attenuation should have contributions from (1) the resonant interaction, and (2) the interaction with order parameter fluctuations. Thus,

$$\alpha = \alpha_{\text{fluctuation}} + \alpha_{\text{resonant}}. \tag{27}$$

α_{resonant} is given by eqs (5) and (7) to be

$$\alpha_{\text{resonant}} = \frac{C_{33}^0 - C_{33}}{V_{33}\, C_{33}^0}\, \omega^2\, \tau_1. \tag{28}$$

If we identify τ_1 as the polarization relaxation time, eq. (28) is the same as the one used by Harnik and Shimshoni (1969) to interpret their attenuation data. The factor $\left(C_{33}^0 - C_{33}\right)/ V_{33}\, C_{33}^0$ on the rhs of eq (28) is a slowly varying functions of temperature. From the Landau-Khalatnikov theory we expect $\tau_1 \propto (T_c - T)^{-1}$. Equation (28), therefore, gives attenuation behaviour of the type $\alpha \propto \omega^2 (T_c - T)^{-1}$. Numerical work to fit the above expression to the observed data shows that the contribution of the resonant interaction to the total attenuation is negligible. This is also seen from the strong deviation of the observed exponents for the frequency and the temperature dependence of attenuation from the ones suggested in eq. (28).

Of the available treatments that take into account the interaction of the sound wave with the fluctuations, the ones by Pytte (1970), Rehwald (1973) and Schwabl (1973) predict a square frequency dependence and, therefore, do not account for our data. The results are, therefore, compared with the expression derived by Kawasaki (1971). For this we adopt the approach taken by Tozaki and Ikushima (1977). Figure 7 shows a plot of the normalized attenuation $\alpha/\alpha\,(T_c)$ as a function of $2\pi(T_c - T)/\omega$. All the data points seem to fall on the same curve within the limits of experimental errors. Since $\alpha\,(T_c) \propto \omega$, the attenuation follows a relation of the form,

$$\alpha \propto \omega f \left(\frac{2\pi\,(T_c - T)}{\omega}\right). \tag{29}$$

If we compare eq. (29) with the generalized form of attenuation given by Kawasaki eq. (10), we find the following results:

(a) It implies that $2W+3\nu'-2=0$. This relation was also conjectured from scaling arguments (Kawasaki 1971). Now since $W \simeq 0$, we get $\nu' = 2/3$. This is in agreement with the observation of Strukov *et al* (1972). They find that for RbH_2PO_4 the specific heat exponent $\alpha' = 0$. From static scaling laws (Stanley 1971), we have,

$$\nu' d' = 2 - \alpha', \tag{30}$$

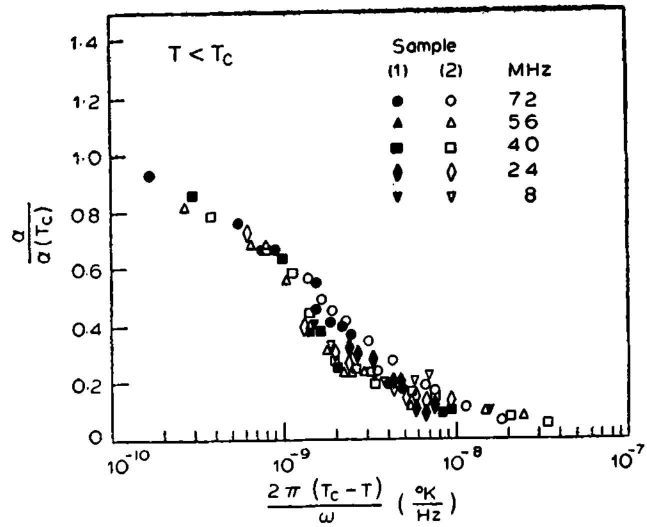

Figure 7. Scaling behaviour of the ultrasonic attenuation in RbH_2PO_4.

d' is the dimension of the system. For $d' = 3$, eq. (30) gives $\nu' = 2/3$.

(b) A further comparison of eqs (29) and (10) implies $f(x) \equiv \mathcal{F}(x^{-1})$. We thus get using eq. (12) $\nu' z = 1$. This gives us $z = 3/2$. There are, however, no predictions of z for KDP type of ferroelectrics.

We now come to the specific predictions which, it may be mentioned, involve approximations. Close to the transition temperature and for high frequencies Kawasaki predicts eq. (17), $\alpha \propto \omega\epsilon^{0}$. This is in close agreement with the behaviour observed in our experiment, $\alpha \propto \omega\epsilon^{0\cdot 16}$. As for other predictions, we do not observe the relation given by eq. (13) which is $\alpha \propto \omega^{2}\epsilon^{-1}$ and which is valid for large values of $T_c - T$. Relation (15) which gives $\alpha \propto (\omega^{2}/\Omega_{\kappa})\,(b_0 - b_1\,(\omega/\Omega_{\kappa})^{1/2})$ for the intermediate temperature region can show an apparent temperature dependence of the form $\alpha \propto \epsilon^{-p}$ where $p < 1$, with suitable constants b_0 and b_1. We do observe $p < 1$ ($p = 0\cdot 69$) in the intermediate temperature region, but more data covering a larger temperature and frequency range are necessary for a detailed comparison.

6. Discussion and conclusions

We have found that the longitudinal mode velocity behaviour in the ferroelectric phase in case of both KH_2PO_4 and RbH_2PO_4 can be well understood in terms of the resonant part of the electrostrictive interaction between the longitudinal sound wave and the order parameter. It is also shown that the elastic behaviour, both for the propagation of shear (X_y) wave and the longitudinal (Z_z) wave can be correlated with the anomaly of the static dielectric constant along the polar axis.

For the ultrasonic attenuation in RbH_2PO_4 the electrostrictive coupling between the longitudinal strain and the order parameter provides a satisfactory explanation, if one takes into account the interaction of the sound wave with the order parameter fluctuations. There is evidence that the dynamic scaling laws hold good in this case. There is, however, need to check these conclusions by further experiments. It will be helpful if one can obtain the ultrasonic data in the paraelectric phase of RbH_2PO_4. Study of the frequency dependence of the velocity will be of further help in understanding this behaviour.

It may be mentioned that an explanation other than the critical scattering cannot be ruled out at present. For example, it will be useful to obtain the effects of the central peak excitation on the ultrasonic absorption from the theory.

The electrostrictive interaction also seems to provide qualitative explanation for the observed attenuation behaviour for KD_2PO_4. In this case the phase transition is of a strong first order character. Consequently, as can be seen from eq. (4), the resonant interaction is expected to be the dominant one in the ferroelectric phase. In this case, therefore, the values of τ obtained by eq. (28) should be of correct magnitude. This is evident from the result of Shimshoni and Harnik (1970) (longitudinal mode) and that of Litov and Uehling (1970) (shear mode).

The case of KH_2PO_4 still presents some problem, in that the values of τ obtained from the longitudinal mode measurements differ from the values obtained from the shear mode measurements. It should be noted, however, that the shear mode measurements in KH_2PO_4 were performed under an electric field of $\sim$ 3–4 kV/cm. The critical field (the electric field required to reduce the discontinuity in the polarization at T_c to zero) is only $\sim$ 200 V/cm. An electric field of $\sim$ 3–4 kV/cm is expected to perturb the phase transition rather strongly. In case of KD_2PO_4 there is no such problem as the electric field of 1·5 kV/cm applied by Litov and Uehling (1970) for the shear mode measurements is much smaller than the critical field of $\sim$ 7·1 kV/cm (Sednenko and Gladkii 1973). It appears, therefore, essential to obtain some quantitative information about the effect of electric field on the phase transition. Measurements of the longitudinal ultrasonic wave propagation, in the presence of an electric field along the polar axis, should help in this case.

Acknowledgements

We are thankful to Messrs M J Mehta, H P Dubbal, S N Malekar and J S Sidhu, members of our laboratory staff, for their technical help and their untiring cooperation during the execution of this work.

References

Barber C R 1950 *J. Sci. Instrum.* **27** 47

Beck M and Granicher H 1950 *Helv. Phys. Acta* **23** 522

Benepe J W and Reese W 1971 *Phys. Rev.* **B3** 3032

Berre B and Fossheim K 1971 *Structural phase transitions and soft modes* eds. Samuelson *et al* (Oslo: Universitets forlaget) p. 225

Brody E M and Cummins H Z 1968 *Phys. Rev. Lett.* **21** 1263

Chabin M and Gilleta F 1977 *Ferroelectrics* **15** 149

Fleury P A 1971 *J. Acoust. Soc. Am.* **49** 1042

Garland C W 1970 *Physical acoustics* eds. W P Mason and R N Thurston (Academic Press) Vol. 7 Ch. 2

Garland C W and Novotony D B 1969 *Phys. Rev.* **17** 9711

Halperin B I and Hohenberg P C 1969 *Phys. Rev.* **177** 952

Harnik E and Shimshoni M 1969 *Phys. Lett.* **A29** 620

Inoue M 1969 *J. Phys. Soc. Jpn.* **26** 420
Jona F and Shirane G 1962 *Ferroelectric crystals* (Oxford: Pergamon Press) p. 76
Kawasaki K 1971 *Int. J. Magnetism* **1** 171
Landau L D and Khalatnikov I M 1954 *Dokl. Akad. Nauk. USSR* **96** 2169
Litov E and Garland C W 1970 *Phys. Rev.* **B2** 4597
Litov E and Uehling A 1968 *Phys. Rev. Lett.* **21** 809
Litov E and Uehling E A 1970 *Phys. Rev.* **B1** 3713
Lüthi B, Moran T J and Pollina R J 1970 *J. Phys. Chem. Solids* **31** 1741
Mishchenko A V, Dovchenko G V and Reshchikova L M 1972 *Sov. Phys. Crystallogr.* (Englis . Trans.) **17** 360
Mnatsakanyan A V, Shuvalov L A, Zheludev I W and Gavrilov I V 1966 *Sov. Phys. Crystallogr.* **11** 412
Peercy P S 1973 *Phys. Rev. Lett.* **31** 380
Pierre Mme C, Duffour J P and Remoissenet M 1971 *Solid State Commun.* **9** 1493
Pytte E 1970 *Phys. Rev.* **B1** 924
Rehwald W 1973 *Adv. Phys.* **22** 721
Schwabl 1973 *Phys. Rev.* **B7** 2038
Sednenko E V and Gladkii V V 1973 *Sov. Phys. Crystallogr.* (English Transl.) **17** 861
Shimshoni M and Harnik E 1970 *Phys. Lett.* **A32** 321
Singh G P and Basu B K 1976a *Phys. Lett.* **A58** 39
Singh G P and Basu B K 1976b *Proc. Nucl. Phys. Solid State Phys. Symp.* **C19**
Singh G P and Basu B K 1978 *Phys. Lett.* **A64** 425
Singh G P and Singh S 1978 (to be published)
Stanley H E 1971 *Introduction to phase transition and critical phenomena* (Oxford: Clarendon Press) p. 196
Suemene Y 1967 *J. Phys. Soc. Jpn.* **22** 735
Strukov B A, Korzhev M A, Baddur A and Kopstik V A 1972 *Sov. Phys. Solid State* (English Transl.) **13** 1569
Tozaki K and Ikushima A 1977 *Phys. Lett.* **A59** 458
Williams R D and Rudnick I 1970 *Phys. Rev. Lett.* **25** 276