CHAPTER 5

ELASTIC PROPERTIES AND PHASE TRANSITIONS IN
LITHIUM AMMONIUM SULPHATE

5.1 Introduction

Lithium ammonium sulphate, LiNH₄SO₄ or LAS is a more extensively studied crystal than lithium hydrazinium sulphate. LAS shows an interesting sequence of phase transitions and the phase transitions around 460 K and 284 K are well known. LAS is ferroelectric from 460 K to 284 K, below which it is ferroelastic. Further a number of phase transitions have been reported in LAS at low temperatures, some of which have not been confirmed.

A variety of experiments carried out on this material by different workers [5.1-5.4] have established the sequence of Phase transitions depicted in Figure 5.1. At room temperature the structure of LAS crystals belongs to a P2₁/cn (C₉) (orthorhombic) space group, with four molecules per unit cell. Both the ferroelectric transition at 460 K and the ferroelastic transition at 285 K are of first order. X-ray results show that there are four molecules per unit cell in phases I and II, eight in phase III and sixteen in phase IV. Hildmann et al [5.5] have shown that phase III is ferroelastic making LAS the first example for a ferroelastic crystal which is not simultaneously ferroelectric. X-ray results of Simonson et al. [5.6], infrared absorption curves of Gerbaux et al. [5.7] and dielectric constant and Raman spectroscopic measurements of Martins et al. [5.8] have established a second order Phase transition occurring at 28 K taking LAS to a C₄ space group (Phase IV) with a doubling of the unit cell volume.

The elastic constants of LAS at room temperature have
Figure 5.1
Sequence of phase transitions in LAS
been measured by earlier workers using ultrasonic [5.3] and Brillouin scattering [5.9-5.11] techniques. The temperature variation of selected elastic constants near the 460K ferroelectric Phase transition has been determined by ultrasonic [5.12] and Brillouin scattering [5.13,5.14] techniques. Also, clear evidence for the ferroelastic transition at 285 K has been obtained in the experimental results on the temperature variation of the elastic constants using Brillouin scattering technique [5.11]. These experimental results and the Landau type theoretical models proposed by Torgashev et.al. [5.15], Luspin et.al. [5.16,5.17] have made it possible to get a clear understanding of the ferroelectric and ferroelastic phase transitions occurring in LAS.

Several questions have been raised about the polar nature of Phase III. Kruglik et.al [5.4] claimed that this Phase is nonpolar with a monoclinic structure belonging to the $P_{2_1}c$ ($C_{2h}$) space group. The nonpolar nature of LAS in Phase III was rejected by Poulet and Mathieu [5.18] who used Raman scattering to study the Phase II $\rightarrow$ Phase III transition. Their results showed that some Raman bands appearing below the transition point at 285 K where an indication of cell doubling, carrying modes from the boundary to the centre of the Brillouin zone. They have described this transition as a first order ferroelastic one but phase III was considered polar, belonging to a $P_{2_1}$ ($C_2^2$) space group. They also proposed that phase III could be a modulated phase with a long modulation period. The polar nature of phase III was supported by Gerbaux et al [5.7] who found a weak anomaly in the dielectric constant and pyroelectric response on both sides of the transition point. Based on their Raman studies, Torgashev et al agreed with Poulet and Mathieu on the doubling of the unit cell but argued that phase III belongs to the $P_{2_1}c$ ($C_{2h}$) space group, in accordance with Kruglik et.al [5.4] and
Simonson et. al [5.6]. Then this phase would be monoclinic and nonpolar with eight molecules per unit cell. The ambiguity is raised by a mode with frequency 24 cm\(^{-1}\) in Raman spectra at 183 K that behaves as a soft mode when the temperature approaches the transition point at 285 K. However, if Phase III has a centre of inversion, then polar modes would only be infrared active. This led Poulet and Mathieu to propose that Phase III is polar, with a structure belonging to a noncentrosymmetric space group, probably \(C_2^2\).

Some of these discrepancies have been addressed by Martins et. al [5.8] who undertook dielectric constant and polarized Raman scattering measurements on LAS below room temperature. They detected a new Phase transition taking place at 256 K which was probably overlooked by earlier workers. Infrared absorption and dielectric measurements by Gerbaux et. al [5.7] also have indicated a transition taking place at this temperature. Specific heat measurements [5.20] also have shown an anomaly at 256 K. Martins et. al. [5.8] have, by analysing various experimental data, suggested that the transition at 256K is second order, order-disorder type and reversible. Their results were not sufficient to decide whether LAS goes from \(C_{2h}^5\) to a new space group at 256 K.

In order to throw more light on the nature of the transitions at 285 K and 256 K, we have carried out a detailed ultrasonic study of the temperature dependence of the elastic constants of LAS at low temperatures in the range 310 to 220 K. This is the first ultrasonic study in LAS in this low temperature range. The absolute values of all the 9 elastic constants of LAS have been determined and are tabulated and compared with the previous measurements. The details of the experimental technique used and the results obtained are described in the following sections.
5.2 Elastic constants of LAS

5.2.1 Introduction

The elastic constants of LAS was first measured by Aleksandrov et al [5.3] by using ultrasonic technique. They have measured and tabulated all the 9 elastic constants and their temperature variation in a small range from 285 K to 305 K. Using Brillouin scattering technique, Hirotsu et al [5.13] investigated the temperature variation of $C_{11}$, $C_{22}$, and $C_{33}$ of LAS in the high temperature range from 293 to 523 K, which included the high temperature transition at 460 K. Luspin et al [5.10] investigated the transverse modes using Brillouin scattering and measured $C_{44}$, $C_{55}$, and $C_{66}$. Wyslouzil et al [5.12] have measured all the 9 elastic constants and their temperature variation in the range 290 K to 540 K, by using the ultrasonic pulse echo overlap method. But they have not given a tabulated data of elastic constants at room temperature. All the 9 elastic constants of LAS were again measured by Mróz et al [5.11] by using Brillouin scattering technique and they have provided a tabulated data of elastic constants and have compared their data with the previous measurements of elastic constants of LAS. They have, for the first time investigated the temperature variation of elastic constants of LAS at the low temperature transition near 285 K. Their measurements were limited to the temperature range from 273 K to 293 K.

On examination of the previous measurements, it can be found that there are wide disagreements between the values of elastic constants reported by various workers. We have resolved these disagreements to some extent by identifying the fact that different workers have taken different choice of axes for this orthorhombic crystal. Mróz et al [5.11], who have recently compared their values with the previous
measurements, have failed to identify this point.

Using the tensor notation of the elastic constants, all the elastic constants can be transformed from one choice of axes to another and it can be seen that there are 6 possible choices for selecting the 3 lattice parameters a, b and c. The conversion scheme for all the elastic constants of LAS under different choice of axes are presently derived and are tabulated in Table 5.1. The lattice parameters given in the table are from the very recent refined X-ray structure work on LAS by Mashiyama and Kasano [5.21].

We have compared the previous measurements after rearranging the elastic constants according to Table 5.1 and this showed much better agreement between the constants reported by previous workers. But even this agreement was not satisfactory because some of the measured elastic constants were showing more than 10% variation between different workers. These variations were clearly the result of inaccurate measurements and an accurate determination of all the elastic constants of LAS was found to be necessary.

We have accurately determined all the 9 elastic constants of LAS and the results are presented in Section 5.2.3. In section 5.2.2, the details of sample preparation are given and in Section 5.2.4 the velocity surface plots of LAS are given.

5.2.2 Sample preparation

Single crystals of LAS were grown by evaporation of an equimolar solution of LiSO$_4$.H$_2$O and (NH$_4$)$_2$SO$_4$ at a constant temperature of 311 K. The details of the apparatus used for the crystal growth have been discussed in Section 2.4. During the growth the crystal was continuously rotated in opposite directions using the crystal rotation mechanism. Large single crystal of LAS, measuring about 5 cm in the c-axis direction
Table 5.1
Conversion table for elastic constants of orthorhombic LAS under different choice of crystallographic axes

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Axes choice (1)†</th>
<th>(2)*</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
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<tbody>
<tr>
<td>5.282 Å = a</td>
<td>c</td>
<td>b</td>
<td>c</td>
<td>b</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>9.131 Å = b</td>
<td>b</td>
<td>a</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>8.780 Å = c</td>
<td>a</td>
<td>c</td>
<td>b</td>
<td>a</td>
<td>b</td>
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<table>
<thead>
<tr>
<th></th>
<th>C_{11}</th>
<th>C_{33}</th>
<th>C_{22}</th>
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<th>C_{22}</th>
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<td>C_{13}</td>
<td>C_{12}</td>
<td>C_{23}</td>
</tr>
</tbody>
</table>

* This choice of axes were adopted for the present work and this choice was also taken by Aleksandrov et al [5.3] and Luspin et al [5.10]

† Choice by Mashiyama and Kasano [5.21]
was obtained after a period of 60 days. LAS usually grows in two different forms, one is the prismatic form and the other is the pseudohexagonal form. The pseudohexagonal form is a twined crystal and is usually obtained from spontaneously nucleated seeds at room temperature. We have grown the untwined prismatic form of LAS for our studies. A drawing of the morphology of the prismatic form of LAS is shown in Figure 5.2.

The crystallographic directions of the grown crystal were determined from interfacial angle measurements. The identification of the correct directions in LAS have been more difficult than in LHS. This is due to the presence of comparatively large number of natural faces in LAS and also due to the confusion existing in literature regarding the choice of axes. Using the lattice parameters, $a = 8.78$, $b = 9.131$ and $c = 5.282$ [5.21], the interfacial angles of LAS were calculated using the crystallographic formula, Eq. (3.01) for orthorhombic lattice. The good agreement between the calculated and measured values of the interfacial angles proved that our direction identification is correct. In Table 5.2 the calculated and measured values of interfacial angles of LAS are given.

The grown crystal of LAS have been cut using the slow speed diamond wheel saw as discussed in Section 3.2 for LHS. The samples have been cut so as to have propagation directions along $a$, $b$ and $c$ axes, [101], [110] and [011] directions. The cut samples in different directions had thickness in the range 0.8 to 1.2 cm. The cut samples were polished carefully using cerium oxide to optical reflection level. The misorientations of the cut samples were less than $1^\circ$.

5.2.3 Velocity measurements and elastic constants

In Section 1.2.3 the details of measuring the elastic
Figure 5.2
Schematic representation of the morphology of prismatic form of LAS
Table 5.2

Calculated and measured values of interfacial angles of LAS
(the angles are given in degrees)

<table>
<thead>
<tr>
<th>Face 1 $h_1 \ k_1 \ l_1$</th>
<th>Face 2 $h_2 \ k_2 \ l_2$</th>
<th>Calculated angles</th>
<th>Measured angles</th>
<th>Difference angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>1 1 0</td>
<td>136.12</td>
<td>135.5</td>
<td>0.62</td>
</tr>
<tr>
<td>1 0 0</td>
<td>1 2 0</td>
<td>117.47</td>
<td>117.5</td>
<td>-0.03</td>
</tr>
<tr>
<td>1 0 0</td>
<td>1 1 1</td>
<td>117.51</td>
<td>117.4</td>
<td>0.11</td>
</tr>
<tr>
<td>1 0 0</td>
<td>1 1 0</td>
<td>136.12</td>
<td>135.5</td>
<td>0.62</td>
</tr>
<tr>
<td>0 1 0</td>
<td>0 1 1</td>
<td>120.05</td>
<td>120.0</td>
<td>0.05</td>
</tr>
<tr>
<td>1 1 0</td>
<td>1 1 1</td>
<td>129.85</td>
<td>128.6</td>
<td>1.25</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 2 0</td>
<td>127.38</td>
<td>127.3</td>
<td>0.08</td>
</tr>
<tr>
<td>1 1 0</td>
<td>-1 1 0</td>
<td>87.75</td>
<td>88.6</td>
<td>-0.85</td>
</tr>
<tr>
<td>1 1 1</td>
<td>0 1 1</td>
<td>152.49</td>
<td>153.7</td>
<td>-1.21</td>
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<tr>
<td>1 1 1</td>
<td>1 1 0</td>
<td>129.85</td>
<td>129.6</td>
<td>0.25</td>
</tr>
<tr>
<td>1 1 1</td>
<td>0 1 0</td>
<td>116.37</td>
<td>116.4</td>
<td>-0.03</td>
</tr>
<tr>
<td>1 1 1</td>
<td>-1 1 0</td>
<td>88.56</td>
<td>88.8</td>
<td>-0.19</td>
</tr>
</tbody>
</table>
constants of orthorhombic crystal have been discussed. The necessary expressions for the same, which relate the measured velocities with the elastic constants, have been obtained and tabulated in Table 1.2. The ultrasonic velocities have been measured using the Pulse Echo Overlap technique and the details of this technique are explained in Section 2.1.2. The basic experimental setup used for the measurements appears in Section 2.2.1. In all the velocity measurements, the correct overlap identification and bond correction have been performed using a computer program developed for the same and the details of the methodology and the program are presented in section 2.3.3. X and Y cut quartz transducers with resonance frequency 10 MHz, excited at their fundamental mode of operation, have been used to generate longitudinal and transverse ultrasonic waves. Specific experimental details regarding the bonding of the transducer to the sample have been discussed in Section 3.4.1 in connection with the measurements in LHS.

Of the 18 propagation modes listed in Table 1.2, measurements have been performed for 12 different modes. Using these 12 measurements all the 9 elastic constants of LAS can be determined with cross checking possible on some of the values. Of the 12 measurements 9 measurements are along the symmetry directions and 3 are in the symmetry planes, a-b, a-c and b-c, in the [110], [101] and [011] directions respectively.

Results of the velocity measurements in LAS are presented in Table 5.3 along with the corresponding elastic constants. In Table 5.4, we compare the results of our measurement of elastic constants of LAS with the previously reported values by different workers. As has been discussed in Section 5.1, there is no general agreement on the choice of axes for this orthorhombic crystal. Hence we have rearranged the elastic constants reported by previous workers using the
<table>
<thead>
<tr>
<th>No.</th>
<th>Mode</th>
<th>Direction of particle motion</th>
<th>Velocity measured ( (v) ) ( \text{km/s} )</th>
<th>Elastic constant ( (\rho v^2) ) ( \text{GPa} )</th>
<th>Involved elastic constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L</td>
<td>a</td>
<td>4.7863</td>
<td>43.57</td>
<td>( C_{11} = \rho v^2 )</td>
</tr>
<tr>
<td>2</td>
<td>T</td>
<td>b</td>
<td>2.9876</td>
<td>16.98</td>
<td>( C_{55} = \rho v^2 )</td>
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<tr>
<td>3</td>
<td>T</td>
<td>c</td>
<td>2.3554</td>
<td>10.55</td>
<td>( C_{66} = \rho v^2 )</td>
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<tr>
<td></td>
<td></td>
<td>Propagation along a-axis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>L</td>
<td>b</td>
<td>4.9531</td>
<td>46.66</td>
<td>( C_{22} = \rho v^2 )</td>
</tr>
<tr>
<td>5</td>
<td>T</td>
<td>a</td>
<td>2.9837</td>
<td>16.93</td>
<td>( C_{66} = \rho v^2 )</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>c</td>
<td>2.9343</td>
<td>16.38</td>
<td>( C_{44} = \rho v^2 )</td>
</tr>
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<td></td>
<td></td>
<td>Propagation along b-axis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>L</td>
<td>c</td>
<td>5.3827</td>
<td>55.11</td>
<td>( C_{33} = \rho v^2 )</td>
</tr>
<tr>
<td>8</td>
<td>T</td>
<td>a</td>
<td>2.3229</td>
<td>10.26</td>
<td>( C_{55} = \rho v^2 )</td>
</tr>
<tr>
<td>9</td>
<td>T</td>
<td>b</td>
<td>2.9179</td>
<td>16.19</td>
<td>( C_{44} = \rho v^2 )</td>
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<td></td>
<td></td>
<td>Propagation along c-axis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>QL</td>
<td>( \perp ) to c</td>
<td>5.0914</td>
<td>49.30</td>
<td>( C_{12} = f_{ab} )</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>( C_{12} = 19.67^+ )</td>
</tr>
<tr>
<td>11</td>
<td>QL</td>
<td>( \perp ) to a</td>
<td>5.4251</td>
<td>55.98</td>
<td>( C_{23} = f_{bc} )</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>( C_{23} = 26.26^+ )</td>
</tr>
<tr>
<td>12</td>
<td>QL</td>
<td>( \perp ) to b</td>
<td>5.2455</td>
<td>52.33</td>
<td>( C_{13} = f_{ac} )</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>( C_{13} = 28.88^+ )</td>
</tr>
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</table>
The abbreviations used have the following meanings:

L - Longitudinal, T - Transverse, QL - Quasi-longitudinal, QT - Quasi-transverse, \( \rho \) = density (1.902 g.cm\(^{-3}\) for LAS), \( v \) = velocity of propagation of respective mode. a, b, c - Crystallographic axis.

\( ^* \) Calculated values using respective formula given below

\[
f_{ab} = \left[ \frac{\left( c^2 C_{11} + s^2 C_{66} - \rho v^2 \right) \left( c^2 C_{66} + s^2 C_{22} - \rho v^2 \right)}{c^2 s^2} \right]^{1/2} - C_{66},
\]

\[
f_{bc} = \left[ \frac{\left( c^2 C_{22} + s^2 C_{44} - \rho v^2 \right) \left( c^2 C_{44} + s^2 C_{33} - \rho v^2 \right)}{c^2 s^2} \right]^{1/2} - C_{44},
\]

\[
f_{ac} = \left[ \frac{\left( s^2 C_{11} + c^2 C_{55} - \rho v^2 \right) \left( s^2 C_{55} + c^2 C_{33} - \rho v^2 \right)}{c^2 s^2} \right]^{1/2} - C_{55}.
\]

where \( s \) = sine and \( c \) = cosine of respective angle \( \theta \). (See Figure 1.1 for definition of \( \theta \))
Table 5.4
Elastic constants* of LAS in comparison with previously measured values (after rearrangement according to Table 5.1).

<table>
<thead>
<tr>
<th>Elastic constant</th>
<th>Different investigations</th>
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<tr>
<td>C_{11}</td>
<td>41.59</td>
</tr>
<tr>
<td>C_{22}</td>
<td>44.10</td>
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<td>49.73</td>
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<tr>
<td>C_{13}</td>
<td>26.1</td>
</tr>
<tr>
<td>C_{23}</td>
<td>22.8</td>
</tr>
</tbody>
</table>

* Piezoelectric couplings neglected
U Ultrasonic measurements
B Brillouin scattering measurements
T Values from tabulated data
Values from the temperature variation curves
[1] Aleksandrov et al [5.3] (1975) at 300 K, axes chosen = (2)
[6] Present work (1994), at 300 K, axes chosen = (2)
(See Table 5.1 for details of axes choice)
conversion scheme given in Table 5.1. It may be noted that the conversion process does not actually change the numerical values but only change the subscript of the notation for elastic constants. Some workers have not indicated their choice of axes and in these cases the choice used by them could be deducted by examining their elastic data. Only Aleksandrov et al [5.3] and Mróz et al [5.11] have given tabulated data of elastic constants and in other cases the values have been obtained from their temperature variation curves which starts from room temperature and goes to high temperatures. There have been only two previous ultrasonic measurements on LAS, one by Aleksandrov et al [5.3] and the other by Wyslouzil et al [5.12].

On comparing the previous results with the present measured values the following observations could be made. The values reported by Aleksandrov et al [5.3] appears to be about 0.95 times smaller than our values. The origin of this difference can possibly be related to a difference in the value of sample density used by them for the calculation of elastic constant from the ultrasonic velocity. We have used the value $\rho = 1.902$ [5.10, 5.11] and Aleksandrov et al [5.3] have not indicated the value used by them but could be $\rho = 1.8$. The Brillouin scattering measurements of Hirotsu et al [5.13] and Luspin et al [5.10] are in agreement with present values. The ultrasonic measurements of Wyslouzil et al [5.12] (no tabulated data given) appears to be inaccurate especially for the longitudinal mode constants. This inaccuracy can be traced to the small sample size (0.5 cm) used by them. With this size of sample the travel time for longitudinal waves in the sample will be less than 2 $\mu$s and an error in overlap identification can considerably affect the velocity measurement. However their interest was mainly the investigation of elastic anomalies near the high temperature phase transition in LAS. The Brillouin scattering measurements
of Mróz et al [5.11] show that the value of $C_{44}$ measured by them is too small when compared to others and this has affected their estimation of $C_{23}$ also.

5.2.4 Velocity surface plots of LAS

In section 1.2.1, we have derived the expressions for the velocities of acoustic waves in the symmetry planes of the orthorhombic lattice. Since LAS belongs to the orthorhombic system, those expressions can be used to compute the velocity of acoustic waves in the symmetry planes of LAS as has been done for LHS in Section 3.6. If the velocities are calculated using the corresponding elastic constants for different values of angle $\theta$ (defined in Figure 1.1) in the range from 0 to 360 degrees with some small step like 2°, then the resulting velocities can be plotted to get a phase velocity surface diagram for the corresponding plane.

For the purpose of plotting the curve on an x-y plane of the paper, we have to convert the calculated velocity $v$ and the angle $\theta$ to the x and y co-ordinates. These conversions can be performed using Equations (3.13) and (3.14).

For plotting the velocity surface in the a-b plane of LAS, the Equations from (1.25) to (1.27) can be used. Here the velocity $v_0$ is a pure shear (S) mode with polarization perpendicular to a-b plane, $v_1$ is a quasilongitudinal (QL) mode and $v_2$ is a quasishear (QS) mode except along symmetry directions a and b where they are pure modes. The plotted velocity surfaces are shown in Figure 5.3.

The velocity surface in the a-c plane can be computed using Equations from (1.34) to (1.36). Here $v_0$ is a pure S mode with polarization perpendicular to the a-c plane, $v_1$ and $v_2$ are QL and QS modes except along symmetry directions a and c. The plotted velocity surfaces are shown in Figure 5.4.

The velocity surface in the b-c plane can be computed
using Equations from (1.42) to (1.44). Here \( v_0 \) is a pure S mode with polarization perpendicular to the b-c plane, \( v_1 \) and \( v_2 \) are QL and QS modes except along symmetry directions b and c. The plotted velocity surfaces are shown in Figure 5.5.

From the above plots, the three velocities in any direction in any of the symmetry planes can be easily found by measuring the length of the straight line drawn from the centre to the curve at the required angle from the symmetry axis. The graphs have been plotted with a scale of 1 cm for 1 km/s of velocity.

5.3 Study of low temperature phase transitions in LAS

5.3.1 Low temperature ultrasonic measurements

We have investigated the temperature variation of all the diagonal elastic constants of LAS in orthorhombic pure mode directions below room temperature in the range 310 to 220 K. This range include the well known phase transition near 285 K and the recently proposed [5.8] phase transition near 256 K. The low temperature measurements are performed in the fabricated cryostat described in Section 2.2.2. Liquid nitrogen is used as the cryogenic fluid. The experimental setup for the measurements are as described in Section 2.2. 10 MHz ultrasonic waves excited by longitudinal and transverse mode quartz transducers are used for velocity measurements. We have used silicon grease as the bond material in these measurements. The change in velocity with temperature with respect to the room temperature value has been measured by carefully adjusting the cw oscillator frequency keeping the selected rf echoes in the phase matched condition. Temperature variation measurements are carried out in temperature intervals of about 1 K and in intervals of about 0.1 K near the transition points. The rate of temperature change in all
Figure 5.3
The velocity surfaces of LAS in a-b plane
Figure 5.4
The velocity surfaces of LAS in a-c plane
Figure 5.5
The velocity surfaces of LAS in b-c plane
these measurements are in the range of 0.1 K to 0.5 K per minute. Measurements are carried out both for cooling and heating cycles. This is to reveal the thermal hysteresis effects of the phase transitions.

One major difficulty for low temperature ultrasonic measurements in LAS is the cracking of the crystal at the 285 K phase transition. Aleksandrov et al [5.3] have also noted this point and they have not been able to make ultrasonic measurements below the transition temperature. Large crystals are required for ultrasonic study and these crystals always develop cracks at the transition temperature even under extremely slow cooling rates. We have found that ultrasonic measurements are still possible below the transition temperature with considerably reduced echo amplitudes. This is achieved by careful tuning and sensitive adjustments of our measuring system. Attenuation measurements could not be performed due to the poor quality of the echo pattern.

The phase transition at 285 K changes the symmetry of the crystal. The crystal goes from the room temperature (phase II) orthorhombic mm2 (C_{2v}) point group to monoclinic 2/m (C_{2h}) point group below the phase transition temperature (phase III). Many of the pure modes in orthorhombic phase are no longer pure modes in the monoclinic phase and combination constants of monoclinic symmetry are only applicable in phase III. With our choice of axes (see choice (2) in Table 5.1) the c-axis coincide with the two fold y-axis in the monoclinic phase. Cell doubling upon transition takes place along orthorhombic a-axis [5.4] which is also made to correspond with monoclinic x-axis. The orthorhombic b-axis is made to correspond with monoclinic z-axis. For the choice of axes in both orthorhombic and monoclinic phases we have followed the convention adopted by IRE standards Committee [5.22] which have been listed by Neighbours and Schacher
The involved constants in both phases for different propagation modes are tabulated in Table 5.5 with our choice of axes. We indicate different modes with a three letter notation; the first letter (a, b or c) indicates the direction of wave propagation, the second letter (l or t) indicates whether the waves are longitudinal or transverse, the third letter (a, b or c) indicates the direction of polarization.

We would like to point out that Mróz et al [5.11] who have provided a table of relations for propagation modes in orthorhombic and monoclinic phases have not clearly defined their choice of axes and we find their table inconsistent with their choice of axes. Further, the relations given by them for monoclinic phase shows some mistakes.

5.3.2 Results and discussion

The temperature variation of the elastic constants $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$ and $C_{66}$, corresponding to the modes indicated in Table 5.5, below room temperature during cooling and heating cycles are shown in Figures 5.6 to 5.16. The phase transition occurring at 285 K is clearly visible in all the figures. There is a clear step like change in the elastic constant values and there is a clear thermal hysteresis of 2.5 K between the cooling and heating cycles for this transition. On cooling the transition takes place at 285.5 K and on heating the transition takes place at 288 K. This has not been reported by previous workers [5.11] who undertook the study of elastic properties near this transition in LAS using Brillouin scattering technique.

It can also be seen that the $C_{22}$ constant in monoclinic phase which correspond with the clc mode (Figures 5.10 and 5.11) shows an anomaly at 242 K on cooling and at 258 K on heating. Similarly a clear anomaly is observed for the
Table 5.5

The involved elastic constants in orthorhombic mm2 and monoclinic 2/m phase of LAS for different modes of propagation

<table>
<thead>
<tr>
<th>Modes</th>
<th>mm2 phase</th>
<th>2/m phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>ala*</td>
<td>( C_{11} )</td>
<td>( \frac{1}{2} \left( C_{11} + C_{55} + \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2} \right) )</td>
</tr>
<tr>
<td>atc</td>
<td>( C_{55} )</td>
<td>( C_{66} )</td>
</tr>
<tr>
<td>atb*</td>
<td>( C_{66} )</td>
<td>( \frac{1}{2} \left( C_{11} + C_{55} - \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2} \right) )</td>
</tr>
<tr>
<td>clc*</td>
<td>( C_{33} )</td>
<td>( C_{22} )</td>
</tr>
<tr>
<td>ctb*</td>
<td>( C_{44} )</td>
<td>( \frac{1}{2} \left( C_{44} + C_{66} + \sqrt{(C_{44} - C_{66})^2 + 4C_{46}^2} \right) )</td>
</tr>
<tr>
<td>cta*</td>
<td>( C_{55} )</td>
<td>( \frac{1}{2} \left( C_{44} + C_{66} - \sqrt{(C_{44} - C_{66})^2 + 4C_{46}^2} \right) )</td>
</tr>
<tr>
<td>blb*</td>
<td>( C_{22} )</td>
<td>( \frac{1}{2} \left( C_{33} + C_{55} + \sqrt{(C_{33} - C_{55})^2 + 4C_{35}^2} \right) )</td>
</tr>
<tr>
<td>bta</td>
<td>( C_{66} )</td>
<td>( \frac{1}{2} \left( C_{33} + C_{55} - \sqrt{(C_{33} - C_{55})^2 + 4C_{35}^2} \right) )</td>
</tr>
<tr>
<td>btc</td>
<td>( C_{44} )</td>
<td>( C_{44} )</td>
</tr>
</tbody>
</table>

* Modes which have been investigated presently
Figure 5.6
Temperature variation of elastic constant of LAS for the cooling cycle of ala mode
Figure 5.7
Temperature variation of elastic constant of LAS for the heating cycle of ala mode
Figure 5.8
Temperature variation of elastic constant of LAS for the cooling cycle of blb mode
Figure 5.8
Temperature variation of elastic constant of LAS for the cooling cycle of blb mode
Figure 5.9
Temperature variation of elastic constant of LAS for the heating cycle of blb mode
Figure 5.10
Temperature variation of elastic constant of LAS for the cooling cycle of clc mode
Figure 5.11
Temperature variation of elastic constant of LAS for the heating cycle of clc mode
Figure 5.12
Temperature variation of elastic constant of LAS for the cooling cycle of ctb mode
Figure 5.13
Temperature variation of elastic constant of LAS for the heating cycle of ctb mode
Figure 5.14
Temperature variation of elastic constant of LAS for the cooling cycle of cta mode
Figure 5.15
Temperature variation of elastic constant of LAS for the cooling cycle of atb mode
Figure 5.16
Temperature variation of elastic constant of LAS for the heating cycle of atb mode
combination constant in atb mode which appears as sudden dip at 242 K on cooling and a distinct slope change at 256 K on heating (Figures 5.15 and 5.16). Further a small slope change is also observed at 255 K in the heating cycle for the combination constant of blb mode (Figure 5.9). These anomalies are indicative of a phase transition occurring in LAS with a thermal hysteresis of about 14 K between the cooling and heating cycles.

Another weak anomaly can be noticed near 272 K for several modes during heating and cooling. For the ala mode a dip can be seen at 272 K during cooling cycle. For the blb mode an anomaly can be found at 272 K for both cooling and heating cycles. For clc mode there is a slope change on cooling and peak on heating can be found at this temperature. The ctb mode shows a slope change near this temperature on heating cycle. The atb mode shows a small slope change at 270 K on heating cycle. A characteristic of this anomaly is that it does not show any thermal hysteresis effect and is present during cooling and heating cycles. A phase transition at this temperature have not been reported or suspected previously by any workers. Examination of the experimental curves of previous workers reveals a correlation with the pyroelectric response curve of Gerbaux et al [5.7]. The pyroelectric signal observed in phase III is showing a continuous increase on heating and reaches a peak value near this temperature and thereafter it sharply falls to a zero value at 285 K transition and recovers after the transition. Thus the anomaly at 272 K can be connected with the temperature at which the pyroelectric response starts to fall on approaching the 285 K transition. It is tempting to argue that this anomaly is connected with the 285 K transition but the possibility of a new phase transition in LAS at 272 K cannot be ruled out.
a) Phase transition at 285 K

As has been reported by earlier workers, the phase transition at 285K is clearly a first order ferroelastic one. In the temperature dependence of elastic constants shown in Figures 5.6 to 5.16, one can notice a clear thermal hysteresis of \( \approx 2.5K \) between the cooling and heating cycles. One expects this kind of a hysteresis in elastic constant values when a crystal undergoes a first order ferroelastic phase transition [5.24]. This small hysteresis can be attributed to the pinning of the ferroelastic domains when the sample is cycled through the transition. The elastic constant data obtained from Brillouin scattering experiments [5.11] do not show this hysteresis, probably because these authors did not make the measurements during cooling and heating cycles. This is the first time this hysteresis in elastic constant data is reported.

A Landau model describing the sequence of phase transitions occurring in LAS has been put forward by Torgashev et al [5.15]. Schranz et al [5.16,5.17] have theoretically analysed the possible couplings between strains and the order parameter involved. Mróz et al [5.11] have put forward a theoretical model for the ferroelastic phase transition in LAS focusing attention on the vicinity of the transition. After writing down the free energy expression and considering the strain \( e_5 \), one can show that the order parameter \( \eta \) is given by

\[
\eta = \left( \frac{C_{55}^0 + 2 G_5 P^2}{l} \right) e_5
\]  

(5.1)

where \( P \) is the polarization. The coupling between \( e_5 \) and \( P \) shifts the transition temperature by a constant value. With the transition to the ferroelastic phase (F), the polarization of the sample vanishes leading to a destabilization of the polarized phase. The effective second order elastic
coefficients experience a discontinuity at $T = T_c$ which is increased by the simultaneous disappearance of polarization. In the paraelastic phase ($P$), $e_s \approx 0$ (not exactly zero due to coupling with polarization) and

$$C_{55}^P = 2(b_2 + \mu P_s^2) \quad (5.2)$$

whereas in the ferroelastic phase ($F$), the relevant combination constant is

$$C_{55}^F = 17b_2 \quad (5.3)$$

such that

$$\Delta C_{55} = C_{55}^F - C_{55}^P$$

$$\approx 15b_2 - 2\mu P_s^2 \quad (5.4)$$

The ferroelastic phase transition is driven by a two component soft mode which couples strongly to the spontaneous strains and to the polarization. Owing to the associated metastability of the phases, thermal hysteresis can be expected to occur. Similar theoretical formulations and arguments apply to the discontinuities exhibited by other strains. These discontinuities and thermal hysteresis are clearly seen in our elastic constant results shown in Figures 5.6 to 5.16. In our results, the thermal hysteresis is observed both for the transition temperature and for the elastic constants. The thermal hysteresis effect of elastic constants is more evident in longitudinal mode constants.

Above observation supports the presence of a metastable phase in LAS below 285 K. Evidence for the presence of a two phase system was also obtained by Smutny and Polomska [5.25] in their study on the effect of electric field on the phase
transition in LAS. A two phase system below the transition was also earlier reported by Aleksandrov et al [5.26]. Martins et al. [5.8], from their Raman scattering study, has recently concluded that the phase between 285 and 256 K is nonpolar but the pyroelectric signal obtained earlier by Gerbaux et al [5.7] in this temperature range shows that LAS is polar in this region. This discrepancy can be explained on the basis of a mixed phase system. The spontaneous deformation of ferroelastic Phase III may produce electric response via the hydrostatic piezoelectric effect along the two fold axis. Signals thus produced can be misinterpreted as pyroelectric response.

b) Phase transition at 256K

Both Gerbaux et.al. [5.7] and Martins et.al.[5.8] have proposed a phase transition taking place in LAS at 256K based on their infrared absorption, dielectric constant and Raman scattering measurements. Change in the slope of the dielectric constant curve [5.8] leads one to believe that the transition at 256K is second order and reversible. The anomalies seen in our elastic constant curves shown in Figures 5.9, 5.10, 5.11, 5.15 and 5.16 are indicative of a transition taking place between 240K and 260K. During the cooling cycle the anomaly is seen at 242K and during the heating cycle it appears at 256K indicating that there is a thermal hysteresis of ≈ 14K for this transition between the cooling and heating cycles. Gerbaux et.al. [5.7] and Martins et.al. [5.8] reported transition only at 256K, probably because these authors made their measurements only during the heating cycle. The thermal hysteresis of the temperature of this transition is evident in the differential scanning calorimetric curves reported by Chhor et al [5.20] but they have interpreted the transition temperature as 248 K which in fact is near the mean value of
According to Martins et al. [5.8], the transition at 256K (or 242K) is a diffuse order-disorder type one involving a reordering of the SO₄ ions. A similar type of mechanism has been proposed for the transition occurring in Lithium Potassium Sulfate crystal [5.27]. The oxygen atoms at the top of the SO₄ tetrahedra freeze in such a way that the symmetry of inversion of the phase is broken and the structure stabilizes with a symmetry belonging to the C₁⁺ or C₂⁺ space group. This transition is observed for the first time in elastic measurements in LAS and the thermal hysteresis of this transition is established for the first time.

c) Modulated structure in LAS: A new model

The results of the previous investigations and our results suggest the need of a new model to resolve the controversies regarding the low temperature phase of LAS. In this model we propose the presence of a modulated structure below the 285 K transition. Earlier Poulet and Mathieu [5.18] on the basis of their Raman scattering experiment has proposed that the low temperature phase could be a modulated one. This idea did not receive much attention after that.

Present ultrasonic investigation shows some difference in elastic behaviour with Brillouin scattering investigation [5.11]. While the ultrasonic results show some anomalous variations near the 285 K transition the Brillouin results show temperature independent straight line curves with step like discontinuities at the transition temperature. While ultrasonic technique is a low frequency technique, Brillouin scattering technique is a very high frequency technique and this difference in behaviour can be interpreted as frequency dispersion of elastic constants. This frequency dispersion of elastic constant is a characteristic feature of an
incommensurate transition [5.28]. Therefore we propose that LAS is undergoing an incommensurate transition at $T_1 = 285$ K or at 272 K where we find an anomaly in many modes. According to this picture the transition at 285 K can still be ferroelastic one and between 285 and 272 K LAS is nonpolar and at 272 K the incommensurate transition takes the crystal to an incommensurate ferroelastic state. If there is no transition at 272 K then the crystal must be entering the incommensurate ferroelastic state at 285 K itself and the elastic anomaly at 272 K may be related to the incommensurate ferroelastic transition at 285 K. In this phase a mixed phase like behaviour can be observed due to the ferroelastic modulation. This modulation can give rise to spatially periodic strain or polarization which can be influenced by external stress or electric fields. The modulation period and amplitude can change with temperature. The pyroelectric signals observed by Gerbaux et al [5.7] can be explained by this temperature dependent periodic polarization. The mixed phase model is no longer required to explain the polar-nonpolar controversy.

Next we propose that the transition at 256 K is the incommensurate to commensurate phase transition or lock in transition $T_c$ which takes LAS to a cell doubled antiferroelastic phase. Thermal hysteresis of the commensurate transition temperature ($T_c$) is observed in a number of crystals which show incommensurate phase [5.29]. In LAS we have established that the transition is taking place at 242 K on cooling and at 256 K on heating which shows a clear thermal hysteresis of 14 K. Weak, higher order and diffuse behaviour of this transition further supports the view that this transition is an incommensurate to commensurate transition.

Evidence for an antiferro order below the 256 K transition can be first found in the work of Martins et al [5.8]. They have found that below 256 K transition there is a modification of the structure leading to two distinct sites
for the SO$_4$ unit. They proposed that the phase below 256 K can be a modulated phase going to a locked phase around 100 K. But no lock-in transition have been reported near 100 K. We propose that the two distinct site for SO found by them is due to the antiferroelastic order.

Martins et al [5.8] have described phase below 256 K as polar belonging to C$_s^1$ or C$_s^2$ space group with no cell doubling. This was in discordance with the X-ray results (at 213 K) of Kruglik et al [5.4] who described this phase as nonpolar C$_{2h}^5$ space group with cell doubling. Recent X-ray structure refinement of LAS by Mashiyama and Kasano [5.21] confirms the low temperature (at 190 K) space group as C$_{2h}^5$ with cell doubling. Further they have found the low temperature phase as a periodically aligned micro-domain structure with alternating polarization. The modulated phase proposed by Martins et al [5.8] from 256 K to 100 K if present would have been found in the refined X-ray work at 190 K [5.21]. On the other hand the recent X-ray result [5.21] that the low temperature phase at 190 K is a periodically aligned micro-domain structure with alternating polarization, is consistent with our model which propose a commensurate antiferroelastic order below 256 K (or 242 K).

The new model discussed above have been mainly based on qualitative arguments and the correctness of it can be established only by further experiments and theoretical formulations.

5.4 Conclusions

In this chapter the measured values of the elastic constants of LAS and the results of low temperature phase transition study in LAS are presented. All the nine elastic constants of orthorhombic LAS are accurately determined and tabulated. Measured velocities in 12 modes of propagation are
also presented in a table. A conversion table is presented to clarify the problem of different choice of axes adopted by different workers. With the help of this table the previous measurements of elastic constants of LAS could be compared correctly with the present values. Using the measured elastic constants the velocity surfaces of LAS are computed in the three orthogonal symmetry planes and the plots are presented.

Temperature variation study of elastic constants are performed for 6 different modes of propagation during cooling and heating cycles.

Our measurements establish a soft mode driven ferroelastic phase transition at 285.5 K which is characterized by a thermal hysteresis of 2.5 K. The observed hysteresis in elastic constants is in accordance with the predictions of the Landau theory. Our experimental results establish an order-disorder type phase transition occurring in LAS at 242 K during the cooling cycle and at 256 K during the heating cycle which is detected for the first time in elastic constant measurements. The 14 K thermal hysteresis of this transition is established for the first time. Based on our results and the earlier workers, the successive phase transitions exhibited by LAS can be redrawn as shown in Figure 5.17. These results indicate that LAS is another interesting member of the sulfate family exhibiting a sequence of phase transitions as the temperature is varied.

Finally, we have proposed a new model for the presently observed low temperature phase transitions in LAS. According to this model an incommensurate ferroelastic phase is proposed below the 285 K transition and the transition at 256 K is considered as a lock in transition to an antiferroelastic order. The new model could resolve some controversies but it was concluded that further research is required to establish the incommensurate phase.
Figure 5.17
Modified sequence of phase transitions in LAS
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