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Ultrasonic dispersion in the phase transition region of ferroelectric materials

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Abstract

Measurements of longitudinal ultrasonic velocity and attenuation have been performed in several ferroelectric materials. Interesting behaviour of the ultrasonic velocity was observed in $Ca_2Sr(C_2D_5CO_2)_6$ (DDSP) single crystals. The temperature dependence of τ in the DDSP crystal was estimated to be $3.5\times10^{-9}/(T-T_c)$ s.

1. Introduction

In recent years, ultrasonic investigation in the vicinity of the ferroelectric phase transition has been recognized as an important method to study the static and dynamic properties of the phase transition [1]. In crystals which are non-piezoelectric in the paraelectric phase, the ultrasonic velocity and attenuation anomalies arising in ferroelectrics can be described by the Landau–Khalatnikov relaxation mechanism [2], in which the polarization relaxation time increases as $(T-T_c)^{-1}$ on approaching the ferroelectric phase transition temperature T_c. The increase in polarization relaxation time manifests itself in temperature- and frequency-dependent anomalies of the dielectric properties near T_c. The dielectric properties have been investigated extensively [3, 4] and dielectric dispersion has been observed at various frequencies in various ferroelectric materials [5]. Such relaxational behaviour must also influence the dynamic elastic properties and cause ultrasonic dispersion. If the relaxation time is relatively short the dispersion appears only at high frequencies and may be observed in Brillouin experiments [6]. In the ultrasonic frequency range 10–90 MHz the velocity dispersion must appear in a very narrow temperature region which experimentally is difficult to resolve. On the other hand, if the polarization relaxation time is long enough (*i.e.* dielectric relaxation is revealed in the megahertz frequency region), the velocity dispersion can be easily observed at ultrasonic frequencies. However, until now, to our knowledge, such dispersion has not been investigated at ultrasonic frequencies.

The main purpose of this paper is to present results showing the ultrasonic velocity dispersion in $Ca_2Sr(C_2D_5CO_2)_6$ (DDSP) single crystals in the 10–90 MHz frequency region. First, however, the temperature and frequency dependences will be presented for ferroelectric $Sn_2P_2S_6$, $PbHPO_4$ (LHP) and diglycine nitrate (DGN) single crystals. For these crystals the condition $\omega\tau<1$ (ω is the angular frequency of the ultrasound and $\tau=\tau_0/(T-T_c)$ is the polarization relaxation time) was valid up to temperatures very close to T_c. Thus velocity dispersion has not been observed. In all these crystals the downward stepwise anomaly of ultrasonic velocity and corresponding attenuation maximum have been observed. The condition $\omega\tau>1$ was fulfilled in a wide temperature range near T_c in crystals of $(CH_3)_2NH_2Al(SO_4)_2\cdot6H_2O$ (DMAAS) because of the extremely long polarization relaxation time. In these crystals we have not observed any slowing down of the ultrasonic velocity at T_c.

2. Experimental details

The ultrasonic velocity and attenuation were measured by the pulse echo method [7]. For excitation and detection of longitudinal ultrasonic waves, z-cut $LiNbO_3$ transducers vibrating on 10 MHz main frequency and on harmonics were used. The crystalline samples were prepared so that both parallel polished faces were perpendicular to the desired crystallographic axis. Silicone oil was used as an acoustic bond. The temperature was stabilized and measured to an accuracy of better than 0.05 K. The estimated accuracy of the absolute ultrasonic velocity measurements was about 3%. The relative changes in ultrasonic velocity were estimated by the shift in the delay time of the detected ultrasonic radio pulse on the screen of the scope with a precision of better than 1 ns. Measurements were always per-

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formed by cooling the sample through the phase transition temperature.

3. Phenomenological theory

The elastic constant evaluated from the ultrasonic experiment is the real part of the complex frequency-dependent elastic constant $c^*(\omega)$. For temperatures close to but below the phase transition temperature T_c in ferroelectric materials, ω can be compared to the inverse relaxation time of polarization, so that dispersion can affect the value of $c^*(\omega)$. In this case, from the Landau–Khalatnikov theory, in the ferroelectric phase

$$c^*(\omega)=c_\infty-\frac{c_\infty-c_0}{1+i\omega\tau} \tag{1}$$

where c_∞ is the elastic constant at high frequencies and c_0 is the static value of the elastic constant in the low temperature phase.

From the general theory of elasticity it is easy to get expressions for the ultrasonic velocity and attenuation:

$$v^2=\frac{1}{\rho}\,\mathrm{Re}c^*$$

$$=v_\infty^2-\frac{v_\infty^2-v_0^2}{1+\omega^2\tau^2} \tag{2}$$

$$\alpha=\frac{1}{2\rho v_0^3}\,\omega\mathrm{Im}c^*$$

$$=\frac{v_\infty^2-v_0^2}{2v_0^3}\,\frac{\omega^2\tau}{1+\omega^2\tau^2} \tag{3}$$

In order to get the expressions for the ferroelectric phase, the free-energy density of a proper uniaxial ferroelectric without piezoeffect in the paraelectric phase can be written as

$$F=F_0+\frac{\alpha}{2}(T-T_c)P^2+\frac{\beta}{4}P^4+\frac{\gamma}{6}P^6+guP^2+\frac{1}{2}c_\infty u^2 \tag{4}$$

where α, β and γ are Landau expansion coefficients, g is the appropriate electrostriction tensor component, u is the elastic strain component and P is the polarization. Using the equation of equilibrium, the static elastic constant can be straightforwardly calculated as

$$c=c_\infty-\frac{2\rho^2}{\beta+2\gamma P^2} \tag{5}$$

Usually ΔP induced by strain is less than the static value of the polarization, P_0, and the P in (5) can be changed to P_0:

$$P_0=\frac{-\beta+[\beta^2-4\alpha\gamma(T-T_c)]^{1/2}}{2\gamma} \tag{6}$$

Then we get

$$c=c_0=c_\infty-\frac{2g^2}{\beta\left(1+\dfrac{T-T_c}{n}\right)^{1/2}} \tag{7}$$

where $n=\beta^2/4\alpha\gamma$.

Rewriting (7) in the form $\Delta c=c_\infty-c_0=\rho v_\infty^2-\rho v_0^2$ (where ρ is the density), one finds in the ferroelectric phase that $(\Delta c)^{-2}$ as well as $(v_\infty^2-v_0^2)^{-2}$ can be expressed by simple linear temperature dependences:

$$(\Delta c)^{-2}=\frac{\beta^2\left(1+\dfrac{T_c-T}{n}\right)}{4g^4} \tag{8}$$

$$(v_\infty^2-v_0^2)^{-2}=\frac{\rho^2\beta^2\left(1+\dfrac{T_c-T}{n}\right)}{4g^4} \tag{9}$$

The relaxation time according to the Landau theory is

$$\tau=\frac{\tau_0}{T_c-T} \tag{10}$$

Then in the phase transition region the ultrasonic velocity dispersion according to (2) must correspond to the maximum ultrasonic attenuation. In the ultrasonic frequency region when τ_0 is comparatively small, 10^{-11}–10^{-12} s K, the velocity dispersion will appear in a very narrow temperature range below the phase transition, which makes it difficult to observe experimentally. In this case the condition $\omega\tau<1$ is valid in the ferroelectric phase and there is no velocity dispersion. If $\tau_0=10^{-6}$–10^{-7} s K, the condition $\omega\tau>1$ is fulfilled in a wide temperature range below T_c and ultrasonic measurement gives the high frequency value of the ultrasonic velocity, v_∞. In this case the velocity anomaly determined by c_∞ can exist, because the fourth-order term Au^2P^2 must be added in (4), which gives the following contribution to c_∞ [8]

$$c'_\infty=c_\infty+AP^2 \tag{11}$$

It is necessary to mention that such a four-phonon interaction remains for comparatively high frequencies and no velocity dispersion can be expected in the ultrasonic frequency region. The most interesting case arises when $\tau_0\approx10^{-9}$ s K; then in the ultrasonic frequency region of tenths of megahertz we expect to observe clear ultrasonic dispersion.

4. Results and discussion

The $Sn_2P_2S_6$ single crystals exhibit a second-order phase transition at $T_c = 339$ K [9]. Here we only present the longitudinal ultrasonic velocity and attenuation behaviour along the Y axis (Fig. 1). The ultrasonic velocity temperature dependence in the gigahertz frequency region obtained from Brillouin experiments [10] is shown in Fig. 1 by triangles and is completely identical to our measurements at 10 MHz frequency. It can be easily concluded that in this frequency region no ultrasonic velocity dispersion exists. Therefore in our measurements we get the low frequency values of the ultrasonic velocity, v_0, in the ferroelectric phase for $Sn_2P_2S_6$. $v_0(T)$ follows the Landau theory (8), because a linear temperature dependence of $(\Delta c)^{-2}$ was obtained. The attenuation peak at T_c was very high and sharp. The temperature dependence of the ultrasonic attenuation is shown in the inset of Fig. 1. The polarization relaxation time estimated from our attenuation measurements was $\tau \approx 10^{-11}/(T - T_c)$ s. This is consistent with the Brillouin measurements [10]. For the crystals of LHP similar results have been obtained. The ultrasonic measurements were performed in the frequency range 10–50 MHz along the Y axis perpendicular to the direction of polarization. No frequency dispersion of the ultrasonic velocity in this frequency range was observed (Fig. 2). The validity of the Landau theory was also checked using eqn. (9) and very good agreement was found. The temperature dependences of the attenuation are shown in Fig. 3. The polarization relaxation time calculated from the attenuation measurements at various frequencies followed the law (10) with $\tau_0 = 3 \times 10^{-11}$ s K in the ferroelectronic phase (see inset of Fig. 3). The value of τ_0 is in the middle of

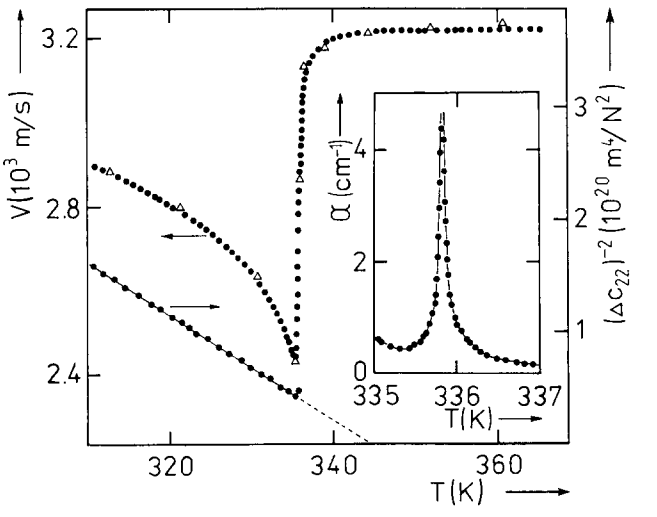

Fig. 1. Temperature dependence of ultrasonic velocity and $(\Delta c_{22})^{-2}$ for $Sn_2P_2S_6$ crystal. Inset shows temperature dependence of attenuation. Ultrasonic frequency 10 MHz.

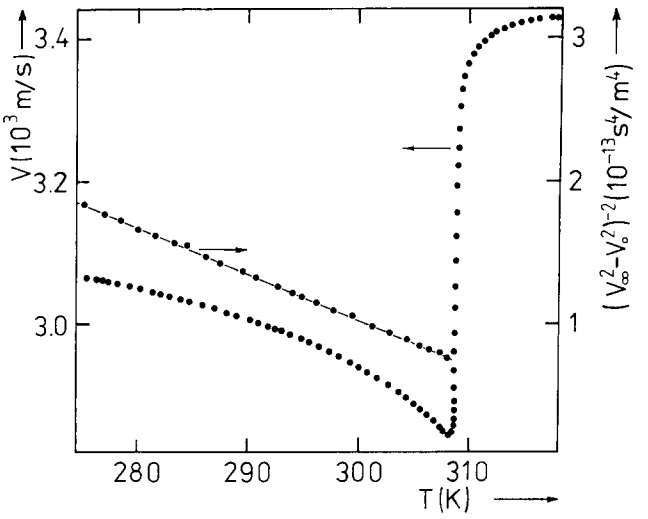

Fig. 2. Temperature dependence of ultrasonic velocity v and $(v_\infty - v_0)^{-2}$ for longitudinal mode along Y axis for LHP crystal.

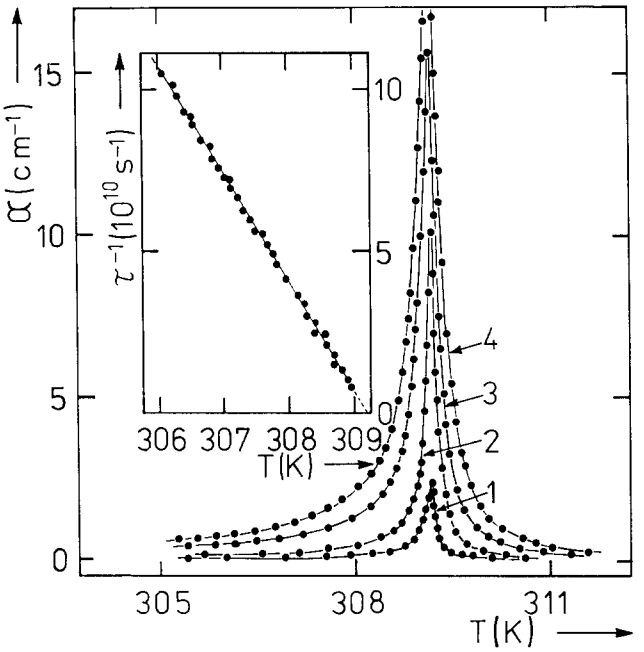

Fig. 3. Temperature dependence of ultrasonic attenuation coefficient in LHP crystal at various frequencies (MHz): 1, 10; 2, 30; 3, 40; 4, 50. Inset shows temperature dependence of τ^{-1}.

the data obtained from Brillouin [11] and IR [12] measurements. The attenuation and velocity frequency dependences for longitudinal ultrasonic waves propagating along the Y axis perpendicular to the polar axis were also measured in DGN crystals at 30 and 50 MHz frequencies near the phase transition at $T_c = 206$ K. These results could also be described according to the Landau theory in the ferroelectric phase. The polarization relaxation time followed the Curie–Weiss law $\tau = 5 \times 10^{-10}/(T_c - T)$ s, which is similar to previous measurements at 10 MHz frequency [13]. The results obtained for $Sn_2P_2S_6$, LHP and DGN crystals reflect

the low frequency regime ($\omega\tau<1$) which was mostly investigated by ultrasonic methods previously [1].

The frequency dependence of the longitudinal ultrasonic velocity was absent in DMAAS single crystals (Fig. 4). As is clearly seen, the result is opposite to that for the above-discussed ferroelectric materials. There was no ultrasonic velocity slowing down near $T_c=152$ K in the polar and perpendicular directions. The excess ultrasonic velocity in the ferroelectric phase is due to the mentioned fourth-order term Au^2P^2 which could be added in the free-energy expansion (11). We do not consider the peculiarities of this behaviour here because a discussion of this was published previously [8]. Also, we should emphasize that in the DMAAS crystals the condition $\omega\tau>1$ was valid in the frequency and temperature range of our investigations.

The most interesting behaviour of the ultrasonic velocity was obtained in ferroelectric DDSP single crystals when the ultrasonic waves propagated along the [100] direction, which is perpendicular to the polar axis of the crystal. In this crystal velocity dispersion was observed in the frequency range 10–70 MHz (Fig. 5). To our knowledge, this is the first observation of velocity dispersion at ultrasonic frequencies. The ultrasonic attenuation maximum (Fig. 6) shifted to lower temperatures with increasing frequency, showing that the relaxation time increased near $T_c=279.2$ K. The values of the attenuation at the maxima were proportional to ω, as they should be according to (3) (when the condition $\omega\tau\approx1$ is fulfilled). The relaxation time of polarization in the ferroelectric phase was found to be $\tau=3.5\times10^{-9}/(T_c-T)$ s (see inset of Fig. 6), which is very close to the value obtained from dielectric measurements [14]. The ultrasonic velocity behaviour far from T_c could be described by including the fourth-order term in the Landau free-energy expansion as was done for the DMAAS crystals above. It is interesting

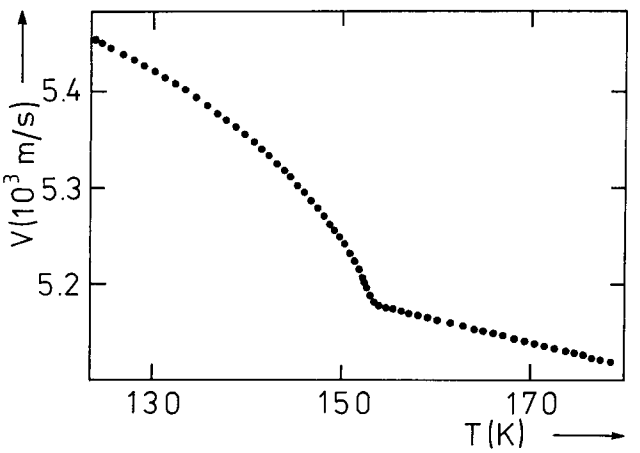

Fig. 4. Temperature dependence of ultrasonic velocity measured perpendicular to polar direction in DMAAS crystal at 30 MHz frequency.

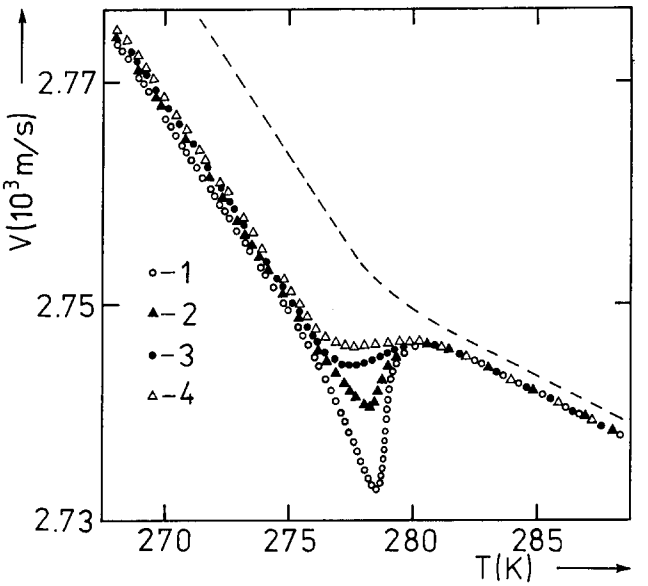

Fig. 5. Temperature dependence of ultrasonic velocity in DDSP crystal at various frequencies (MHz): 1, 10; 2, 30; 3, 50; 4, 70. Dashed curve represents Brillouin data from ref. 15.

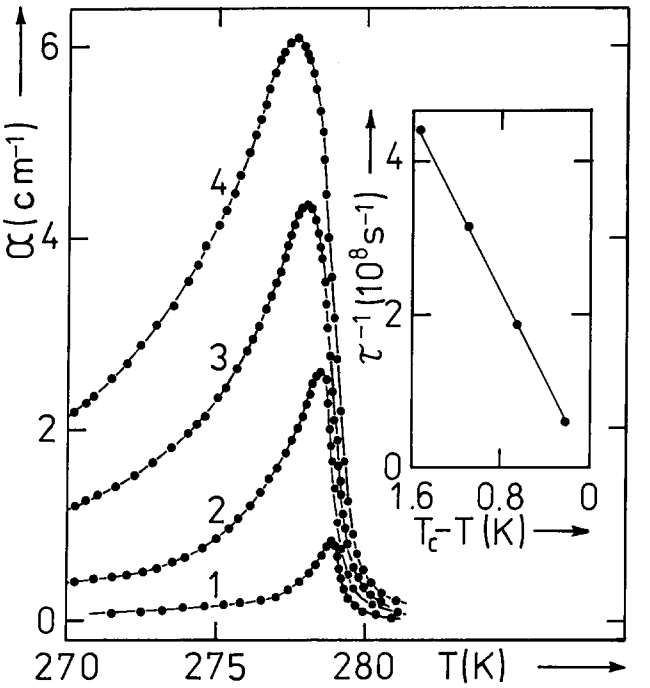

Fig. 6. Temperature dependence of ultrasonic attenuation in DDSP crystal at various frequencies (MHz): 1, 10; 2, 30; 3, 50; 4, 70. Inset shows temperature dependence of reciprocal polarization relaxation time.

to note that at these temperatures the ultrasonic velocity data were in good agreement with values obtained from previous Brillouin-scattering experiments [15]. At gigahertz frequencies of those experiments the slowing down at T_c was not observed as it should be, because there the condition $\omega\tau>1$ is valid in a wide temperature range in the ferroelectric phase.

Ultrasonic velocity and attenuation measurements performed in several uniaxial ferroelectric materials with the longitudinal waves propagating perpendicular to the polar axis indicate that the results in the ferroelectric phase can be well described by the Landau–Khalatnikov theory. Also, the velocity behaviour near T_c at ultrasonic frequencies can be very different depending on the polarization relaxation time.

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References

1 W. Rehwald, in K.A. Müller and H. Thomas (eds.), *Topics in Current Physics*, Vol. 23, Springer, New York, 1981, p. 190.
2 L.D. Landau and I.M. Khalatnikov, *Dokl. Akad. Nauk SSSR, 96* (1954) 469.
3 A. Brilingas, R.L. Davidovich, J. Grigas, S. Lapinskas, M.A. Medkov, V. Samulionis and V. Skritskii, *Phys. Status Solidi A, 96* (1986) 101.
4 R. Mizeris, J. Grigas, L.A. Shuvalov and A.I. Baranov, *Ferroelectrics Lett., 7* (1987) 83.
5 J. Grigas, J. Banys and R. Sobiestianskas, *Ferroelectrics, 133* (1992) 199.
6 Y. Tsujimi, T. Yagi, H. Yamashita and I. Tatsuzaki, *J. Phys. Soc. Jpn., 50* (1981) 184.
7 A. Kezionis, A. Orliukas, K. Paulavicius and V. Samulionis, *Mater. Sci. Forum, 76* (1991) 229.
8 R. Sobiestianskas, J. Grigas, V. Samulionis and E.F. Andreyev, *Phase Transitions, 29* (1991) 167.
9 V. Valevichius, V. Samulionis and V. Skritskii, *Ferroelectrics, 79* (1988) 225.
10 A.I. Ritus, N.C. Roslik, Yu.M. Vysochansky, A.A. Grabar and V.Yu. Slivka, *Fiz. Tverd. Tela, 27* (1988) 2225.
11 B.B. Lavrencic, M. Copic, M. Zgodnik and J. Petzelt, *Ferroelectrics, 21* (1978) 325.
12 J. Kroupa, J. Petzelt, G.V. Kozlov and A.A. Volkov, *Ferroelectrics, 21* (1978) 387.
13 B.A. Strukov, S.V. Rodin, K.A. Minayeva and I.A. Lenchik, *Fiz. Tverd. Tela, 30* (1988) 810.
14 E. Nakamura, K. Deguchi, T. Nishikara and T. Yagi, *Ferroelectrics, 109* (1990) 57.
15 T. Yagi, H. Fujisaki and A. Sakai, *J. Phys. Soc. Jpn., 56* (1987) 2535.