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Acoustic anomalies in NH_4LiSO_4 near the uniaxial ferroelectric phase transition at $T_c \simeq 460$ K

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Abstract. The velocity and attenuation of the longitudinal ultrasonic wave propagating along the a axis perpendicular to the ferroelectric b axis with frequencies ranging from 10 to 90 MHz were measured around the ferroelectric phase transition in NH_4LiSO_4. The data have been analysed in terms of the Landau theory including small fluctuation corrections. A crossover in the order parameter dynamics from dipole to Ising-type behaviour is observed in the paraelectric phase of NH_4LiSO_4. This crossover manifests itself in the specific temperature dependence of the elastic constants and sound attenuation above T_c.

1. Introduction

Ammonium lithium sulphate (ALS) NH_4LiSO_4 undergoes at least two phase transitions (Pepinsky *et al* 1958, Mitsui *et al* 1975). The present work reports ultrasonic measurements around the ferroelectric phase transition at $T_c \simeq 460$ K, and gives a theoretical model to explain the data.

ALS is built of corner-sharing SO_4 and LiO_4 tetrahedra which occupy in the high-temperature disordered phase D_{2h}^{16} ($Z = 4$) two equivalent orientations with equal probability, having a mirror symmetry plane between these two orientations perpendicular to the b axis (Itoh *et al* 1981). The orientation of the crystal axis has been chosen as given by Wyslouzil *et al* (1986). In the low-temperature ferroelectric phase C_{2v}^9 ($Z = 4$) the SO_4 and LiO_4 tetrahedra occupy only one of the two orientations. This phase is weakly ferroelectric with the spontaneous polarization along the b direction. The phase transition is slightly first order (Iskornev and Flyorov 1977, Tomaszewski *et al* 1979).

We are here concerned with a detailed acoustic investigation of this phase transition. Ultrasonic studies can provide information about both the static and the dynamic behaviour near phase transitions. Indeed, a considerable amount is already known about the acoustic behaviour of ALS from careful ultrasonic (Wyslouzil *et al* 1986, Schranz *et al* 1987a) and Brillouin (Hirotsu 1983, Luspin *et al* 1984, 1985) measurements. Hirotsu (1983) has shown that longitudinal acoustic waves are coupled to the order parameter P_y via quadratic terms of the form $\sum k_i u_i P_y^2$ and $\sum k_i u_i^2 P_y^2$ and Wyslouzil *et al* (1986) have developed concisely the Landau theory. Schranz *et*

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al (1987a, b) have shown that there exists a peculiar behaviour in the c_{66} mode and explained it as the onset of a ferroelastic transition and its suppression due to the occurence of the ferroelectric transition. A united Landau theory of the ferroelectric and ferroelastic phase transitions in ALS was proposed by Mroz *et al* (1989). The phase diagram describing the whole sequence of phase transitions in ALS based on a two-dimensional order parameter was developed by Torgashev *et al* (1984).

Concerning the dynamics, the relaxation time of the order parameter near the ferroelectric phase transition has been studied by Yamamoto *et al* (1983) and Luspin *et al* (1984) using Brillouin scattering measurements. The results for the relaxation time in the ferroelectric phase yielding $\tau = 9 \times 10^{-11}(T_1 - T)^{-1}$ s (Yamamoto *et al* 1983) and $\tau = 1.1 \times 10^{-11}(T_1 - T)^{-1}$ s (Luspin *et al* 1984) are rather different; this can be attributed to the different resolving powers of the apparatus used. Both results are based on the Landau–Khalatnikov theory.

The critical behaviour in the specific heat of ALS near $T_c \simeq 460$ K was studied by Sandvold (1987). The data have been analysed in terms of critical exponents which were not compatible with 3D Ising behaviour. To explain his value of $\alpha \simeq 0.5$ he suggested that the ferroelectric phase transition in ALS is close to a tricritical point.

In the present study we have analysed the anomalies in the elastic constants and sound attenuation in terms of Landau theory including small fluctuation corrections. Since ALS belongs to the weak ferroelectric group this induces some peculiarities in the order parameter dynamics (Tagantsev *et al* 1987). Because of the extremely small value of the Curie constant $C_+ = 5.6$ K (Mitsui *et al* 1975), ALS is a good candidate for the observation of a crossover in the order parameter dynamics from dipole to Ising type (see, e.g., Smolenskii *et al* 1985). This crossover should show up in the real and imaginary parts of the elastic susceptibilities, as will be discussed below.

We present our results on the acoustic velocity and attenuation of longitudinal waves ($k \| a$) as a function of temperature and frequency and describe the data using the Landau theory including small fluctuation corrections with the aim of obtaining a consistent picture of the paraelectric-to-ferroelectric phase transition in ALS. The experimental procedure is summarized briefly in section 2, the results are discussed in section 3, and a summary is given in section 4.

2. Experimental procedure

The high-purity single crystal of ALS used in the present study was obtained from an aqueous solution of threefold-purified ALS using a two-tank growth procedure (Wyslouzil 1985). The samples for ultrasonic experiments were of good optical quality and were cut with a diamond saw. The orientation of the crystal was obtained using a polarization microscope and samples were prepared by grinding with Al_2O_3 powder of size 12.5 and 5 μm and using a precision lapping machine with diamond pastes (3–1 μm) in Diaplastol from Ernest Winter und Sohn GmbH as a lapping fluid. The accuracy of orientation was better than $\pm 1°$. The sample dimensions were about 5 mm×10 mm×10 mm. The accuracy of the linear dimension along the a axis was better than ± 2 μm and the end planes were parallel to within 1×10^{-3} rad. The density of the samples was taken to be 1.900 ± 0.001 g cm^{-3} (Wyslouzil *et al* 1986).

Overtone polished 10 MHz Y-cut $LiNbO_3$ transducers (diameter, 0.125 in) from Valpay Fisher were used on their fundamental, third, fifth, seventh and ninth harmonic resonances. The transducers were bonded to the (100) faces by using UHU

PLUS bond. The specimen was mounted in the sample chamber (Wyslouzil 1985) with a controlled temperature gradient along the sample. The temperature gradient was constant along the sample to within 0.02 K during the measurement. The measurements were performed by increasing or decreasing the temperature at a rate of about 0.2 K min^{-1} far from T_c and at 0.02 K min^{-1} in a range of about 10 K around T_c. After heating the sample to the temperature at which the paraelectric phase was obtained, the temperature was kept at least 15 K above T_c for at least 12 h before starting the cooling run.

The pulse echo overlap method (Papadakis 1976) with one transducer was used to determine the velocity of sound. The measurements were performed for 10 and 30 MHz in the temperature range 300–530 K, and for the frequencies 50, 70 and 90 MHz in the temperature range 460–480 K. However, at the higher frequencies the signal tended to disappear in a range of 2 K around T_c.

The ultrasonic attenuation coefficient was measured together with the velocity by using the exponential-comparator method (Truell *et al* 1969) for frequencies 10, 30, 50, 70 and 90 MHz in the temperature range 300–475 K. In sample 1 the reflected ultrasound pulses have shown a sufficiently exponential decay pattern in the whole temperature range; in samples 2 and 3, probably because of wedge-shaped bonding, a Bessel modulation of the echoes was observed. For sample 1 the relative accuracy of the attenuation coefficient was estimated to be about ±5%.

The absolute temperature of the sample under investigation was determined using a platinum resistance thermometer of resistance 100 Ω at 273 K. The temperature of the sample was derived from the measured value of resistance (four-wire technique) using a fourth-degree polynomial fit to the tabulated DIN 43 760 data, leading to an absolute accuracy of the calculated temperature of ±0.5 K and a relative accuracy of ±0.005 K.

3. Results and discussion

In this section we report the experimental results of the acoustic measurements and describe the data in the framework of the phenomenological Landau theory including small fluctuation corrections (Levanyuk *et al* 1969, Yao *et al* 1981).

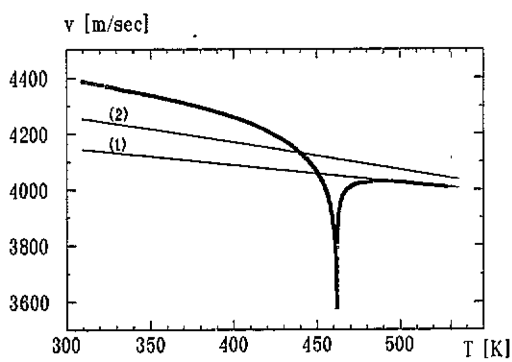

Figure 1. Temperature dependence of the ultrasonic velocity of the longitudinal sound wave propagating along the *a* axis at 10 MHz around the ferroelectric phase transition: curve (1), bare velocity determined from a linear fit to the experimental data in the region 500–525 K; curve (2), bare velocity determined from a fit to equation (7) (see text).

The temperature dependence of the velocity v of sample 2 at 10 MHz is shown in figure 1. Note that we found no significant difference between the velocities in the whole accessible frequency region (as far as we were able to measure v at these frequencies) nor between the different samples.

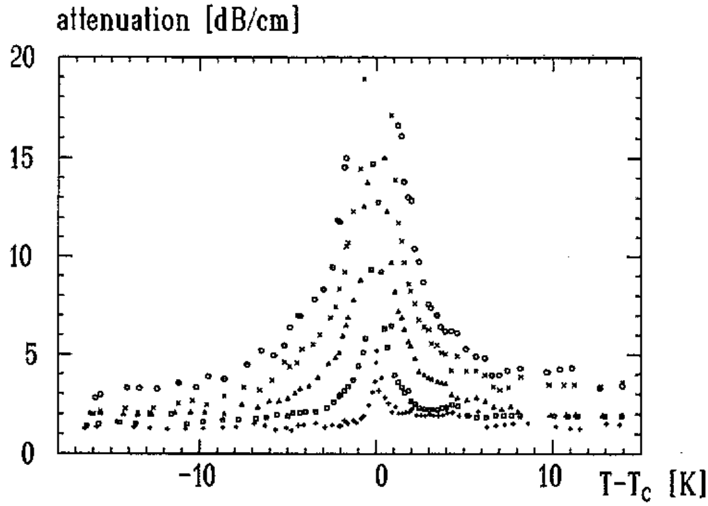

Figure 2. Temperature dependence of the sound attenuation for a longitudinal wave propagating along the [100] direction for various frequencies: +, 10 MHz; □, 30 MHz; △, 50 MHz; ×, 70 MHz; ○, 90 MHz.

Figure 2 shows the temperature dependence of the sound attenuation α for sample 1 for a longitudinal wave propagating along the [100] direction for 10, 30, 50, 70 and 90 MHz. The phase transition temperature $T_c = 462.0$ K has been determined from the maximum value of attenuation at 10 MHz. Note that the measurement of α was done in the heating run for $T < T_c$. Here, the attenuation coefficients were measured for all five frequencies by slowly stepwise increasing the temperature. The generator and the receiver of ultrasound pulses (Matec) was tuned carefully in the vicinity of the resonant frequency of the transducer, such that the attenuation had a minimum value (Truell *et al* 1969).

In the cooling run for $T < T_c$ (after the sample had traversed T_c), the attenuation reached much higher values than in the heating run when the sample had not been above T_c before (similar to what was observed by Wyslouzil *et al* (1986)) and we were not able to observe an ultrasonic signal at frequencies higher than 30 MHz (probably because of the appearance of new domains).

Analogously for $T > T_c$ the attenuation coefficient was measured in a heating and a cooling run. Here the measured values in both runs do not differ significantly.

The next step was to determine the critical part of the attenuation: $\alpha_{crit}(T) = \alpha(T) - \alpha_{0t}$. We have done this by subtracting a linearly temperature-dependent background attenuation $\alpha_{0t} = \alpha_0 + k(T - 445\ \text{K})$ (where α_0 is the background attenuation at 445 K). The values for α_0 and k are given in table 1.

The temperature dependence of this critical part of the attenuation divided by the squared frequency f^2 is shown in figure 3 for frequencies 30–90 MHz. This procedure leads to α_{crit}/f^2-values that are independent of the frequency in the whole temperature range (except in the close vicinity $\Delta T \simeq 1$ K of T_c, where we were not able to measure the attenuation for higher frequencies because of its high

Table 1. Values for α_0 and k.

f (MHz)	α_0 (dB cm^{-1})	k (dB cm^{-1} K^{-1})
30	1.3	0.0133
50	1.75	0.0000
70	1.75	0.0333
90	2.4	0.0167

value). The relation $\alpha_{\text{crit}} \propto \omega^2$ (figure 3) implies that $\omega\tau \ll 1$ is fulfilled in a large temperature range.

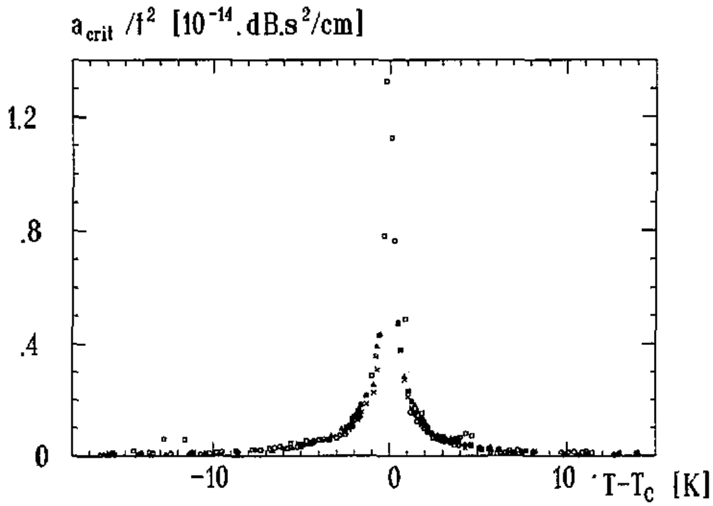

Figure 3. Temperature dependence of the critical part of the sound attenuation divided by the squared ultrasonic frequency for various frequencies: □, 30 MHz; △, 50 MHz; ×, 70 MHz; ○, 90 MHz.

Before the ALS data can be analysed in terms of the theoretical expressions given below, it is necessary to establish the temperature-dependent bare velocity $v_0(T)$. This velocity is shown in figure 1 (line (1)) as the best fit through the data points far above T_c (500–525 K). The bare velocity is expressed as $v_0(T) = 4286.210 - 0.525\,79T(\text{K})\ \text{m s}^{-1}$. Note that $v_0(T)$ and $v(T)$ cross at $T < T_c$ because of biquadratic coupling (Wyslouzil *et al* 1986) between the strain and order parameter.

To describe the present experimental data we use the phenomenological Landau theory with small fluctuation corrections (Levanyuk *et al* 1969, Yao *et al* 1981).

The Landau free energy for the ferroelectric phase transition including the coupling between the order parameter P_y, the strains u_{ij} and the variables P_x, P_z which do not belong to the soft-mode branch can be written (Wyslouzil *et al* 1986) as

$$F = F_0 + \int \mathrm{d}V \left(\frac{a_{11}}{2} \left(P_x^2 + P_z^2\right) + \frac{a_{22}(T - T_0)}{2} P_y^2 + r_{1122} u_{11} P_y^2 + r_{2222} u_{22} P_y^2 + r_{3322} u_{33} P_y^2 + c^0_{ijkl} u_{ij} u_{kl} + \kappa \delta_{il} \delta_{km} \frac{\partial P_i}{\partial x_k} \frac{\partial P_l}{\partial x_m} - \tfrac{1}{2} P_i E_i \right) \qquad (1)$$

where c^0_{ijkl} are the bare elastic constants, r_{ijkl} are the electrostriction coefficients, and we have included only invariants which are important for the following discussion. $a_{11} > 0$ is temperature-independent and for simplicity we assume isotropic dispersion in the (x, z) plane. We have neglected anisotropy of the tensor $\kappa_{iklm} = \kappa\delta_{il}\delta_{km}, \kappa > 0$.

Passing over to Fourier transforms of the function $P_i(r)$, we find for the inverse of the wavevector-dependent susceptibility $\chi^{-1}_{ij}(q)$ the form

$$\chi^{-1}_{ij}(q) = a_{ij}\delta_{ij} + 4\pi q_i q_j/\epsilon q^2 + \kappa q^2. \tag{2}$$

The term $4\pi q_i q_j/\epsilon q^2$ arises from the long-range dipolar interaction, where ϵ is the dielectric constant and q_i/q are the direction cosines of q. Diagonalization of $\chi^{-1}_{ij}(q)$ yields the three different eigenvalues λ_1, λ_2 and λ_3 where only one of them (λ_2) is temperature-dependent:

$$\lambda_2 = a_{22}(T - T_0) + \kappa q^2 + (4\pi/\epsilon)\cos^2\vartheta. \tag{3}$$

Here ϑ is the angle between q and the direction of the spontaneous polarization P_y, a_{22} is related to the Curie–Weiss constant $C_+ = 4\pi/a_{22}$, and λ_1 and λ_2 are temperature-independent eigenvalues of $\chi^{-1}_{ij}(q)$. To obtain equation (3) in this form, a_{11} was assumed to be sufficiently large: $a_{11} \gg 2\pi$. In the presence of this high anisotropy the fluctuations of P_x and P_z need not be taken into account, simplifying the equations for the elastic constants and attenuation.

From the coupled equations of motion for the strain and order parameter fluctuations the real and imaginary parts of the elastic constants above T_c have been calculated as (Levanyuk *et al* 1969, Yao *et al* 1981)

$$\mathrm{Re}\left[c^{\mathrm{fl}}_{ijlm}(\omega)\right] = c^0_{ijlm} - \frac{4k_B T r_{iji'j'} r_{lml'm'}}{(2\pi)^3} \times \int_0^{k_m} \mathrm{d}^3q \, \frac{b_{i'p}b_{j'q}b_{l'q}b_{m'p}\left[\lambda_p(q) + \lambda_q(q)\right]}{2\lambda_q\left\{\omega^2\tau_0^2 + 4\left[\lambda_p(q) + \lambda_q(q)\right]^2\right\}} \tag{4a}$$

and

$$\mathrm{Im}\left[c^{\mathrm{fl}}_{ijlm}(\omega)\right] = \frac{4k_B T}{(2\pi)^3}\omega\tau_0 r_{iji'j'} r_{lml'm'} \int_0^{k_m} \frac{\mathrm{d}^3q\, b_{i'p}b_{j'q}b_{l'q}b_{m'p}}{2\lambda_q\left\{\omega^2\tau_0^2 + 4\left[\lambda_p(q) + \lambda_q(q)\right]^2\right\}}. \tag{4b}$$

The matrix of elements b_{ij} transforms the quadratic form $\chi^{-1}_{ij}(q)$ of equation (2) into diagonal form. $\omega/2\pi$ is the applied sound frequency and τ_0 is the temperature-independent single-'spin' relaxation time. With $\omega\tau \ll 1$ for ALS in the whole temperature range and the coupling between the longitudinal strains and P_y^2 of equation (1), equations (4*a*) and (4*b*) for longitudinal waves $k \| a$ can be simplified to

$$\Delta c^{\mathrm{fl}}_{1111} = -\frac{k_B T r^2_{1122}}{(2\pi)^3} \int_0^{k_m} \mathrm{d}^3q \, \frac{b^4_{22}(\vartheta)}{4\lambda_2^2(q)} \tag{5a}$$

$$\Delta\alpha^{\mathrm{fl}}_{1111} = \frac{\omega^2\tau_0}{2\rho v^3(\omega)} \frac{k_B T}{(2\pi)^3} r^2_{1122} \int_0^{k_m} \mathrm{d}^3q \, \frac{b^4_{22}(\vartheta)}{8\lambda_2^3(q)} \tag{5b}$$

where $v(\omega)$ is the measured velocity of sound and ρ is the density of the sample. α^{fl} is the damping in the presence of fluctuations. Since we are interested in the anomalies of the elastic constant and sound attenuation, we have omitted terms with $p, q \neq 2$ in equations (4*a*) and (4*b*).

In the present approximation ($a_{11} \gg 2\pi$) the transformation matrix element b_{22} becomes independent of ϑ and reduced to unity. Inserting λ_2 from equation (3) into (5*a*) and (5*b*) and performing the integration, we obtain

$$\Delta c^{\mathrm{fl}}_{1111} = -\left[r^2_{1122}k_{\mathrm{B}}T/4(4\kappa\pi)^{1.5}\right]\epsilon^{0.5}\left[\ln\left(1+[1+(T-T_0)/T_{\mathrm{k}}]^{1/2}\right) - \ln\left(-1+[1+(T-T_0)/T_k]^{1/2}\right)\right] \tag{6a}$$

where

$$T_{\mathrm{k}} = 4\pi/a_{22}\epsilon = C_+/\epsilon$$

and

$$\Delta\alpha^{\mathrm{fl}}_{1111} = [\omega^2/2\rho v^3(\omega)][r^2_{1122}k_{\mathrm{B}}T\epsilon^{3/2}/4\kappa^{3/2}(4\pi)^{5/2}] \times [T_{\mathrm{k}}/(T-T_0)][1+(T-T_0)/T_{\mathrm{k}}]^{-1/2}. \tag{6b}$$

Equations (6*a*) and (6*b*) represent the effect of thermal fluctuations which are effective above and below the phase transition.

According to equations (4*a*) and (4*b*) and the form of the invariants in the free-energy expansion (1) the real and imaginary parts of the longitudinal elastic constants associated with the interaction between a sound wave and polarization fluctuations are independent of the propagation direction of the sound wave. In contrast with this the elastic response due to relaxation of P_y is effective only below T_0 and strongly dependent on the direction of sound propagation (Strukov *et al* 1977). For clarity we have omitted this term in our equations.

Now we can use the relations (6*a*) and (6*b*) to describe the experimental data. Since we are concerned with one elastic constant we omit the indices in the following discussion.

3.1. Real part of the elastic susceptibility Δc_{fl}

Using equation (6*a*) we can discuss different temperature regimes. For $T - T_0 \ll T_{\mathrm{k}}$, $\Delta c_{\mathrm{fl}} \propto \ln(T - T_0)$, which is expected for uniaxial ferroelectrics in the dipole regime (Levanyuk *et al* 1969). Far from T_0, for $T - T_0 \gg T_{\mathrm{k}}$ equation (6*a*) reduces to $\Delta c_{\mathrm{fl}} \propto 1/\sqrt{T - T_0}$, which corresponds to the 'Ising limit' ($4\pi/\epsilon = 0$ in equation (3)).

For temperatures $T > T_0 + T_{\mathrm{k}}$ a crossover from dipolar to Ising behaviour is expected. In this region the fluctuation corrections Δc_{fl} to the elastic constant can be approximated by

$$\Delta c_{\mathrm{fl}} \propto \ln\left\{1 + [T_{\mathrm{k}}/(T-T_0)]^{1/2}\right\}. \tag{7}$$

Using equation (7) the experimental data have been fitted (with a non-linear fitting procedure), resulting in a very good agreement in the region $T_c + 0.1$ K $< T < T_c + 25$ K (figure 4). The temperature T_0 has been calculated to be $T_0 =$

$T_c - (0.4 \pm 0.1)$ K, which is consistent with the weak first-order character of the phase transition. It should be noted that $T_k = C_+/\epsilon = 0.5$ K has been determined from Mitsui *et al* (1975) and held constant during the fitting procedure. Only very far from T_c at $T - T_c > 30$ K are the experimental points somewhat higher indicating the necessity to determine the $c_0(T)$-value from the region further away from T_c. As one can estimate from equation (7) the temperature range in which fluctuations are important is large (much more than 60 K), but unfortunately the crystal starts to decompose at a temperature higher than 540 K (Loiacono *et al* 1980). Therefore we have also tested the possibility of fitting the data using the bare elastic constant in the paraelectric phase of the form $c_0(T) = c_0(0) + kT$. Fitting the experimental data to equation (7) with $c_0(0)$ and k as a free parameter we gained excellent agreement for the whole region under consideration (figure 5). The fitted values for $c_0(0) = 39.132$ MPa and $k = -0.01524$ MPa K^{-1} are a little higher than those determined from the temperature range 500–525 K and are shown in figure 1 (as curve (2)). The asymptotic behaviour of the $\Delta c_{11} \propto 1/\sqrt{T - T_0}$ is shown in figure 5.

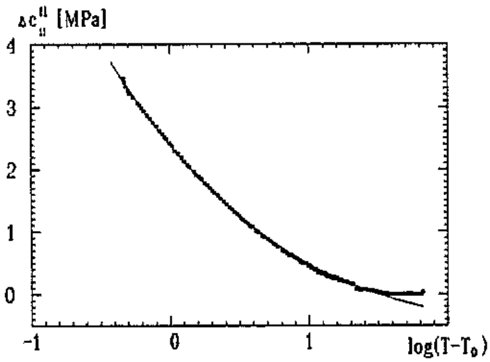

Figure 4. Temperature dependence of the critical part Δc_{11}^{fl} of ALS in the paraelectric phase: □, experimental data, where the bare elastic constant c_0 has been determined by a linear fit to the experimental data in the temperature range 500–525 K; ——, line given by the crossover function of equation (7).

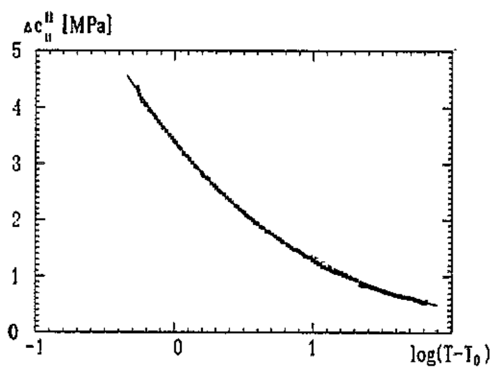

Figure 5. Temperature dependence of the critical part Δc_{11}^{fl} of ALS in the paraelectric phase: □, experimental data with the bare elastic constant $c_0(T)$ given by equation (7); ——, line given by the crossover function of equation (7) describing a crossover from dipolar to Ising behaviour (see text); ----, limiting case $\Delta c \propto (T - T_0)^{-1/2}$ for Ising-type fluctuations.

A corresponding analysis can be performed for the critical part of the sound attenuation (6*b*).

3.2. Imaginary part of elastic susceptibility $\Delta\alpha_{fl}$

For $T - T_0 \ll T_k$, equation (6*b*) reduces to $\Delta\alpha_{fl} \propto 1/(T - T_0)$ as expected for dipolar behaviour (Levanyuk *et al* 1969), and far from T_0, an Ising-type fluctuation contribution to $\Delta\alpha_{fl} \propto 1/(T - T_0)^{3/2}$ is found from equation (6*b*).

Since $T_k \simeq 0.5$ K in ALS, a crossover in the order parameter dynamics from dipole to Ising type can also be observed in the sound attenuation. Figure 6 shows the temperature dependence of the critical part of the sound attenuation and a fit using the crossover function (6*b*). The temperature T_0 was determined as $T_0 = T_c - (0.35 \pm 0.11)$ K. The asymptotic behaviour of $\Delta\alpha_{fl}$ is also shown in figure 6.

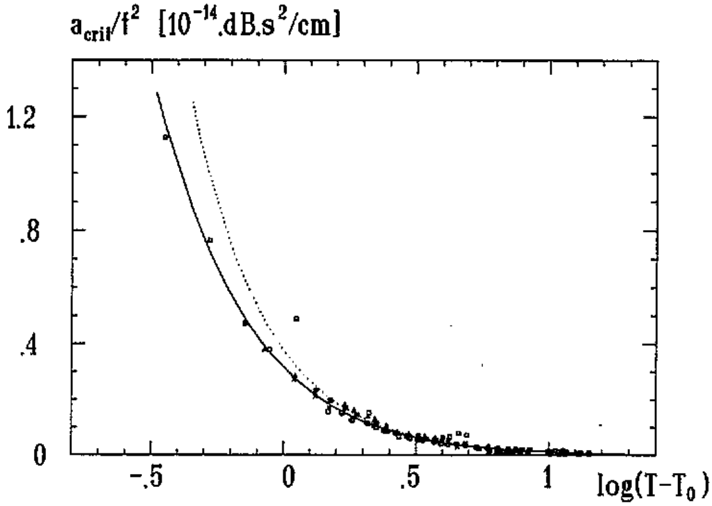

Figure 6. Temperature dependence of the critical part of the sound attenuation divided by the squared frequency: experimental data □, 30 MHz; △, 50 MHz; ×, 70 MHz; ○, 90 MHz; ——, corresponding fit obtained using the crossover function (6*b*); ----, limiting case for Ising-type fluctuations $\Delta\alpha_{fl} \propto (T - T_0)^{-1.5}$.

At the end of this section, we determine the temperature dependence of the relaxation time $\tau(T)$. In the single-relaxation-time approximation $\tau(q = 0, T) = \tau_0/\lambda_2(q = 0)$ the relation

$$\Delta\alpha_{fl} = -\left[\omega^2/2\rho v^3(\omega)\right](\Delta c_{fl}/2)\,\tau(q = 0, T) \qquad (8)$$

holds as obtained from equations (5*a*) and (5*b*).

By calculation of $\tau(T)$ from equation (8), one can use two possibilities for fitting c_0 (see figure 1). We have tried both possibilities and found that the difference in the temperature dependence of τ is negligible and only the value of τ_0 shows differences of about 20%. Because of the large temperature range in which fluctuations are important, it seems that the fit in curve (2) for c_0 is better and therefore we discuss here only the results for this fit.

Figure 7 shows the temperature dependence of the inverse relaxation time above and below T_c. Above T_c, $\tau(T) = \tau_0^+/(T - T_0)^\gamma$ with $\tau_0^+ = (1.8 \pm 0.4) \times 10^{-10}$ s,

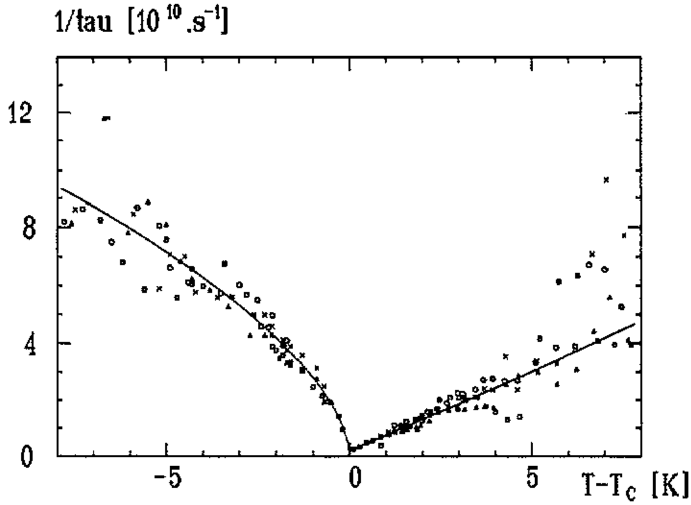

Figure 7. Temperature dependence of the inverse relaxation time $1/\tau$ above and below T_c: experimental data □, 30 MHz; Δ, 50MHz; ×, 70 MHz; ○, 90 MHz; ——, corresponding fits obtained for $T < T_c$ using $1/\tau = (1/\tau_0)P_y^4$ and for $T > T_0$ using $\tau = \tau_0^+(T - T_0)^{-1}$.

$\gamma = 1.02 \pm 0.08$ and $T_0 = T_c - (0.40 \pm 0.05)$ K is fulfilled in a large temperature range.

As already mentioned, below T_c there are two contributions to the sound attenuation: the relaxational contribution and the fluctuational contribution. Because of the first-order nature of the phase transition in ALS it is difficult to separate these two contributions below T_c. The temperature dependence of $1/\tau$ below T_c has been fitted to the equation $1/\tau \propto P_y^4$ (figure 7). The temperature dependence of P_y^2 has been determined from the transverse elastic constant $\Delta c_{44} \propto P_y^2$ obtained by Wyslouzil (1985). From this fit τ_0^- has been determined as $\tau_0^- = (0.34 \pm 0.06) \times 10^{-10}$ s.

4. Summary

We have measured the temperature and frequency dependences of the acoustic velocity and attenuation of longitudinal waves propagating along the non-polar axis in the uniaxial ferroelectric NH_4LiSO_4. The results have been analysed in terms of the phenomenological Landau theory, including small fluctuation corrections.

A crossover in the order parameter dynamics from a dipolar ($(T - T_0)/T_k \ll 1$) to an Ising ($(T - T_0)/T_k \gg 1$) type of behaviour leads to the anomalies in the elastic constants and sound attenuation above the ferroelectric phase transition of ALS. Such a crossover can be in principle observed if the parameter T_k = Curie constant/dielectric constant (crossover temperature) appearing in the fluctuation correction is small compared with T_0. This implies that the dipole–dipole interactions of the order parameter fluctuations are small compared with the characteristic energies responsible for the phase transition. Because of the weak dipolar interactions, indicated also by the small value of T_k, the crossover from Ising to dipolar behaviour appears in our case rather near to T_0, implying Ising-type fluctuation behaviour in a large temperature range. Thus the fluctuation corrections to the elastic constant around the phase transition can be described in the first approximation with the Ising limit contributions. However, this leads to a shift of T_0 to lower temperatures (about 0.3 K) and to a larger value of χ^2 in the fitting procedure. This probably also explains the value $\alpha \simeq 0.5$ which has been found by Sandvold (1987) for the critical exponent of the specific heat of ALS.

Using the value of $T_k = 0.5$ K obtained from dielectric measurements of Mitsui *et al* (1975) we were able to describe the temperature dependence of the elastic constant and sound attenuation in ALS over a wide temperature range above T_c. Similar results have been obtained by Smolenskii *et al* (1985) for the uniaxial ferroelectric TSCC. In this case the relation $T_k = 7\ \mathrm{K} \ll T_c = 130$ K is also fulfilled. In the case of TGS, $T_k \simeq T_c \simeq 320$ K and the observation of the crossover is impossible.

The analysis of the sound attenuation yielded for the temperature dependence of relaxation time above T_c the relation $\tau^+ = 1.8 \times 10^{-10}(T - T_0)^{-1.02}$ s. Below T_0 it is difficult to decouple the fluctuation contribution and the relaxation contribution to the sound attenuation, especially because of the first-order nature of the phase transition in ALS. From our analysis we have found $\tau^- = 0.34 \times 10^{-10}(T_c - T)^{-0.51}$ s. Our value of $\tau_0^- = 0.34 \times 10^{-10}$ s is comparable with the value of $\tau_0^- = 0.9 \times 10^{-10}$ s found by Yamamoto *et al* (1983) and the value of $\tau_0^- = 0.11 \times 10^{-10}$ s determined by Luspin *et al* (1984). It should be noted that the exponent $\gamma = 1.02 \pm 0.08$ is consistent with the mean-field value $\gamma = 1$. The non-linear behaviour of $1/\tau \propto P_y^4$ below T_c is not in contradiction to the mean-field behaviour but shows the importance of higher-order terms in the free-energy expansion.

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