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On the ferroelastic phase transition of $LiNH_4SO_4$: a Brillouin scattering study and theoretical modelling

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Abstract. Brillouin spectroscopy was used to study the elastic properties of $LiNH_4SO_4$ in the vicinity of the ferroelastic first-order transition occurring at approximately 285 K. Eleven acoustic modes were observed in the temperature range from 273 to 293 K. Their sound velocities and the temperature dependences of the corresponding elastic constants were calculated from the measured frequency shifts. The measured elastic constants exhibited step-like dicontinuities at the transition temperature and were interpreted using a symmetry-adapted Landau free-energy expansion. The order parameter for the ferroelectric phase transition at 460 K was chosen to be an infrared-active soft mode; while for the ferroelastic phase transition at 285 K, a two-component soft mode from the X point of the Brillouin zone was chosen. Both of these order parameters are coupled to polarisation and strains.

1. Introduction

Lithium ammonium sulphate (LAS), $LiNH_4SO_4$, is known to exhibit an interesting sequence of structural phase transitions. Several experimental studies of this crystal (Dollase 1969, Kruglik *et al* 1978, Itoh *et al* 1981) established the sequence of phase transitions which is represented schematically in figure 1. Both the ferroelectric transition at $T_1 = 460$ K and the ferroelastic transition at $T_2 = 285$ K are of first order. Moreover, the $C_{2v}^9(mm2) \rightarrow C_{2h}^5(2/m)$ transition is associated with the doubling of the volume of the unit cell.

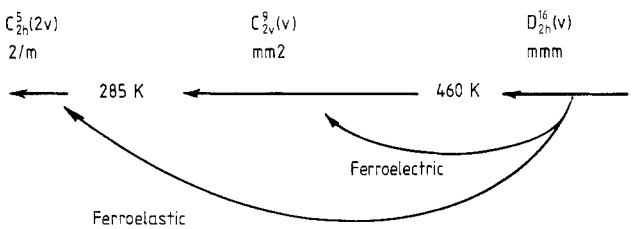

Figure 1. The sequence of phase transitions of LAS. The prototype phase for the ferroelastic phase 2/m is the high-temperature orthorhombic phase mmm.

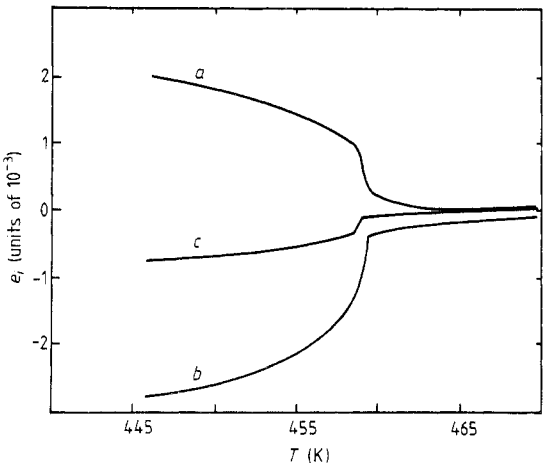

Figure 2. Spontaneous deformation e_i near the ferroelectric phase transition, along the crystallographic axes a, b and c, respectively, obtained from the plots of lattice parameters in Tomaszewski and Pietraszko (1979).

The first order of the ferroelectric transition has been determined unambiguously by measuring (i) the discontinuity in spontaneous polarisation (Mitsui *et al* 1975) as $\Delta P_s \simeq 0.2 \times 10^{-2}$ C m^{-2}, (ii) a thermal hysteresis effect and the latent heat of the transition (Iskornev and Flyorov 1977), and (iii) discontinuities of lattice parameters (see figure 2) and the volume of the sample (Tomaszewski and Pietraszko 1979). The dielectric constant measured along the axis of spontaneous polarisation has been found to have two anomalies (Mitsui *et al* 1975), one at 460 K and the other at 285 K.

From optical studies of Aleksandrov *et al* (1975), it is known that LAS exhibits ferroelastic properties below 285 K. Two types of domain walls inclined at an angle of 90° were observed. It was possible to reorient these domains under the action of appropriate mechanical stress. However, the ultrasonic studies of LAS performed in the temperature range 285–300 K by the same authors do not indicate that the monoclinic phase III is ferroelastic.

Recent experiments of Smutný and Polomska (1984) discovered that, on heating a sample of LAS, a double hysteresis loop existed for polarisation P as a function of the applied electric field E. This indicates metastability of the ferroelectric and para-electric phases around 285 K in the presence of external fields. The para-electric phase became less and less stable on heating and its eventual disappearance was signalled by the emergence of a single hysteresis loop. Mitsui *et al* (1975), for example, found a single hysteresis loop at 346 K which means that the para-electric phase is unstable at this temperature. Close to 285 K, the value of spontaneous polarisation reached its saturation value of approximately $P_0 = 10^{-2}$ C m^{-2} in the absence of external fields (Smutný and Polomska 1984). Supercooling of the ferroelectric phase was possible by as much as tens of kelvins and a gradual growth of regions of the ferroelastic phase was simultaneously observed (Smutný and Polomska 1984). These observations are in agreement with earlier reports given by Aleksandrova *et al* (1977). Finally, it was also found by Smutný and Polomska (1984) that the transition temperature T_2 decreased linearly with the magnitude of the applied electric field.

The standard theory of ferroelastic phase transitions (Toledano *et al* 1983) predicts the appearance of a soft acoustic mode as T approaches the critical temperature. No such behaviour was observed in the case of LAS. The closest analogue would be the observed partial softening of the c_{55} elastic constant measured by ultrasound (Wyslouzil *et al* 1986) as T approached 460 K. An interesting analysis of this effect has recently been presented and suggests that a transition to the ferroelastic phase is being suppressed by a coupling with other degres of freedom (Schranz *et al* 1987a). This will be discussed in more detail in § 3. In the proximity of the ferroelastic transition, however, all the measured elastic constants either change linearly with temperature or remain constant between 300 and 285 K.

The question of whether the ferroelastic phase is polar below 285 K is still open. Some authors (Kruglik *et al* 1978, Mitsui *et al* 1975, Smutńy and Polomska 1984, Simonson *et al* 1984) claim that LAS is centrosymmetric between 285 and 28 K and therefore allows no spontaneous polarisation. Although no hysteresis loops are observed below 285 K (Gerbaux *et al* 1982), pyro-electric measurements (Loiacono *et al* 1980) indicate a non-zero pyro-electric coefficient giving rise to claims that the 285 K transition is of polar–polar type. It is conceivable that the polar nature hinted at, in these experiments, may be entirely due to the metastability of the ferroelectric phase mentioned earlier.

To date all the papers concerned with Brillouin studies of LAS (Hirotsu *et al* 1981, Hirotsu 1983, Yamamoto *et al* 1983, Luspin *et al* 1985, Schranz *et al* 1987b) have been devoted to the high-temperature ferroelectric phase transition at 460 K. Since this crystal exhibits extremely weak scattering at room temperature, there are no direct results for the purely transverse modes.

In this paper, experimental results of high-resolution Brillouin spectroscopy are presented in the vicinity of the mm2 → 2/m transition. A symmetry-based phenomenological Landau model is applied to provide a theoretical description of the results obtained. The model is based on the ideas presented earlier by Torgashev *et al* (1984) and several other theoretical papers on this topic.

2. Experimental procedure and results

Single crystals of LAS were grown isothermally, at 315 K, from an aqueous solution containing the initial salts at the stoichiometric ratio. Large (20 cm^3) crystals grown this way showed pseudo-hexagonal symmetry with pseudo-hexagonal twins visible in polarised light. We have taken the choice of axes proposed by Gerbaux *et al* (1982). Samples of four different orientations were prepared from the untwinned part of the crystal to measure the sound velocities propagating along the crystallographic axes and the bisectors of these axes. The samples were typically of dimensions $4 \times 4 \times 5$ mm^3 and were immersed in silicon oil to maintain their homogeneous temperature distribution during the experiments. We utilised values of refractive indices (at wavelength 514.5 nm) and density presented, $n_a = 1.5024$, $n_b = 1.4937$, $n_c = 1.4947$ and $\rho = 1.902$ g cm^{-3}, from Luspin *et al* (1985).

The spectrometer has been described in detail elsewhere (Ahmad *et al* 1982). The incident radiation was produced by the single-mode argon-ion laser (Coherent Radiation 52) operating at $\lambda = 514.5$ nm. The laser beam, always polarised perpendicular to the scattering plane, was limited to 80 mW. The scattered light was analysed with piezo-electrically scanned triple-pass Fabry–Perot interferometer (Burleigh RC-110), a cooled photomultiplier tube (ITT FW 130), and the photon electronics of a data acquisition and

Table 1. ρv^2 as a function of the elastic constants in the orthorhombic (mmm) and monoclinic (2/m) phases for pure longitudinal (L) and pure transverse (T) modes in the mmm phase for QL and QT modes.

Phonon	Modes[a]	mm2 phase	2/m phase
[101]	L $^*\gamma_1$	c_{11}	$\frac{1}{2}\{c_{11}+c_{55}+[(c_{11}-c_{55})^2+4c_{15}^2]\}^{1/2}$
	$T_1\gamma_2$	c_{66}	c_{66}
	$T_2\gamma_3$	c_{55}	$\frac{1}{2}\{c_{11}+c_{55}-[(c_{11}-c_{55})^2+4c_{15}^2]\}^{1/2}$
[010]	L $^*\gamma_4$	c_{22}	c_{22}
	$T_1\gamma_5$	c_{44}	$\frac{1}{2}\{c_{44}+c_{66}+[(c_{44}-c_{66})^2+4c_{46}^2]\}^{1/2}$
	$T_2{}^*\gamma_6$	c_{66}	$\frac{1}{2}\{c_{44}+c_{66}-[(c_{44}-c_{66})^2+4c_{46}^2]\}^{1/2}$
[001]	L $^*\gamma_7$	c_{33}	$\frac{1}{2}\{c_{33}+c_{55}+[(c_{33}-c_{55})^2+4c_{35}^2]\}^{1/2}$
	$T_1{}^*\gamma_8$	c_{55}	$\frac{1}{2}\{c_{33}+c_{55}-[(c_{33}-c_{55})^2+4c_{35}^2]\}^{1/2}$
	$T_2{}^*\gamma_9$	c_{44}	c_{44}
[110]	L $^*\gamma_{10}$	$\frac{1}{4}\{c_{11}+c_{22}+2c_{66}+[(c_{22}-c_{11})^2+4(c_{12}+c_{66})^2]^{1/2}\}$	
	$T_1\gamma_{11}$	$\frac{1}{4}\{c_{11}+c_{22}+2c_{66}-[(c_{22}-c_{11})^2+4(c_{12}+c_{66})^2]^{1/2}\}$	
	$T_2\gamma_{12}$	$\frac{1}{2}\{c_{44}+c_{55}\}$	
[011]	L $^*\gamma_{13}$	$\frac{1}{4}\{c_{22}+c_{33}+2c_{44}+[(c_{33}-c_{22})^2+4(c_{23}+c_{44})^2]^{1/2}\}$	
	$T_1{}^*\gamma_{14}$	$\frac{1}{4}\{c_{22}+c_{33}+2c_{44}-[(c_{33}-c_{22})^2+4(c_{23}+c_{44})^2]^{1/2}\}$	
	$T_2\gamma_{15}$	$\frac{1}{2}\{c_{55}+c_{66}\}$	
[101]	L $^*\gamma_{16}$	$\frac{1}{4}\{c_{11}+c_{33}+2c_{55}+[(c_{33}-c_{11})^2+4(c_{13}+c_{55})^2]^{1/2}\}$	
	$T_1{}^*\gamma_{17}$	$\frac{1}{4}\{c_{11}+c_{33}+2c_{55}-[(c_{33}-c_{11})^2+4(c_{13}+c_{55})^2]^{1/2}\}$	
	$T_2\gamma_{18}$	$\frac{1}{2}\{c_{44}+c_{66}\}$	

[a] The asterisks (*) indicate which modes were observed in our experiment.

stabilisation system (Burleigh DAS-1). Any drifts due to the laser, electronics or Fabry–Perot were automatically compensated by the DAS-1. Another important feature of the DAS-1 was the ability to spend more time in accumulating counts in selected regions of the spectrum where transverse components were expected to appear. Free spectral ranges of 16.50 and 25.00 GHz were used to analyse the spectra, with estimated shift errors of 0.03 and 0.05 GHz, respectively.

The sound velocities v were deduced from the measured frequency shifts $\Delta\nu$ using the Brillouin equation, which in the case of 90° scattering geometry applied in our experiment takes the form

$$v = \lambda\Delta\nu(n_i^2 + n_s^2)^{-1/2} \tag{1}$$

where λ is the wavelength of incident light, and n_i and n_s are the refractive indices for the incident and scattered light, respectively.

We have observed 11 acoustic modes in the temperature range 273–293 K. The relevant $\rho v^2 = f(c_{ijkl})$ relations for the mm2 and 2/m phases are given in table 1. The temperature dependences of the frequencies of pure longitudinal and pure transverse modes are plotted in figure 3. All these modes exhibit linear temperature behaviour in the entire region studied. In all cases a small step change of the frequency shift (about 2%) was observed at T_2. Because of the low signal-to-noise ratio below T_2, we could not observe the γ_9 mode over the whole temperature region studied. The temperature dependences of the second-order elastic constants calculated from Brillouin shifts presented in figure 3 are plotted in figure 4. All elastic constants are temperature-independent except c_{55}, for which the step change at T_2 is twice as high as the accuracy of our measurements.

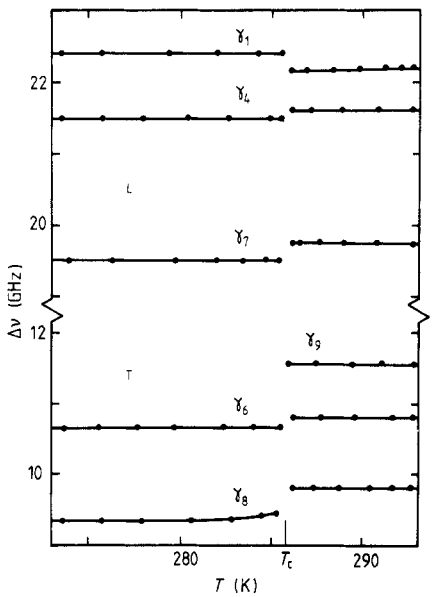

Figure 3. Temperature dependences of the Brillouin shifts $\Delta\nu$ for the pure longitudinal (L) modes γ_i ($i = 1$, 4 and 7) and the pure transverse (T) modes γ_i ($i = 6$, 8 and 9).

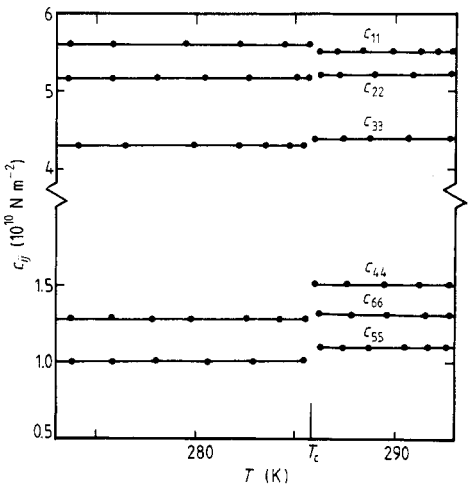

Figure 4. Temperature dependences of elastic constants calculated for the mm2 phase.

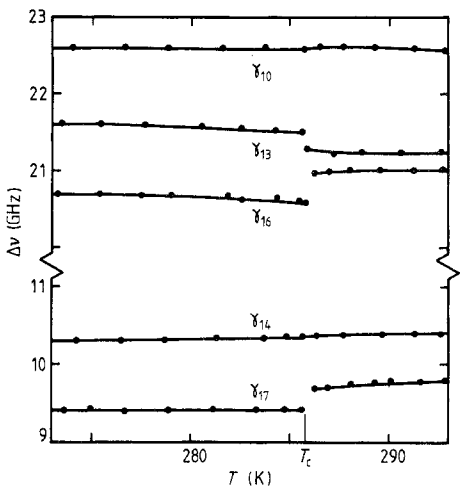

Figure 5. Temperature dependences of the Brillouin shifts $\Delta\nu$ for the quasi-longitudinal (QL) and quasi-transverse (QT) modes γ_i (i = 10, 13, 14, 16 and 17).

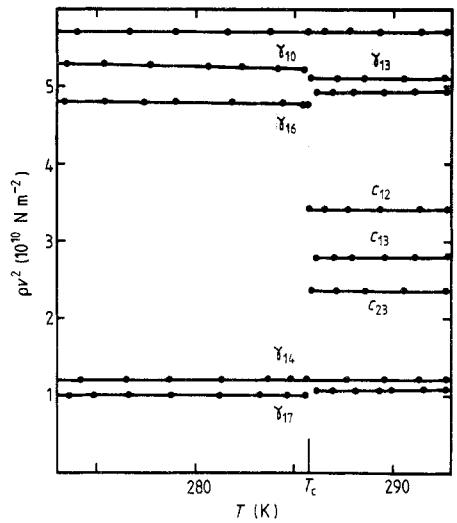

Figure 6. Temperature dependences of ρv^2 for γ_i presented in figure 5 and c_{12}, c_{13} and c_{23} elastic constants calculated from the mm2 phase.

The measured frequency shifts γ_i of the quasi-longitudinal (QL) (i = 10, 13 and 16) and quasi-transverse (QT) modes (i = 14 and 17) are plotted in figure 5. The observed temperature behaviour is similiar to that observed for the pure modes. In a few cases (i = 13, 16 and 17) we found a step-like behaviour at T_2. The appropriate values of ρv^2 are plotted in figure 6. Using these values we have calculated the remaining elastic constants c_{12}, c_{13} and c_{23} of the orthorhombic phase mm2. Since the solution of $\rho v^2(c_{ijkl})$ for the γ_i (i = 10, 13, 14, 16, 17) modes gives two sets of values for c_{12}, c_{13} and c_{23}, the correct elastic constants were obtained by checking the consistency of the velocity extremums in the pure-mode directions (Vacher *et al* 1972). All these components were found to be temperature-independent.

Finally, in table 2 we compare our elastic constants to those previously obtained for LAS using Brillouin spectroscopy (Hirotsu *et al* 1981, Hirotsu 1983, Yamamoto *et al* 1983,

Table 2. Comparison of elastic constants of LAS at 293 K (in units of 10^{10} N m^{-2}).

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}
Aleksandrov *et al* (1975)[a]	4.167	4.416	4.978	1.541	0.989	1.580	1.97	2.61	2.28
Hirotsu *et al* (1981), Hirotsu (1983), Yamamoto *et al* (1983)[b]	5.45	4.62	4.45	—	—	—	—	—	—
Luspin *et al* (1985)[c]	—	—	—	1.61[d]	1.06	1.64	—	—	—
Present experiment	5.52	5.22 ± 0.08	4.38	1.51	1.08 ± 0.05	1.31	3.41	2.77 ± 0.15	2.36

[a] Ultrasonic method.
[b,c] Brillouin spectroscopy.
[d] There is an error in the calculation of c_{44}; the correct value is 1.22.

Luspin *et al* 1985) and the ultrasonic method (Aleksandrov *et al* 1975). All measurements were performed in a cooling mode only such that we did not determine the thermal hysteresis of the measured quantities. The phase transition temperature was found to be 285.8 ± 0.4 K. The main aim of our experiment was to determine whether or not LAS exhibits acoustic phonon softening. No such effect was found; however, the observed step-like discontinuities of the elastic constants occurring simultaneously with a discontinuous drop of the spontaneous polarisation (Smutný and Polomska 1984) call for a theoretical explanation. In the following section we present a phenomenological model in an attempt to provide a theoretical description of the observed phenomena.

3. Theoretical model

A Landau model describing the sequence of phase transitions occurring in LAS has recently been put forward by Torgashev *et al* (1984). In addition, a discussion on the theoretical description of the ferroelectric transition has been presented by Luspin *et al* (1985) and Hirotsu *et al* (1981). Also, Schranz *et al* (1987a, b) analysed theoretically the possible couplings between strains and order parameters. Moreover, since LAS is isomorphous with $(NH_4)_2SO_4$, certain similarities between model free energies can be found useful in our analysis. A paper has recently been published (Bagpai *et al* 1987) presenting a theory of the improper ferroelectric phase transition for $(NH_4)_2SO_4$. In our presentation we will use the ideas developed earlier for LAS by other authors but will try to focus on the vicinity of the ferroelastic phase transition in order to relate it to the experimental findings of § 2.

Note first that below 460 K LAS is a pseudo-proper ferroelectric whose order parameter is the infrared-active soft-mode Q (Hirotsu *et al* 1981, Torgashev *et al* 1984) which belongs to the B_{3u} representation at the Γ point of the Brillouin zone of the paraelectric space group D_{2h}^{16}. Spontaneous polarisation P belongs to the same representation B_{3u} and thus the two quantities can be coupled bilinearly in the free-energy expansion. The compressional strains e_1, e_2 and e_3 belong to the A_{1g} representation; thus the lowest-order couplings between these and Q are of the form e_iQ^2 (Hirotsu *et al* 1981). In the next order we find $e_ie_jQ^2$ (Hirotsu *et al* 1981, Luspin *et al* 1985). The shear strains e_4, e_5 and e_6 belong to the representations B_{3g}, B_{2g} and B_{1g}, respectively, and they couple to Q via $e_i^2Q^2$ ($i = 4, 5, 6$).

Since the improper ferroelastic phase transition at T_2 involves the doubling of the unit cell, its order parameter should be a two-component soft mode from the X point of the Brillouin zone of D_{2h}^{16} and should belong to the B_{2g} representation (Torgashev *et al* 1984). It is denoted by (η_1, η_2). However, for simplicity it can be assumed that $\eta_1^2 = \eta_2^2 = \eta^2$ which results in a more tractable form of the free energy. Torgashev *et al* (1984) postulated a phenomenological free-energy expansion involving both the order parameter Q and (η_1, η_2). When carried to sixth order such a free energy was found to account properly for the sequence of transitions in question. However, these authors did not include strain variables in their analysis; these are found to be all-important in the present study.

Accordingly, we shall generalise the expansion of Torgashev *et al* (1984) to include strain components e_i ($i = 1, 2, 3, 4, 5, 6$) and focus special attention on the spontaneous strain e_5. The various strain components are allowed to interact amongst themselves, which is reflected in second- and third-order coupling terms. The starting form of the

free energy is then

$$F = A_2Q^2 + A_4Q^4 + A_6Q^6 - \chi^{-1}QP + \tfrac{1}{2}\Delta P^2 + m\eta^2Q^2 + \sum_{i=1,2,3} d_ie_iQ^2$$
$$+ \sum_{i,j=1,2,3} f_{ij}e_ie_jQ^2 + \sum_{i=4,5,6} g_ie_i^2Q^2 + \tfrac{1}{2}\sum_{i=1}^{6} c_{ii}^0e_i^2 + B_2\eta^2$$
$$+ B_4\eta^4 + B_6\eta^6 - le_5\eta + \sum_{i=1,2,3} h_ie_i^2\eta^2 + \sum_{i=4,6} k_ie_i\eta^2$$
$$+ \tfrac{1}{2}\sum_{i\neq j=1}^{6} c_{ij}^0e_ie_j + \tfrac{1}{3}\sum_{i,j,k} c_{ijk}^0e_ie_je_k. \tag{2}$$

We have assumed here that D_{2h}^{16} is the prototypic phase and that both transitions are of first order. Consequently, it is assumed that $A_2 = a(T - T_1^0)$, $B_2 = b(T - T_2^0)$ with $T_1^0 \gg T_2^0$ while $A_4 < 0, A_6 > 0$ and $B_4 < 0, B_6 > 0$; and the remaining parameters of the expansion in equation (2) are assumed to be constant. Obviously, it is not possible to do exact calculations using equation (2) as the model free energy for the system. Besides, this expansion has too many free parameters which could not be determined from the various experimental data, and as such would lead to interpretational problems. Therefore, we have decided to simplify this free energy as much as possible even at the cost of an extra approximation.

First of all, minimising equation (2) with respect to P yields a linear relationship between spontaneous polarisation P and the ferroelectric transition's order parameter, i.e.

$$Q = \chi\Delta P. \tag{3}$$

This allows us to recast the free energy in a form which uses P rather than Q, namely substituting Q of equation (3) into equation (2) and regrouping all the terms appropriately gives

$$F = a_2P^2 + a_4P^4 + a_6P^6 + M\eta^2P^2 + \sum_{i=1,2,3} D_ie_iP^2 + \sum_{i,j=1,2,3} F_{ij}e_ie_jP^2$$
$$+ \sum_{i=4,5,6} G_ie_i^2P^2 + \tfrac{1}{2}\sum_{i=1}^{6} c_{ii}^0e_i^2 + B_2\eta^2 + B_4\eta^4 + B_6\eta^6 - le_5\eta$$
$$+ \sum_{i=1,2,3} h_ie_i^2\eta^2 + \sum_{i=4,6} k_ie_i\eta^2 + \tfrac{1}{2}\sum_{i\neq j=1}^{6} c_{ij}^0e_ie_j$$
$$+ \tfrac{1}{3}\sum_{i,j,k} c_{ijk}^0e_ie_je_k \tag{4}$$

where the new coefficients are $a_2 = \chi^2\Delta^2A_2 - \Delta/2$, $a_4 = \chi^4\Delta^4A_4$, $a_6 = \chi^6\Delta^6A_6$, $M = \chi^2\Delta^2m$, $D_i = \chi^2\Delta^2d_i$, $F_{ij} = \chi^2\Delta^2f_{ij}$ and $G_i = \chi^2\Delta^2g_i$. It can readily be seen that, as a result of the coupling between Q and P, and ignoring interactions with the remaining modes, the ferroelectric (first-order) transition temperature is shifted from

$$T_Q = T_1^0 + A_4^2/(4A_6) \qquad \text{for } \chi = 0 \tag{5a}$$

to

$$T_1 = T_1^0 + \frac{1}{2\chi^2\Delta a} + \frac{\chi^2\Delta^2A_4}{4A_6} \qquad \text{for } \chi \neq 0. \tag{5b}$$

These temperatures correspond to the triply degenerate minimum of the free energy as a function of polarisation. The direction of this shift depends on the particular values of χ, Δ and a. Confining ourselves to the vicinity of T_1 we can evaluate the effect of this transition on the behaviour of the elastic modes. In general, since T_1 is far above T_2, the coupling between e_i and η is far less significant. Minimising F with respect to e_i we thus obtain, neglecting higher-order terms in the expansion,

$$e_i \simeq -(D_i/c_{ii}^0)P^2 \qquad \text{for } i = 1, 2, 3 \tag{6}$$

and

$$e_i \simeq -\left[\left(\sum_{j,k=1,2,3} \frac{D_j D_k}{c_{jj}^0 c_{kk}^0}\right) \Big/ (2G_i P^2 + c_{ii}^0)\right] P^4 \qquad \text{for } i = 4, 5, 6. \tag{7}$$

We see that the compressional strains respond much more strongly to the changes in polarisation than the shear strains which do so in the next order of approximation. Therefore, at T_1, we expect all the strains to experience a discontinuity as a result of polarisation jumping to $\Delta P \simeq 0.2 \times 10^{-2}\,\mathrm{C\,cm^{-2}}$. The discontinuities occurring for the compressional modes have been measured by Tomaszweski and Pietraszko (1979) and are significant. Those occurring for the shear strains have not been measured and are expected to be very small. It should be emphasised that these strains become non-zero before a spontaneous symmetry-breaking occurs in the elastic subsystem.

In the same temperature range one is also expecting a discontinuity in the second-order elastic constants. Calculating their effective values as $c_{ii}^{\mathrm{eff}} = \partial^2 F/\partial e_i^2$ yields

$$c_{ii}^{\mathrm{eff}} = c_{ii}^0 + 2F_{ii}P^2 + 2h_i\eta^2 \qquad \text{for } i = 1, 2, 3 \tag{8}$$

$$c_{ii}^{\mathrm{eff}} = c_{ii}^0 + 2G_i P^2 \qquad \text{for } i = 4, 5, 6. \tag{9}$$

This indicates that the equilibrium values of the effective elastic constants should exhibit a marked discontinuity at T_1 and, in addition, be temperature-dependent below T_1 since $P = P(T)$ with an approximate formula for $P(T)$ which is obtained from equation (4) as

$$P \simeq \pm[-2a_4 \pm (4a_4^2 - 12a_2a_6)^{1/2}/6a_6]^{1/2} \tag{10}$$

where we have neglected the modifying effect of the couplings between P and the elastic modes. Equations (8) and (9) appear to be in good qualitative agreement with the experimental plots of c_{11}, c_{22} and c_{33} presented by Hirotsu *et al* (1981) and c_{55} by Schranz *et al* (1987b). There is a marked discontinuity of c_{55} at T_1 but it is not evident that the compressional elastic constants show any such effect. In both cases, however, a strong temperature dependence appears to resemble a square-root function as equations (8)–(10) would indicate.

The controversy surrounding the ultrasonic measurements of c_{55} close to T_1 also appears to be related to our expanson of equation (4). Since the frequency involved in ultrasound experiments is $\nu_{\mathrm{US}} = 25\,\mathrm{MHz}$ which is much less than $\nu_{\mathrm{BS}} = 10\,\mathrm{GHz}$ for Brillouin scattering, it is conceivable that in the former experiment the c_{55} mode exhibits metastable behaviour caused by relaxational coupling to the η-order parameter. Then using equation (4) with the neglect of the polarisation mode, we find that $e_5 \simeq (c_{55}^0)^{-1} l\eta$ and hence its effective second-order constant is

$$c_{55}^{\mathrm{US}} \simeq B_2(c_{55}^0/l)^2 = b(c_{55}^0/l)^2(T - T_2). \tag{11}$$

In figure 7 we have plotted c_{55}^{US} following Wyslouzil *et al* (1986) and Schranz *et al* (1987b) and extrapolated the high-temperature branch showing that the intercept with the

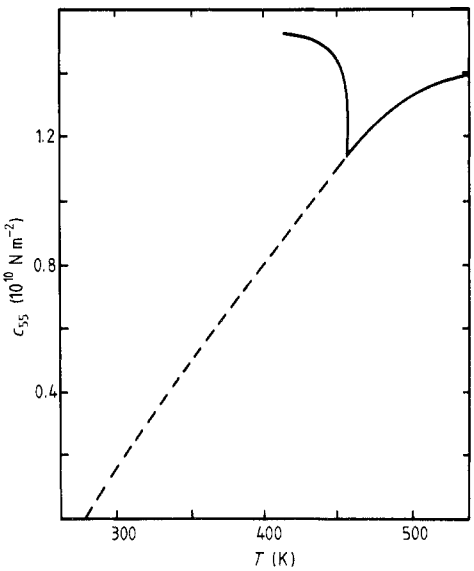

Figure 7. An extrapolation of c_{55} following Schranz *et al* (1987b).

vertical axis is indeed very close to $T_2 = 285$ K as is consistent with our argument. This is in close correspondence with a more elaborate analysis presented by Schranz *et al* (1987b). Thus, the results observed by the ultrasonic measurements can be interpreted as precursor effects for the ferroelastic transition at T_2.

In order to analyse the situation in the vicinity of the ferroelastic transition temperature T_2 we first minimise the free energy equation (4) with respect to spontaneous strain and find a relationship between η and e_5, i.e.

$$\eta = [(c_{55}^0 + 2G_5P^2)/l]e_5. \tag{12}$$

Allowing only the most dominant terms which arise upon substitution of equation (12) into equation (4) yields

$$\begin{aligned} F \simeq\ & a_2P^2 + a_4P^4 + a_6P^6 + \sum_{i=1,2,3} D_ie_iP^2 + \sum_{i,j=1,2,3} F_ie_ie_jP^2 \\ & + \sum_{i=4,6} G_ie_i^2P^2 + \tfrac{1}{2}\sum_{\substack{i=1\\ i\neq 5}}^{6} c_{ii}^0e_i^2 + \tfrac{1}{2}\sum_{i\neq j=1}^{6} c_{ij}^0e_ie_j \\ & + \tfrac{1}{3}\sum_{i,j,k} c_{ijk}^0e_ie_je_k + b_2e_5^2 + b_4e_5^4 + b_6e_5^6 + \mu e_5^2P^2 \end{aligned} \tag{13}$$

where the new coefficients are

$$b_2 = -\tfrac{1}{2}c_{55}^0 + B_2(c_{55}^0/l)^2 \qquad b_4 = B_4(c_{55}^0/l)^2$$
$$b_6 = B_6(c_{55}^0/l)^2 \qquad \mu = M(c_{55}^0/l)^2.$$

Again, as with the ferroelectric transition, the transition temperature in the ferroelastic transition has been shifted because of coupling between η and e_5.

Furthermore, it is known (Smutný and Polomska 1984) that in the vicinity of the ferroelastic transition temperature T_2, the value of spontaneous polarisation is almost equal to the saturation level ($P_s \simeq 1.09 \times 10^{-2}$ C m^{-2}). Consequently, above T_2 we may consider P^2 to be essentially constant. The actual transition temperature T_2 is defined such that

$$b_2 = b_4^2/4b_6 \qquad \text{at} \qquad T = T_2 \tag{14}$$

which means that the free energy F of equation (13) is triply degenerate with respect to e_5 at T_2. The ferroelastic phase becomes metastable slightly above T_2; at $T = T_2^*$ such that

$$b_2 = b_4^2/3b_6 \tag{15}$$

at $T = T_2^*$ which is expected to be just above T_2. The ferroelastic phase remains metastable below T_2, down to T_2^{**} such that

$$b_2 = 0 \tag{16}$$

at $T = T_2^{**}$ which is expected to be much below T_2. Therefore, in the range $T_2^{**} < T < T_2^*$ there is coexistence of the two elastic phases (see figure 8). At $T = T_2$, the

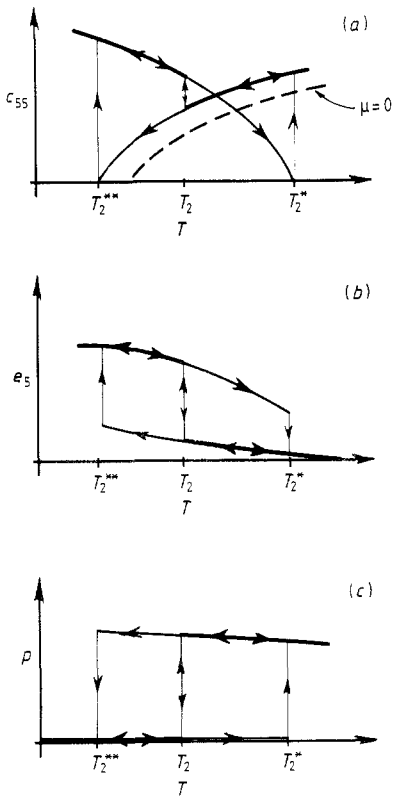

Figure 8. Schematic illustration of the thermal hysteresis effects in the vicinity of T_2 for (*a*) the elastic constant, (*b*) the spontaneous strain, and (*c*) the polarisation of the sample. Thick lines: stable phase. Thin lines: metastable phase.

spontaneous strain e_5 experiences a sudden jump as a result of the transition to the ferroelastic phase, its magnitude being

$$\Delta e_5 \simeq (-b_4/6b_6)^{1/2}. \tag{17}$$

It should also be noted that coupling between e_5 and P shifts the two characteristic temperatures T_2 and T_2^{**} by an approximately constant value as we replace b_2 with $b_2 + \mu P_s^2$ in equations (14) and (16). The other temperature T_2^* is unchanged since $P = 0$ in the ferroelastic phase. Simultaneously with the transition to the ferroelastic phase at T_2 the polarisation of the sample vanishes and can be interpreted as a result of the polarised phase becoming unstable. This would happen if

$$a_2 + \mu(\Delta e_5)^2 \geqslant a_4^2/3a_6 \qquad \text{at} \qquad T = T_2. \tag{18}$$

Thus, the onset of ferroelasticity leads to a destabilisation of the polarised phase.

The effective second-order elastic coefficient experiences a discontinuity at $T = T_2$ which is somehow increased by the simultaneous disappearance of polarisation. In the para-elastic (P) phase, $e_s \simeq 0$ (not exactly zero due to the coupling with P) and

$$c_{55}^{\mathrm{P}} \simeq 2(b_2 + \mu P_s^2) \tag{19}$$

whereas, in the ferroelastic (F) phase,

$$c_{2s}^{\mathrm{F}} \simeq 17b_2 \tag{20}$$

such that $\Delta c_{55} = c_{55}^{\mathrm{F}} - c_{55}^{\mathrm{P}} \simeq 15b_2 - 2\mu P_s^2$. Owing to the associated metastability of phases, a thermal hysteresis effect is expected to occur. We have schematically represented the effect of the hysteresis in figure 8. If the shift of the critical temperature T_2 resulting from the coupling between e_5 and P is large enough, then the plot of c_{55} below T_2 may be almost a straight line parallel to the horizontal axis as is evident from our experiment (see figure 4). This is because, for temperatures sufficiently removed from the temperature for which $b_2 = 0$, b_2 ceases to be visibly temperature-dependent.

Similar arguments apply to the analysis of discontinuities exhibited by other strains. In these cases, however, the effects first appear in higher orders so that the result is less pronounced.

Finally, we wish to comment on two other related effects. Smutný and Polomska (1984) demonstrated that, as a result of applying an external electric field E, T_2 decreased almost linearly with the magnitude of E. Consider the balance of energy between the polarised and para-elastic phase for $T > T_2$ and the non-polar and ferroelastic phase for $T \leqslant T_2$. Then we find that at $T > T_2$, $P \simeq P_s$ and $e_5 \simeq 0$. On the other hand, at $T \leqslant T_2$, $P \simeq 0$ and $e_5 \simeq$ constant. Therefore, the relationship between E and the shifted critical temperature T_2^{E} is

$$-EP_s \simeq \alpha(T_2^{\mathrm{E}} - T_2) \tag{21}$$

where $\alpha = \partial c_{55}^{\mathrm{P}}/\partial T$. This is in agreement with the result of Smutný and Polomska (1984) since it is a linear relationship leading to a decrease of T_2^{E} below T_2 as E increases.

The other comment we wish to make concerns the analysis of the latent heat L_c of transition around T_1 carried out by Tomaszewski and Pietraszko (1979). The measured value of L_c is $L_c = 2.2\ \mathrm{J\ g^{-1}}$ (Iskornev and Flyorov 1977) which yields the entropy jump at T_1 as $\Delta S^{\mathrm{exp}} = 0.56\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Using the Clausius–Clapeyron relation $\Delta S = \Delta V/(\mathrm{d}T_c/\mathrm{d}p)$ Tomaszewski and Pietraszko (1979) found that with $\Delta V = 0.17\ \text{Å}^3$ and $\mathrm{d}T_c/\mathrm{d}p = 9\ \mathrm{K\ kbar^{-1}}$, the calculated value of entropy jump is only half of ΔS^{exp}, namely

$\Delta S^{th} = 0.28$ J mol^{-1} K^{-1}. We note, then, that this calculation neglected to account for the change of entropy due to the polarisation degree of freedom, namely $\Delta P/(\mathrm{d}T_c/\mathrm{d}p)$. Using our equation (4) for F and considering only its first three terms yields

$$\Delta S = S(T \geqslant T_1) - S(T \leqslant T_1) = \partial F/\partial T = a(\Delta P)^2 > 0 \tag{22}$$

where $a = \partial a_2/\partial T$. This has the correct sign and we believe accounts for the difference between ΔS^{exp} and ΔS^{th}. Using the value of ΔP at $T = T_1$ gives $a = 7 \times 10^4$ J m^4) mol^{-1} K^{-1} C^{-2}.

4. Conclusions

In this paper we have presented the results of Brillouin scattering experiments for LAS in the vicinity of the ferroelastic phase transition. From the measured frequency shifts we were able to calculate the sound velocities and the temperature dependences of the elastic constants for 11 acoustic modes. The results exhibit step-like discontinuities at the transition temperature.

We have presented an overview of recent experimental and theoretical investigations on LAS. A recent theoretical model of Torgashev *et al* (1984) was used to describe the situation, especially as it pertains to the elastic degrees of freedom. We have made several useful transformations and approximations of the Landau-type free energy of the system in order to be able to focus on polarisation and spontaneous strain in the vicinity of the ferroelectric and, then, the ferroeleastic phase transition. The ferroelectric transition is driven by an infrared-active mode which couples both to polarisation and strains. This results in an abrupt emergence of polarisation and somewhat less dramatic but also unambiguous shifts in the equilibrium values of elastic strains.

The ferroelastic phase transition is driven by a two-component soft mode which couples strongly to spontaneous strain e_5, to the remaining strains, and to polarisation. The otherwise unobserved softening of this mode becomes evident through ultrasonic measurements and clarifies the underlying mechanism of the transition. At the transition temperature, polarisation vanishes while elastic constants undergo abrupt shifts. This, as well as thermal hysteresis effects and the dependence of the critical temperature on an external field, can be interpreted with the use of our theoretical model.

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