Investigation of the Elastic Properties of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ as a Function of Temperature and Pressure

by

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Abstract

A high resolution acoustic interferometer is used to study the elastic properties of $Rb_4LiH_3(SO_4)_4$ as a function of temperature and pressure. The temperature and pressure ranges in our investigation were 4 $K$-300 $K$ and 0 $kbar$-10 $kbar$, respectively. At ambient pressure, a phase transition at $T_c = 132 \pm 0.3$ $K$ is observed using the sound velocity measurements as a function of temperature. At room temperature, the occurrence of a phase transition at a pressure of $P_c = 8.4 \pm 0.2$ $kbar$ is discovered through sound velocity measurements as a function of pressure. Attempt has also been made to distinguish the x and y direction in the monoclinic phase. The results turn out to be still equivalent along these two directions. Using the sound velocity measurements as a function of temperature under different pressures, the temperature-pressure phase diagram of $Rb_4LiH_3(SO_4)_4$ is derived. It is found that $T_c$ increases rapidly with pressure at a rate of $19 \pm 1 K/kbar$. Using the sound velocity measurements, the temperature and pressure dependence of five of the seven independent elastic constants of $Rb_4LiH_3(SO_4)_4$ are obtained. To our knowledge, we are the first to investigate the elastic constants as a function of pressure. We observed that the elastic constant $(C_{11} - C_{12})/2$ shows incomplete softening at $T_c$ or $P_c$. In the high symmetry phase, this elastic constant exhibits a nonlinear temperature or pressure dependence. A Landau model involving both temperature and pressure as external parameters is proposed. Our calculations agree well with our experimental results.
Our model predicts that the actual soft acoustic mode shows complete softening at $T_c$. It also predicts that the actual soft acoustic mode propagates along the direction away [110] by $-5^\circ$. 
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Chapter 1

Introduction

Over the last few decades, due to their interesting physical properties and application potentials, ferroelastic crystals have been the subject of numerous theoretical and experimental studies. According to Aizu [1], ferroelastics has been defined as materials in which homogeneous stress may be used to order and switch the orientation of structural domains. Thus, ferroelastic crystals are analog to ferroelectric crystals where, in that case, the electric domains can be aligned by the application of a homogeneous electric field. While all ferroelectric crystals are known to be also ferroelastic, ferroelastic compounds are not necessarily ferroelectric at the same time [2]. Thus, the central physical feature of ferroelastic crystals is their lattice distortion associated with the occurrence of spontaneous strain in the ferroelastic phase. Moreover, when a stress is applied, hysteretic behavior of the macroscopic spontaneous strain is observed. This strain-stress hysteresis is one of the characteristics of ferroelastic crystals.

The properties of the ferroelastic materials have been exploited in many applications. As the domains in a ferroelastic can be made to shrink or expand by applying an uniaxial stress, single-domain crystal can be obtained as required by some appli-
cations, e.g. in nonlinear optics [59]. By applying uniaxial stress, one can also pole
or switch the domain of a ferroelastic single crystal. This property has been used
for creating periodically spaced domain walls in some ferroelastic crystals, and the
spacing of the walls can be from 70 mirons to 0.5 micron [3]. The result is a tunable
optical grating. The switchability of ferroelastic domains and the consequent mobility
of the domain walls have additional applications [4]. Micropositioner with a memory,
variable acoustic delay line, tailored domain patterns for resonator applications and
focusing acoustic transducers, are some examples of potential applications. Near the
phase transition, ferroelastic crystals also exhibit some interesting properties. For
example, in the vicinity of the transition temperature a small stress can be used to
induce a large strain which result in a large variation in the birefringence property
of the crystal. This property has found application in acoustic-optic modulators [59].
Since for ferroelastic crystals, one of the acoustic velocity typically tends to zero as
the transition temperature is approached, the modulation efficiency, which is inverse
proportional to the acoustic velocity, is considerably high. The feature that some
elastic constants show a strong temperature dependence near the transition temper­
ature has been used in smart structures (materials or structures with the ability to
respond in a pre-designed manner to changing environmental conditions) [59].

Although the existence of crystals with the stoichiometry $A_4LiH_3(BO_4)_4$, where
$A = Rb, NH_4, K$ and $B = S, Se$, was reported more than a hundred years ago,
their ferroelastic properties have been discovered only recently. That aroused the
interest of scientists and consequently a large number of studies followed. However,
till now, these investigations are focused on the understanding of the structure and
properties of these crystals. The application of these crystals cannot be reasonably
predicted until their properties are known. From the reported results, we know that
at room temperature almost all these crystals are isomorphous and possessed the
tetragonal symmetry [5–7]. However, there was a disagreement about the actual symmetry group to which they should be ascribed. For $K_4LiH_3(SO_4)_4$, Electron Spin Resonance (ESR) investigations [8] led to the conclusion that the point group $4/m$ is the most likely. However, for $Rb_4LiH_3(SO_4)_4$ the inverted torsional pendulum and piezoelectric series resonance studies [9] and the Brillouin scattering studies [10] suggested that the prototype symmetry should be the point group $4mm$. Later investigations [6, 7, 11–16] finally reached a consensus and showed that this class of compounds has a room-temperature phase corresponding to the tetragonal point group 4. Moreover, at low temperatures most of these crystals undergo a structural phase transition from the tetragonal point group 4 to the monoclinic point group 2. In spite of their structure similarity, the transitions they undergo below room temperature usually show different features. For example, while the Brillouin scattering study [14] of $Rb_4LiH_3(SO_4)_4$ indicates that the transition at about 130 K is ferroelastic, the ferroelastic nature of the transition at 115 K in $K_4LiH_3(SO_4)_4$ was not confirmed [14]. Though both compounds $Rb_4LiH_3(SO_4)_4$ and $(NH)_4LiH_3(SO_4)_4$ undergo ferroelastic phase transitions, the temperature behavior of the soft elastic constants are believed to be different [6]. While the effective elastic constant for the soft mode in $(NH)_4LiH_3(SO_4)_4$ vanishes at $T_c$ [16]. The soft mode in $Rb_4LiH_3(SO_4)_4$ shows incomplete softening at $T_c$ [14]. To our knowledge, $Rb_4LiH_3(SO_4)_4$ is the only ferroelastic compound whose soft mode shows incomplete softening at $T_c$. Because of the unusual elastic properties displayed by $Rb_4LiH_3(SO_4)_4$, we choose this particular ferroelastic compound as our research object.

Despite the large number of investigations realized on $Rb_4LiH_3(SO_4)_4$, our knowledge about some of its properties is far from complete. The compound $Rb_4LiH_3(SO_4)_4$ was initially assumed to have the chemical formula corresponding to $LiRb_5(SO_4)_2 \cdot 1.5H_2SO_4$ [9, 10, 12, 17, 18]. However, the density value calculated
from X-ray data using this formula disagreed with the measured value [14]. The following chemical analyses led to its present form for which a better fit was obtained. So far four structural phase transitions have been observed for this crystal in the temperature range going from 4 $K$ to 495 $K$. Piskunowicz et al. [19] reported that three structural transitions happened at 440, 454, and 470 $K$, respectively. These three phase transitions were later confirmed by Differential Thermal Analysis (DTA) study [20], however the observed transition temperatures (458 $K$, 470 $K$, and 490 $K$) are somewhat different from those reported by Piskunowicz et al [19].

Comparatively, the phase transition below room temperature is well studied, the transition temperature was found to be around 132 $K$ [6, 10, 15, 17–19, 21]. Besides, it was already well established that the transition belongs to the second order (continuous transition). In conformity with this, neither latent heat nor thermal hysteresis has been observed in the transition [9, 10, 18, 19]. The ferroelastic character for this crystal is also known. In the low temperature phase, two kinds of birefringent domains has been observed by using a polarization microscope [9]. The domains are separated by mutually perpendicular walls in the planes (100) and (010). Such 90° domain structure was later confirmed by the observations conducted by Piskunowicz et al. [19] and Mielcarek et al. [22]. Moreover, the strain-stress hysteresis was also observed by applying normal stress along [100] or [010] directions [9, 18]. Given these facts, the phase below room temperature is undoubtedly ferroelastic. Since it was also found that the direction of the spontaneous electric polarization remain unchanged around 132 $K$ [18], the transition is ferroelastic and non-ferroelectric.

In determining the symmetry of this crystal at room temperature, results obtained from different techniques used to be inconsistent. Brillouin scattering measurements [10, 17] suggested that the phase transition type is 4$mm \rightarrow mnm2$. This conclusion was corroborated by inverted torsional pendulum and piezoelectric series resonance
measurements [9] and the observations of domain walls [18]. However, the X-ray investigation [23] showed that \( Rb_4LiH_3(SO_4)_4 \) possesses the symmetry of space groups \( P4_1 \) or \( P4_3 \) at room temperature. The X-ray anomalous scattering and optical-activity measurements [11] further point out that \( Rb_4LiH_3(SO_4)_4 \) is consisted of 87% of laevorotatory crystal in space group \( P4_1 \) and 13% of dextrorotatory crystal in the space group \( P4_3 \). However, recent neutron scattering measurements [6] only confirmed the existence of space group \( P4_1 \) at room temperature. Despite the uncertainty about the existence of \( P4_3 \), given that the two space groups both possess the same point group symmetry, it is safe to say that the crystal belongs to the tetragonal point group 4 at room temperature. This assignment of the point group for the prototype phase was supported by ultrasonic velocity and dielectric permittivity measurements [12] and Brillouin scattering [14] and Raman scattering studies [15]. For such a prototype symmetry, the ferroelastic transition theory [24] requires that the low-temperature ordered phase to be monoclinic 2. However, direct evidences about the structure of the low-temperature phase are scarce and inconsistent. On the one hand, X-ray studies [23] suggested the presence of orthorhombic distortion in the low temperature phase. On the other hand, X-ray investigations reported by Zuniga et al. [11] show that the low temperature phase should belong to monoclinic space group \( P2_1 \) and point group 2. Very recent results, from neutron scattering measurements [6], support the conclusion of the latter group.

A ferroelastic phase transition is usually accompanied by the onset of spontaneous strains which in turn lead to anomalous temperature behavior on the elastic properties. Such variations have been observed in \( Rb_4LiH_3(SO_4)_4 \) by various types of experiments, however, the results are not fully consistent. For example, during a ferroelastic phase transition with a symmetry change \( 4 \rightarrow 2 \), one expects to see the softening of the elastic constant \( C_{11} - C_{12} \) and \( C_{66} \). However, in the inverted torsional
pendulum measurements, the appearance of a soft mode associated with the elastic constants $C_{11} - C_{12}$ is observed [9]. According to the Brillouin scattering studies [10], only the elastic constant $C_{66}$ gets softened while ultrasonic studies [12] show that both $C_{11} - C_{12}$ and $C_{66}$ get softened. Despite this disagreement, there is a common feature that emerges, they all indicate incomplete softening.

So far several Landau theory models have been put forward by different research groups, however none of them can describe the overall elastic properties of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$. These models can be divided into two classes. One assumes that the spontaneous strain (or strains) is the order parameter of the Landau free energy, i.e. assuming that the transition corresponds to a proper ferroelastic transition [12, 14, 19]. The other assumes that the order parameter is not the strain but has the same symmetry as the spontaneous strain (or strains) [10, 21]. In this case, the transition is classified as a pseudo-proper ferroelastic transition. Though the proposed models agree qualitatively with some of the observations, their predictions are still not fully consistent with the measurements.

The aim of this project is to investigate the elastic properties of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ as a function of both temperature and pressure, in the meantime, to verify if the softening of the effective elastic constant associated with the soft mode is indeed incomplete. This is realized via sound velocity measurements using an acoustic interferometer. These measurements also enable us to derive the temperature-pressure diagram of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$. The diagram covers the temperature range 4 K-300 K for pressures up to 7 kbar. Attempt has also been made to distinguish the x and y direction in the monoclinic phase. The result will reveal some properties of the domains which appear in this phase. In order to explain the experimental features, we also present a Landau model using both temperature and pressure as the external parameters. This model is based on the assumption that the observed ferroelastic phase transition has a
pseudoproper character. The validity of this model is verified using our experimental data. Unexpectedly, it predicts that the effective elastic constant associated with the soft mode shows complete softening at the transition.

The acoustic interferometer used in this project is very suitable for the investigation of the elastic properties of crystals. The advantage of this technique lies in its high resolution ($1 ppm$), two or three order of magnitude greater than that of Brillouin scattering (its resolution is in the order of 1%). Consequently, our technique can detect small variation in sound velocity and, in some cases, discover phase transitions that have been missed by other techniques. Another advantage should be attributed to its versatility. With the same experimental set up, we can measure the sound velocity as a function of both temperature and pressure. However, the samples used in our measurements normally need to be larger in size than those used in X-ray scattering or Brillouin scattering. In this particular case, this requirement should not be considered as a disadvantage since large single crystals of $Rb_4LiH_3(SO_4)_4$ can be easily obtained.
Chapter 2

Crystalline Elasticity

As the aim of this project is to investigate the elastic properties of $Rb_4LiH_3(SO_4)_4$, we first introduce some essential background knowledge about crystalline properties, such as, the strain, stress and elastic constant tensors. Then we will discuss how the elastic energy can be obtained. Finally, we describe how the Christoffel equation is used in order to determine the relation between the velocity of some specific plane waves and the independent elastic constants of the crystal. A detailed discussion about the elastic properties of crystals can be found in the book “Elastic Waves in Solids” written by E. Dieulesaint and D. Royer [60].

2.1 Static Elasticity

2.1.1 Strain and Stress

Under the action of external forces, materials are generally deformed to some extent. Before discussing deformations in general, we first consider a simple case, the stretching of a string (one dimensional), see Fig. 2.1. Under the action of a force $F$, the string stretches. The section between $M_0$ and $N_0$ extends from the original length
CHAPTER 2. CRYSTALLINE ELASTICITY

Figure 2.1: Deformation of a string. Under the action of a force $F$, the length increment for the portion $\Delta x$ is $\Delta u$. The strain is described as the limit of the ratio $\Delta u/\Delta x$ when $\Delta x$ goes to 0 [60].

$\Delta x$ to $\Delta x + \Delta u$. The deformation of this section is then $\Delta u$ and the deformation per unit length can be written as

$$ e = \frac{\Delta u}{\Delta x} \quad (2.1) $$

which represents the strain. In the case of a two dimensional body, the deformations induced by external forces do not necessarily involve only the variations in length but also some angular distortions, as shown in Fig. 2.2. The variations in length along x-axis and y-axis are represented by the quantities $e_{xx}$ (or $e_{11}$) and $e_{yy}$ (or $e_{22}$), respectively, while the angular distortions or shear deformations are represented by the quantities $e_{xy}$ (or $e_{12}$) and $e_{yx}$ (or $e_{21}$). These four quantities constitute a $2 \times 2$ second-rank tensor, which is often expressed in the form of a matrix. Due to similar considerations, the deformations of a three dimensional body induced by external forces are described by a $3 \times 3$ strain tensor. Its nine elements can be arranged in a
Figure 2.2: The deformations of a two dimensional body under the action of forces $F_1$ and $F_2$. Under the action of $F_1$ and $F_2$, the lengths along both x-axis and y-axis change, so did the angle between two points of the body with respect to the origin $0$.

3 × 3 matrix as following

$$
(e_{ij}) = \begin{pmatrix}
e_{11} & e_{12} & e_{13} \\
e_{21} & e_{22} & e_{23} \\
e_{31} & e_{32} & e_{33}
\end{pmatrix}
$$  \hspace{1cm} (2.2)

where $(e_{ij})$ represents the strain tensor with $i, j$ running from 1 to 3. Its diagonal components are a measurement of the extensions along the three axes of an orthogonal reference frame associated with the crystal axes. The off-diagonal components describe the shear deformations of the medium. For small deformations, which are considered here, the strain components can be expressed as [60]

$$
e_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right]
$$  \hspace{1cm} (2.3)

where $e_{ij}$ is the component of the strain tensor in the i-th row and j-th column and $u_i$ ($u_j$) is the i-th (j-th) component of the displacement $\vec{u}$ of the point where the
deformation is observed. From Eq. 2.3, we see that the element of the strain tensor remains invariant under the interchange of indices $i$ and $j$, i.e.

$$e_{ij} = e_{ji} \quad (2.4)$$

In other words, for small deformations the strain tensor is symmetric and can be rewritten as

$$\begin{pmatrix}
e_{11} & e_{12} & e_{13} \\
e_{12} & e_{22} & e_{23} \\
e_{13} & e_{23} & e_{33}
\end{pmatrix}$$

where the number of independent strain components reduces to 6.

The force acting on a unit area in the solid is defined as the stress. There are nine stress components $T_{11}, T_{12}, T_{13}, T_{21}, T_{22}, T_{23}, T_{31}, T_{32}, T_{33}$. The nine components form a second-rank tensor called the stress tensor $(T_{ij})$, where $i, j = 1, 2, 3$. The component $T_{ij}$ represents a force applied in the $i$ direction acting on a unit area normal to the $j$-axis. The number of independent stress components is reduced from nine to six based on the following considerations. Let's consider an elementary cube which remains in static equilibrium under the action of stress $T_{ij}$, see Fig. 2.3. The force applied to the upper face in the $x$-direction corresponds to the stress component $T_{xy}$ or $T_{12}$. As required by the equilibrium condition, the force applied to the bottom in the negative $x$-direction must also be $T_{12}$ since the magnitude of these two forces are equal. Similarly, the forces applied to the right and left faces of the cube in the $y$-direction correspond to $T_{21}$. As the cube is in static equilibrium, the condition that the total torque must be zero requires that $T_{12} = T_{21}$. Generalizing this result, we have that

$$T_{ij} = T_{ji} \quad (2.6)$$

and, as for the strain tensor, the stress tensor is also symmetric.
Figure 2.3: For a body in equilibrium, the net force acting on that body must vanish. The total torque acting on that body must also vanish, so that $T_{12} = T_{21}$ [61].

2.1.2 Elastic Constants

A medium is said to be elastic, if it returns to its initial state after the external forces are removed. In an elastic material, for sufficiently small deformations, the strain is directly proportional to the stress. In this linear limit, the relation between stress $T$ and strain $e$ is adequately described by the generalized Hooke's law:

$$T_{ij} = C_{ijkl} \cdot e_{kl} \quad i, j, k, l = 1, 2, 3$$ (2.7)

where repeated indices are implicitly summed over (Einstein convention), so that the coefficients $C_{ijkl}$ represent the components of a fourth-rank tensor called elastic stiffness tensor. As each index in $C_{ijkl}$ runs from 1 to 3, the elastic stiffness tensor has 81 components. However, as the stress tensor and the strain tensor are both symmetric, the elastic constants must have the properties

$$C_{ijkl} = C_{jikl}; \quad C_{ijkl} = C_{ijlk}.$$ (2.8)

Based on these symmetry properties, the elastic stiffness tensor has a maximum of 36 independent components instead of 81. Using Eq. 2.3, these symmetries also allow
CHAPTER 2. CRYSTALLINE ELASTICITY

us to express Hooke’s law Eq. 2.7 in terms of the displacements:

\[ T_{ij} = C_{ijkl} \frac{\partial u_l}{\partial x_k} \]  \hspace{1cm} (2.9)

The symmetry properties Eq. 2.8 also enable us to label the independent elastic moduli of the elastic stiffness tensor by only two indices. In the standard Voigt notation, the correspondence shown here is used:

\[
\begin{align*}
(11) & \leftrightarrow 1 & (22) & \leftrightarrow 2 & (33) & \leftrightarrow 3 \\
(23) & = (32) & & \leftrightarrow 4 & (31) & = (13) & \leftrightarrow 5 \\
& & & (12) & = (21) & \leftrightarrow 6 .
\end{align*}
\]  \hspace{1cm} (2.10)

So that the 36 independent constants can be arranged in a 6 × 6 matrix,

\[ C_{\alpha \beta} = C_{ijkl} \]  \hspace{1cm} (2.11)

with \( \alpha \leftrightarrow (ij) \), \( \beta \leftrightarrow (kl) \), where \( \alpha \) and \( \beta \) range from 1 to 6. This so-called matrix notation can be extended to the stress and strain tensors. The 6 × 6 elastic constant matrix is symmetric based on the following thermodynamic consideration. From the first law of thermodynamics, we know that the internal energy variation per unit volume is

\[ dU = \delta W + \delta Q \]  \hspace{1cm} (2.12)

where \( \delta Q \) is the heat received per volume and \( \delta W \) is the work done to that volume. However, during a change in strain \( de_{ik} \), the work done by the external forces can be expressed as

\[ \delta W = T_{ik} \, de_{ik} \]  \hspace{1cm} (2.13)

and for a reversible transformation, the second law of thermodynamics tell us

\[ \delta Q = T \, dS \]  \hspace{1cm} (2.14)
where $T$ is the absolute temperature and $S$ the entropy. Therefore,

$$dU = T_{ik} \, de_{ik} + T \, dS$$

(2.15)

and

$$T_{ik} = \left( \frac{\partial U}{\partial e_{ik}} \right)_S .$$

(2.16)

From the Hooke’s law Eq. 2.7, we also know that

$$C_{ijkl} = \left( \frac{\partial T_{ij}}{\partial e_{kl}} \right) ; \quad C_{kl} = \left( \frac{\partial T_{kl}}{\partial e_{ij}} \right) .$$

(2.17)

Inserting 2.16 into them, we obtain

$$C_{ijkl} = \left( \frac{\partial^2 U}{\partial e_{ij} \partial e_{kl}} \right)_S = C_{kl}$$

(2.18)

or

$$C_{\alpha\beta} = C_{\beta\alpha} .$$

(2.19)

The above property reduces the number of independent elastic constants to 21, as shown hereunder.

$$C_{\alpha\beta} = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\
C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\
C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66}
\end{pmatrix}$$

(2.20)

This elastic constant tensor corresponds to the triclinic symmetry wherein the only symmetry operation is the identity operation.

For crystals of higher symmetry, this number may be reduced further using their symmetry properties which require that some elastic constants must be zero or equal
to each other. Under symmetry operations, the atoms in the crystal recover its original configuration and, therefore all its physical properties should remain unchanged including the elastic stiffness tensor associated with that crystal. However, as these symmetry operations are equivalent to a series of transformations of the reference frame, they will result in the transformation of the elastic tensor of the crystal. Before we discuss the transformation property of a fourth-rank tensor, let’s first consider a simple case, the transformation of a first-rank tensor or vector. Taking the position vector \(\mathbf{r}\) for example, under a rotation of the Cartesian reference frame, the three components of \(\mathbf{r}\) \((x_1, x_2, x_3)\) are transformed as

\[
\begin{pmatrix}
x'_1 \\
x'_2 \\
x'_3 \\
\end{pmatrix} =
\begin{pmatrix}
\alpha_1^1 & \alpha_1^2 & \alpha_1^3 \\
\alpha_2^1 & \alpha_2^2 & \alpha_2^3 \\
\alpha_3^1 & \alpha_3^2 & \alpha_3^3 \\
\end{pmatrix}
\begin{pmatrix}
x_1 \\
y_2 \\
z_3 \\
\end{pmatrix}
\]

where \(x'_1, x'_2, x'_3\) are the three components of \(\mathbf{r}\) in the new frame, and the transformation matrix is called the \(\alpha\) matrix. Using Einstein convention, the above transformation can be rewritten as

\[
x'_i = \alpha_i^j x_j .
\]

Other vectors, such as the velocity, obey the same transformation rule. Accordingly, a second-rank tensor obey the transformation rule of

\[
T'_{ij} = \alpha_i^p \alpha_j^q T_{pq} .
\]

and a fourth-rank tensor, such as the elastic moduli tensor, should transform under a change of the orthonormal reference frame according to

\[
C'_{ijkl} = \alpha_i^p \alpha_j^q \alpha_k^r \alpha_l^s C_{pqrs}
\]

where \(\alpha_i^p, \alpha_j^q, \alpha_k^r, \alpha_l^s\) are components of the transformation matrix of the frame. If the transformation corresponds to a symmetry operation, the invariance condition
requires that $C_{ijkl} = C_{pqrs}$, i.e.

$$C_{ijkl} = \alpha_i^p \alpha_j^q \alpha_k^r \alpha_l^s \ C_{ijkl}.$$ (2.25)

Thus all the elastic moduli vanish unless $\alpha_i^i \alpha_j^j \alpha_k^k \alpha_l^l = 1$. Taking the crystal $Rb_4LiH_3(SO_4)_4$ for example, its low symmetry phase belongs to monoclinic point group 2. Relative to the triclinic crystals, it possesses an additional symmetry, i.e. invariant under a 180° rotation around the z-axis. Given that the $\alpha$ matrix for this symmetry operation is

$$\alpha = \pm \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ (2.26)

the invariance condition implies that all components of the elastic stiffness tensor with odd number of index 3 (for which $\alpha_i^i \alpha_j^j \alpha_k^k \alpha_l^l = -1$) vanish. Therefore, the elastic moduli with indices 1113, 2213, 3313, 1312, 1123, 2223, 3323 and 2312, or those with subscripts of 15, 25, 35, 56, 14, 24, 34 and 46 in the Voigt notation (see relation 2.10) must be zero. Therefore, only 13 independent elastic constants are left for the monoclinic crystals:

$$C_{\alpha \beta} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{22} & C_{23} & 0 & 0 & C_{26} \\ C_{13} & C_{23} & C_{33} & 0 & 0 & C_{36} \\ 0 & 0 & 0 & C_{44} & C_{45} & 0 \\ 0 & 0 & 0 & C_{45} & C_{55} & 0 \\ C_{16} & C_{26} & C_{36} & 0 & 0 & C_{66} \end{pmatrix}$$ (2.27)

In the high symmetry phase, the crystal $Rb_4LiH_3(SO_4)_4$ has the symmetry of tetragonal point group 4. In addition to the symmetry of monoclinic point group 2, it acquires new symmetry, a 4-fold rotation symmetry around the z-axis (which is taken
along the c-axis of the crystal). Relative to the tensor of the monoclinic phase, the 4-fold symmetry, which is represented by the element \( C_4 \) (rotating \( 90^\circ \) around z-axis), further reduces the number of independent elastic constants. Applying \( C_4 \) (counter clockwise), the coordinates transform as

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix}
\rightarrow
\begin{pmatrix}
  y \\
  -x \\
  z
\end{pmatrix}
\]  

hence the elastic constants transform as

\[
C_{22} = C_{2222} \rightarrow C_{1111} = C_{11} \quad (2.29)
\]
\[
C_{23} = C_{2233} \rightarrow C_{1133} = C_{13} \quad (2.30)
\]
\[
C_{55} = C_{1313} \rightarrow C_{2323} = C_{44} \quad (2.31)
\]
\[
C_{26} = C_{2212} \rightarrow -C_{1121} = -C_{16} \quad (2.32)
\]
\[
C_{36} = C_{3312} \rightarrow -C_{3321} = -C_{36} = 0 \quad (2.33)
\]

As a result, the independent elastic constants for the tetragonal phase are reduced to 7, as shown below

\[
C_{\alpha\beta} = \begin{pmatrix}
  C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\
  C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\
  C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
  0 & 0 & 0 & C_{44} & 0 & 0 \\
  0 & 0 & 0 & C_{44} & 0 & 0 \\
  C_{16} & -C_{16} & 0 & 0 & 0 & C_{66}
\end{pmatrix} \quad (2.35)
\]
2.1.3 Elastic Energy

The energy provided by the external forces during the deformation is stored in the medium as elastic energy. In the approximation of the Hooke’s law (recall the expression for the energy of a stretched spring), this energy can be written as

\[ U = \frac{1}{2} C_{\alpha\beta} e_{\alpha} e_{\beta} \]  

(2.36)

where the indices \( \alpha, \beta \) range from 1 to 6. The energy \( U \) is called the elastic potential energy, it stands for the internal energy variation per unit volume. Using Eq. 2.36, the elastic energy for the tetragonal phase of \( Rb_4LiH_3(SO_4)_4 \) is found to be

\[
F(e_i) = \frac{1}{2} C_{11} (e_1^2 + e_2^2) + \frac{1}{2} C_{44} (e_4^2 + e_5^2) + \frac{1}{2} C_{33} e_3^2 + \frac{1}{2} C_{66} e_6^2 \\
+ C_{12} e_1 e_2 + C_{13} (e_1 + e_2) e_3 + C_{16} (e_1 - e_2) e_6
\]  

(2.37)

which will be referred to in chapter 5.

2.2 Plane Wave Propagation

Unlike liquids, solids can sustain shear deformations and, therefore can transmit both longitudinal and transverse waves. Moreover, in an anisotropic medium, such as a crystal, normally three different waves can propagate in a given direction. However, in most cases, none of these waves is purely longitudinal or transverse. Consequently, the three waves one observed in a given direction are often referred as quasi-longitudinal, fast quasi-transverse and slow quasi-transverse wave. The polarizations of these three waves are always mutually orthogonal.

The properties of the three waves come from the equation of motion which is the result of Newton’s second law and the Hooke’s law. The force density of stressed material is [60]

\[ f_i = \frac{\partial T_{ij}}{\partial x_j} \]  

(2.38)
which gives rise to the acceleration $\partial^2 u_i/\partial t^2$ for the unit volume mass $\rho$, where $u_i$ is the $i$-th component of the displacement $\bar{u}$. According to Newton's second law, the equation of motion for an elastic medium can be written as

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial T_{ij}}{\partial x_j}. \quad (2.39)$$

Making use of Eq. 2.9, the equation of motion becomes

$$\rho \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_l}{\partial x_j \partial x_k} \quad (2.40)$$

which represents a set of wave equations for which the plane wave function

$$u_i = u_{0i} \ e^{i(k \cdot r - \omega t)} \quad i = 1, 2, 3 \quad (2.41)$$

is a proper solution. Here, $k$ represents the wave vector, $\omega$ is the frequency, and $u_{0i}$ is the wave polarization (i.e. the particle displacement direction). Inserting Eq. 2.41 into Eq. 2.40 and putting $u_{0i} = \delta_{il} u_{0l}$, we obtain

$$(\rho \omega^2 \delta_{il} - C_{ijkl} k_j k_k) u_{0l} = 0 \quad (2.42)$$

Dividing Eq. 2.42 by $k^2$, it takes the form

$$(\rho v^2 \delta_{il} - C_{ijkl} n_j n_k) u_{0l} = 0 \quad (2.43)$$

where $v = \omega/k$ is the phase velocity, and $n_j, n_k$ are the cosine direction of $k$ with respect to the axes of $x, y, z$. The equation above is the well-known Christoffel equation. After introducing a second rank tensor

$$\Gamma_{il} = C_{ijkl} n_j n_k \quad (2.44)$$

the Christoffel equation becomes

$$(\Gamma_{il} - \rho v^2 \delta_{il}) u_{0l} = 0. \quad (2.45)$$
This shows that the polarization $u_{0i}$ is an eigenvector of the propagation tensor $\Gamma_{il}$ with eigenvalue $\rho v^2$. Therefore, for a given propagation direction, the velocities of the waves can be found by solving the secular equation:

$$|\Gamma_{il} - \rho v^2 \delta_{il}| = 0 .$$ (2.46)

It will generally give three different velocities which correspond to the three waves propagating in this direction. As the elements of the $\Gamma_{il}$ tensor contain the elastic constants, the wave velocities are thus related to the independent elastic constants of the crystal. The polarization for each wave can be determined by searching for the eigenvector of the propagation tensor using Eq. 2.45. For convenience, the propagation directions are usually chosen to be along the crystallographic axes or its bisectors so that the Christoffel equation can be easily solved. For illustration, let consider waves propagating along the $z$ direction. In this case, the cosine directions are $n_1 = 0$, $n_2 = 0$, $n_3 = 1$ and the propagation tensor $\Gamma_{il}$ can be written as $\Gamma_{il} = C_{i33l}$, or

$$
\Gamma_{il} = \begin{pmatrix}
C_{55} & C_{45} & C_{35} \\
C_{45} & C_{44} & C_{34} \\
C_{35} & C_{34} & C_{33}
\end{pmatrix}
$$ (2.47)

For most crystals, this tensor can be further simplified. Taking the tetragonal phase of $Rh_4LiH_3(SO_4)_4$ for example, we know that $C_{35} = C_{34} = C_{45} = 0$ and $C_{44} = C_{55}$. Therefore,

$$
\Gamma_{il} = \begin{pmatrix}
C_{44} & 0 & 0 \\
0 & C_{44} & 0 \\
0 & 0 & C_{33}
\end{pmatrix}
$$ (2.48)

As the matrix of the tensor $\Gamma_{il}$ is already diagonalized, finding the eigenvalues is
straightforward

\[ \lambda_1 = C_{33}, \quad \lambda_2 = \lambda_3 = C_{44} \]  \hspace{1cm} (2.49)

As the eigenvalue of the propagation tensor is equal to \( \rho v^2 \), the velocities for the three waves propagating in this direction can be expressed in terms of the elastic constants as

\[ v_1 = \sqrt{\frac{C_{33}}{\rho}} \quad v_2 = v_3 = \sqrt{\frac{C_{44}}{\rho}} \]  \hspace{1cm} (2.50)

Substituting \( \lambda_1, \lambda_2, \lambda_3 \) into Eq. 2.45, their corresponding eigenvectors (or the polarizations) are found to be

\[ u_1 \rightarrow (0, 0, 1) \quad u_2 \rightarrow (0, 1, 0) \quad u_3 \rightarrow (1, 0, 0) \]  \hspace{1cm} (2.51)

where the eigenvectors have been normalized. It is easy to see that the polarization \( u_1 \rightarrow (0, 0, 1) \) of the first wave is parallel to the wave vector (the z-direction) and, therefore belongs to the longitudinal mode. The polarizations of the other two waves are perpendicular to the wave vector and, consequently belong to the transverse modes. The velocities and modes of the sound waves propagating along \([100], [010] \) and \([110] \) for both phases of \( Rb_4LiH_3(SO_4)_4 \) can be determined in the same way and the results are given in Table 2.1. For clarity, the long expressions for \( \rho v^2 \) corresponding to the modes \( L[110] \) and \( T_y[110] \) in the monoclinic phase are left out, where \( L \) and \( T \) represent longitudinal and transverse, while the subscripts represent the direction of polarization for a direction of propagation given in the bracket. As shown in Table 2.1, the elastic constants can be obtained from measuring velocities along different crystal directions. We also see that, in order to get the independent elastic constants for the tetragonal phase, we need to measure the modes \( L[100], T_y[100], T_z[100], L[001], L[110], T_{[110]}[110] \).
Table 2.1: The \( \rho v^2 \) as a function of the elastic constants in the tetragonal (4) and monoclinic (2) phases, where L is longitudinal, \( T_j \) is transverse wave with polarization along the j-direction. For clarity, long expressions for the modes L and \( T_{[110]} \) along [110] are omitted.
Chapter 3

Experimental Setup

Acoustic measurements play an important role in the investigation of the elastic properties of crystals. One of the most useful techniques is the pulse echo method. In this chapter, we will describe how the ultrasonic velocity can be measured using the standard pulse echo method. However, this method does not always have sufficient sensitivity to detect changes in the sound velocity close to a phase transition. Thus, we will also present how it is possible to achieve resolution as high as a few parts per million using an experimental technique called acoustic interferometer. Moreover, as one of the goals of this project is to study the pressure effect on the elastic properties of $Rb_4LiH_3(SO_4)_4$, the procedure of applying and measuring the pressure will also be presented here.

3.1 Crystal Structure of $Rb_4LiH_3(SO_4)_4$

The $Rb_4LiH_3(SO_4)_4$ crystals were grown in the Crystal Physics Laboratory of Adam Mickiewicz University, Poland [14]. Their chemical composition was determined by atomic spectroscopy ($Li^+$, $Rb^+$) and chemical analysis ($SO_4^{2-}$) [21]. The structure
consists of tetrahedral sulphate groups arranged together with \( Rb \) atoms on layers stacked perpendicularly to the c-tetragonal axis. The four \( Rb \) atoms and \( SO_4 \) groups are distributed on two consecutive layers. The \( Li \) atoms are intercalated every two layers and are surrounded by tetrahedra of \( O \) atoms [11]. At room temperature the crystals belong to space group \( P4_1 \) of the tetragonal system. The unit cell contains four layers of \( Rb_4LiH_3(SO_4)_4 \) molecules, see Fig. 3.1. After rotating 90° around the axis and moving up \( \frac{1}{4}c \), the crystal recovers its original configuration. In the low temperature phase, the second- and the fourth-layer molecules are slightly displaced from their tetragonal position. The symmetry operation becomes a 180° rotation followed by a \( \frac{1}{2}c \) translation along the axis. That means that the crystal possesses the symmetry of space group \( P2_1 \). The lattice parameters, determined by X-ray measurements [11], correspond to \( a = 7.615 (2) \; Å, \; c = 29.458 (6) \; Å \) with a density of 2.81 \( g/cm^3 \).

3.2 Sound Velocity Measurements

As stated previously, the independent elastic constants of a material can be derived from sound velocity measurements. However, in order to obtain all the independent elastic constants, these measurements must be realized along some specific directions for different acoustic modes. For crystals \( Rb_4LiH_3(SO_4)_4 \), we need to perform these measurements at least along [100], [001], [110] and [011] directions. Thus, a series of samples with parallel faces perpendicular to the crystallographic axes and the bisectors of these axes were prepared. The samples used in our measurements were cut from large colorless and transparent single crystals. In order to get a good signal, two opposite faces of the sample were polished using silicon carbide to the degree that they became smooth and parallel to each other. After all these operations, the
Figure 3.1: An illustration of the symmetry of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ at room temperature. Here the horizontal bars represent the $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ molecules. The vertical line represents the screw axis. The parallelogram represents the unit cell.
sample dimensions were approximately $5\text{mm} \times 5\text{mm} \times 3\text{mm}$. The orientations of the samples has been checked using polarized light. Since $Rb_4LiH_3(SO_4)_4$ is a birefringence crystal with optic axis along $c$-axis, the polarization of a linearly polarized light will normally be modified after the light passes through this crystal. When this crystal is put between two polarizers with their transmission axes rotated $90^\circ$, as the crystal is rotated around its $z$-axis, no significant variation in the intensity of the transmitted light is observed. However, if the crystal is rotated around the $x$-axis (or $y$-axis), a large change in the intensity of the transmitted light is observed every time the crystal is rotated by $90^\circ$. This method was used for all samples to confirm their orientations.

The sound velocity can be measured using the standard pulse-echo method, as illustrated in Fig. 3.2. The tiny device bonded on the top surface of the sample is a transducer which consists essentially of a thin piezoelectric crystal and two electrodes. As an oscillating electrical field is applied to the electrodes, the transducer mechanically vibrates at the same frequency due to the piezoelectric effect. Thus, in this standard approach, a pulsed radio frequency signal induces an ultrasonic pulse in the crystal, and subsequently the ultrasonic pulse travels back and forth between the crystal’s extremities owing to reflection at the boundaries. Each time that the sound wave returns to the transducer, a small fraction of its mechanical energy is converted into electrical signal (inverse piezoelectric effect). If the acoustic attenuation is not too large, this process will repeat several times, and a multi-echo pattern can be observed on an oscilloscope, as depicted in Fig. 3.2. In this reflection configuration, the time $\Delta t$ for a round trip can be determined by measuring the time between two consecutive echoes. Since the length $L$ of the sample along which the wave is propagating is normally measured before mounting the transducer, the calculation of the
Figure 3.2: A pulsed rf signal is sent to the transducer. Several electrical pulses come out. The reflection configuration and consecutive echoes are shown here. Here the piston tip is used to produce a gentle force on the transducer due to a small compressed spring, also shown in Fig. 3.6.
velocity is then given by

\[ v = \frac{2L}{\Delta t}. \] (3.1)

The typical length of samples used in these experiments is between 3 mm and 5 mm which gives a time of flight between 1 μs and 3 μs. Considering that the uncertainties on the sample's length and the time of flight are 0.01 mm and 0.01 μs, respectively, the resolution for the absolute velocity determination is normally around 0.5%. Thus, the standard pulse-method does not always have sufficient sensitivity to detect changes in the sound velocity close to a phase transition. In principle, the resolution can be improved by increasing the length of the crystal. But this method is limited by the finite space of the sample holder and the acoustic attenuation of the crystal. Even with this improvement, the resolution would still be in the order of 0.05%. So we need a new approach with higher resolution. We will see in the next section how it is possible to improve the resolution to a few parts per million by using a device called acoustic interferometer.

### 3.3 The Acoustic Interferometer

An acoustic interferometer can achieve a resolution as high as a few part per million by measuring the relative change in velocity \( \Delta v/v \) instead of the absolute velocity. As shown in Fig.3.3, a continuous radio frequency signal, generated by a RF Synthesizer (6061A *Synthesized RF Generator*), is divided into two parts by a power splitter. The first part is used as the reference signal, the second part is sent to a gate (Gate 1) which cuts the signal into short pulses of about 1 μs at a repetition rate of 1000 pulses per second. These electrical pulses arrive at the transducer after passing through a circulator. The main purpose of the circulator is to prevent any reflected signal from entering the synthesizer. As described in section 3.2, the transducer converts the elec-
Figure 3.3: Block diagram of the acoustic interferometer.
trical pulse into mechanical vibrations and consequently produces an ultrasonic wave in the crystal. The sound wave gets reflected at each extremity of the crystal. Each time it reaches the transducer, a small portion of its mechanical energy is converted into electrical signal. Then this electrical multi-echo signal enters the circulator at position 2 and comes out at position 3. Before being amplified, the initial pulse is cut off from the echo pattern by a second gate (Gate 2) in order to prevent saturation of the low noise rf amplifier. The phase differences between the reference signal and the reflected signal are then compared using a phase detector, which gives a signal proportional to the phase difference. A typical multi-echo pattern one observes on the oscilloscope is shown in Fig. 3.4. In this particular case, we can see that the first, the third and the fourth echo are in phase, and that the second echo is out of phase. This figure also shows that the amplitude of the echo decreases with the time of flight. This is a result of the acoustic attenuation as the wave propagates in the crystal. The amplitude of one of these echoes (usually the first one) is measured using the boxcar, which is in fact measuring the phase difference between the reference signal and the echo. For the n-th echo, the phase difference $\Phi_n$ is

$$\Phi_n = 2\pi f \Delta t_n$$

(3.2)

where $f$ is the frequency of the sound wave, i.e. the frequency of the electrical signal and $\Delta t_n$ is the time of flight of the n-th echo. As the distance travelled by the n-th echo is $2nL$ ($L$ is the length of the sample), $\Delta t_n$ can be expressed as

$$\Delta t_n = \frac{2nL}{v}.$$  

(3.3)

Combining the last expression with equation 3.2, we obtain an expression for the relative phase of the n-th echo which is given by

$$\Phi_n = \frac{4\pi nLf}{v}.$$  

(3.4)
Figure 3.4: A typical multi-echo pattern on the Oscilloscope. The time $\Delta t$ between the first and second echo is the time of flight for the sound wave to travel from the top to the bottom and back. The time between the first and the third is then $2\Delta t$, and so on.

From the equation 3.4, we can derive the expression for the relative phase change of the n-th echo

$$\frac{\Delta \Phi_n}{\Phi_n} = \frac{\Delta f}{f} + \frac{\Delta L}{L} - \frac{\Delta v}{v} .$$

(3.5)

The last expression shows that any phase variation caused by external parameters (the change in temperature $T$, the change in pressure $P$, and so on) can be offset by adjusting the frequency of the electrical signal. In fact, we can keep $\Delta \Phi$ being equal to zero, thus the relative change in the sound velocity can be expressed in terms of
the relative change in the frequency $\Delta f/f$ as well as the relative change in the length of the crystal $\Delta L/L$:

$$\frac{\Delta v}{v} = \frac{\Delta f}{f} + \frac{\Delta L}{L}. \quad (3.6)$$

For measurements as a function of temperature, the change of the sample's length $\Delta L$ can be easily estimated using the thermal expansion coefficient. It turns out that in most cases $\Delta L/L$ is an order of magnitude smaller than $\Delta v/v$. If we neglect the change in the crystal's length with temperature, the relative change in velocity can be approximated by

$$\frac{\Delta v}{v} \approx \frac{\Delta f}{f}. \quad (3.7)$$

Therefore, under the condition $\Delta \Phi = 0$, the relative change in velocity can be calculated from the frequency shift $\Delta f$ and the frequency $f$. In this project, apart from investigating the temperature dependence of the sound velocity, we also study the effect of pressure on the velocity. In the later case, the variation of the sample's length can be found using the isothermal compressibility. The calculation shows that the relative change of the sample's length is negligible relative to that of the frequency. Thus, the method used in calculating the relative change in velocity caused by temperature can also be used for pressure. In both cases, the procedure is the same.

Each time the Boxcar detects a phase difference, the computer adjusts the frequency of the Synthesizer in order to bring the phase difference back to zero. The computer is also used to record the frequencies, which are subsequently used to calculate the relative change in velocity. In this technique, the frequency stability of the synthesizer is really what ensures the high resolution of the interferometer. The frequency used in this experiment is normally around 30 $MHz$ with frequency adjustment as small as 10 $Hz$. Consequently, a resolution as high as 1 part per million can be achieved using this technique.
3.4 The Pressure Cell and the Sample Holder

One of the goals of this project is to derive the temperature-pressure phase diagram of $Rb_4LiH_3(SO_4)_4$. For this, we need to measure the temperature dependence of the sound velocities under different pressures. This was achieved by putting the sample-transducer assembly into a pressure cell. As shown in Fig. 3.5, the body of the pressure cell is a hollow cylinder, made of Cu-Be alloy so that it can sustain pressures up to 12 kbar. The teflon cell and the sample holder are placed in the chamber of the cylinder. After the obturator and the piston (plug) are introduced, the cell is closed by two screws. For the purpose of transmitting pressure, the teflon cell is filled with 3methyl – 1 – butanol solution. The advantage of this solution lies in its low freezing temperature. At ambient pressure, it has a freezing temperature of 123 K which is below the critical temperature ($T_c = 132 K$) of the phase transition observed in $Rb_4LiH_3(SO_4)_4$ at ambient pressure. At pressure as high as 10 kbar, the freezing point of this solution is still well below the transition temperature of $Rb_4LiH_3(SO_4)_4$. This ensures that the pressure applied on the crystal is quasi-hydrostatic as long as the temperature is not well below $T_c$. The pressure is exerted by a hydraulic unit. Applying a force to the pusher, the Piston (Plug) will be pushed forward. As the liquid inside the Teflon cell is almost incompressible, hydrostatic pressure builds up in the compressed Teflon cell. At the desired pressure, the cap screw is tightened, and the hydrostatic pressure is locked inside the cell. In order to hold the sample and the transducer together a small sample holder is used. As shown in Fig. 3.6, the transducer is held on the surface of the sample by the piston tip which produces a gentle force on the transducer due to a small compressed spring. To improve the coupling, the transducer is often bonded to the surface of the sample with a thin layer of glue. After the sample is mounted, the sample holder is connected to the obturator.
Figure 3.5: A schematic drawing of the pressure cell. The sample is immersed in a 3methyl - 1 - butanol solution contained in a teflon cell.
Figure 3.6: A close look at the sample holder and its structure.
The sample holder is then put into the 3methyl-1-butanol solution contained in the Teflon cell. After that, the obturator bearing the teflon cell is introduced in the body of the pressure cell.

3.5 Pressure and Temperature Measurements

The pressure in the pressure cell is determined by measuring the resistance of the lead wire which is mounted next to the sample. To improve the accuracy of the measurement, a four contact configuration is adopted. The pressure dependence of the resistance of lead has been well studied [53, 67]. It is found that at temperature $T$ the ratio $R(P, T)/R(0, T)$ (where $R(P, T)$ and $R(0, T)$ correspond to the lead wire resistances measured at pressures $P$ and $0$ kbar, respectively) is temperature independent [67]. Using the expression for the pressure as a function of the normalized resistance of the lead, pressures at various temperatures can be determined. It turned out that due to the thermal contractions of the different elements of the cell, the pressure in the pressure cell changes with temperature. At temperatures around 100 K, a pressure drop of a few kbar is often observed. A typical pressure-temperature curve is given in Fig. 3.7. From this curve, we see that the hydraulic pressure decreases with cooling till 125 K, at which the liquid in the Teflon cell freezes, then remains constant. In this particular case, we observed a pressure drop of 2 kbar. The pressure was measured using this method to an accuracy of 0.1 kbar.

In our experiment, the temperature is controlled and measured by a Lake Shore 340 temperature controller. Calibrated cernox resistors are used as the temperature sensors. For sound velocity measurements realized at ambient pressure, the sensor was mounted on the sample holder. However, for measurements as a function of pressure, the sensor was mounted on the outside wall of the pressure cell. The cooling or
Figure 3.7: Pressure as a function of temperature. The pressure at room temperature is 3.7 kbar.

heating rate is regulated by the temperature controller through a heater located at the bottom of the cryostat. The temperature measurement in this experiment has an accuracy of 0.01 K.
Chapter 4

Experimental Results

The experimental goal of this project was to investigate the elastic properties of $Rb_4 LiH_3(SO_4)_4$ as a function of temperature and pressure. Consequently, in order to determine as many independent elastic constants as possible, we measured the sound velocities of longitudinal and transverse waves propagating along specific crystallographic directions of single crystals of $Rb_4 LiH_3(SO_4)_4$. In this chapter, we essentially present the results of sound velocity measurements realized as a function of temperature and pressure. From these measurements, five of the seven independent elastic constants of the high temperature phase (tetragonal structure) of $Rb_4 LiH_3(SO_4)_4$ are obtained. We also derived the pressure-temperature phase diagram of $Rb_4 LiH_3(SO_4)_4$ between 4 K and 300 K. The aim of this chapter is, therefore, to present the experimental results, a detailed analysis of the results will be presented in Chapter 5.
4.1 Sound Velocities and Elastic Constants at Ambient Pressure

In order to describe the elastic properties of $Rb_4LiH_3(SO_4)_4$, we need to determine all its independent elastic constants. As stated previously, the elastic constants can be obtained through a series of sound velocity measurements. As long as the crystal structure is known, the specific relations between the velocity and the independent elastic constants for any acoustic modes can be derived using the Christoffel equations (see Eq. 2.45). Thus, in general, the sound velocity can always be written as

$$v = \sqrt{\frac{C_{\text{eff}}}{\rho}} \quad (4.1)$$

where $\rho$ represents the crystal density and $C_{\text{eff}}$ stands for an effective elastic constant associated with the measured acoustic mode. At room temperature, as the crystal structure of $Rb_4LiH_3(SO_4)_4$ belongs to the tetragonal point group 4 [6], the effective elastic constants for some specific modes and directions correspond to the expressions given in Table 2.1. However, for this investigation, we limited our measurements to the modes and directions listed in Table 4.1. From Table 4.1, we immediately see that the elastic constants $C_{33}$ is directly proportional to the square of the sound velocity of longitudinal mode propagating along the z-axis, $V_{L[001]}$. A similar observation stands for $C_{44}$ which is associated with the velocity of transverse mode propagating along the x-axis with its polarization along the z-axis, $V_{T_x[100]}$. Unfortunately, the relations between the remaining elastic constants and velocities are not so straightforward. However, as $C_{16}$ is known to be relative small [14, 21], we see that the velocity of the longitudinal mode propagating along the x-axis, $V_{L[100]}$, is dominated by $C_{11}$ while the velocity of transverse mode polarized along y-axis, $V_{T_y[100]}$, should give a good estimate for $C_{66}$. Finally, using the obtained values for $C_{11}$ and $C_{66}$, the elastic
### Table 4.1: Expressions of $\rho V^2$ as a function of the elastic constants for the acoustic modes measured in this project.

Note that these equations are only valid for the tetragonal structure. Here \( L \) represents longitudinal modes, \( T_j \) stands for transverse modes polarized along the \( j \)-direction. In this Table, \( V_{L[100]} \) represents the velocity of longitudinal mode propagating along the x-axis and \( V_{T_y[100]} \) represents the velocity of transverse mode propagating along the x-axis and polarized along the y-axis, and so on.
constant $C_{12}$ can then be derived from the velocity of transverse mode propagating along the [110] direction with its polarization perpendicular to the z-axis, $V_{T[110]}$. Thus, using our sound velocity measurements, listed in Table 4.2, along with the reported crystal density ($\rho = 2.81 \text{ g/cm}^3$) [14] of $Rb_4LiH_3(SO_4)_4$, it is possible to obtain some of the room temperature independent elastic constants. The elastic constants obtained in this project, along with results obtained by other groups [14, 21] are presented in Table 4.3. Our results agree particularly well with those reported by B. Mróz et al. [14] obtained via Brillouin scattering measurements. They also agree with those obtained by T. Breczewski et al. [21] except for $C_{12}$ for which they obtained a significantly lower value. The fact that we were able to reproduce the published values for the elastic constants of $Rb_4LiH_3(SO_4)_4$ indicates that all samples used in

<table>
<thead>
<tr>
<th>Direction</th>
<th>Mode</th>
<th>$v$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>..</td>
<td>L</td>
<td>3450 ± 30</td>
</tr>
<tr>
<td>[100]</td>
<td>$T_y$</td>
<td>1840 ± 20</td>
</tr>
<tr>
<td>..</td>
<td>$T_z$</td>
<td>1560 ± 20</td>
</tr>
<tr>
<td>..</td>
<td>L</td>
<td>3930 ± 30</td>
</tr>
<tr>
<td>[001]</td>
<td>$T_x$</td>
<td>1540 ± 20</td>
</tr>
<tr>
<td>..</td>
<td>$T_y$</td>
<td>1570 ± 20</td>
</tr>
<tr>
<td>..</td>
<td>L</td>
<td>3980 ± 60</td>
</tr>
<tr>
<td>[110]</td>
<td>$T_{[110]}$</td>
<td>1300 ± 10</td>
</tr>
<tr>
<td>..</td>
<td>$T_z$</td>
<td>1650 ± 20</td>
</tr>
</tbody>
</table>

Table 4.2: Sound velocities obtained at room temperature. The directions and modes were chosen according to Table 2.1. Here, $L$ stands for longitudinal modes, and $T_j$ represents transverse modes with its polarization along the j-direction.
Table 4.3: Elastic constants of $Rb_4LiH_3(SO_4)_4$ for the tetragonal structure at 295 $K$.

For comparison, data obtained by two other groups are also presented.

4.1.1 Temperature Dependence of Sound Velocities

The temperature dependence of the sound velocity for all the modes listed in Table 4.1 has been investigated between 4 $K$ and 300 $K$. In Fig. 4.1, we present the temperature dependence of the velocities of longitudinal modes propagating along [001] and [100], respectively. Along both directions, we observe a drop in the velocity at a temperature of $132.2 \pm 0.3$ $K$. According to specific heat measurements and optical studies [18], this temperature corresponds to the occurrence of a second order ferroelastic transition in $Rb_4LiH_3(SO_4)_4$. This transition was initially described as a tetragonal to orthorhombic structural change corresponding to a $4mm \rightarrow mm2$ symmetry change [9,10,17]. However, recent x-rays measurements [11] seem to indicate
Figure 4.1: Temperature dependence of the sound velocity of longitudinal modes propagating along the z-axis ($V_{L[001]}$) and x-axis ($V_{L[100]}$), respectively.
that the low temperature phase is rather monoclinic and that a $4 \rightarrow 2$ type symmetry change is a more appropriate designation. Our measurements also indicate that the sound velocity of longitudinal waves propagating along the z-axis ($L[001]$ mode) changes by 1.2% at the transition temperature, while it drops by 5% for longitudinal waves propagating along x-axis ($L[100]$ mode). At temperatures above the transition, the velocity increases almost linearly with cooling for the $L[001]$ mode. However, for the longitudinal mode propagating along the x-axis, the velocity shows a temperature dependence which is clearly nonlinear. Initially, it increases with cooling from room temperature and then decreases with further cooling. As we will see in Chapter 5, this unusual temperature dependence can be associated with a soft mode. In the low temperature phase, the velocities along both directions increase monotonically with cooling with no sign of any other phase transitions. Let add that results presented in Fig. 4.1 agree very well with those reported by Hempel et al. [12] and Breczewski et al. [21]. For example, for the $L[100]$ mode, our measurements of the magnitude of the velocity variation in the transition is comparable with the drop 5.6% observed by Breczewski et al. [21]. However, our results do not agree so well with Brillouin scattering measurements [14]. In that case, the velocity does not show any jump at the transition temperature. The fact that they failed to detect a velocity drop of 5% cannot be ascribed to their lower resolution of about 1%.

Among all the acoustic modes measured in this project, the one corresponding to transverse waves propagating along [110] and polarized perpendicularly to the z-axis shows the largest temperature dependence, see Fig. 4.2. In comparison with $L[100]$ mode, the velocity for this mode starts to decrease at a much higher temperature and decreases more rapidly. From 300 $K$ to 140 $K$, the velocity decreases by about 50%. Due to the high acoustic attenuation near $T_c$, the signal is invariantly lost. For that reason, only measurements in the temperature range between 140 $K$ and 300 $K$ are
Figure 4.2: Temperature dependence of the sound velocity of transverse waves propagating along [110] with their polarization normal to the z-axis, $V_{T[110][110]}$. 

$T_c = 132$ K
presented in Fig. 4.2. For that particular mode, the rapid decrease in the velocity is obviously a precursor effect associated with the softening of a normal mode well above \( T_c \). However, the velocity for this mode does not behave as a typical soft mode since it does not seem to decrease to zero at the transition temperature \( T_c \). By extrapolating the velocity curve down to \( T_c \), we find that the velocity at the transition temperature is approximately 540 m/s. Furthermore, the temperature dependence is nonlinear. All these observations are consistent with results reported by both Mróz et al. [14] and Breczewski et al. [21].

The temperature dependence of the velocities of two transverse modes, \( T_y[100] \) and \( T_z[100] \), are presented in Fig. 4.3. Both curves show an observable change in velocity at the transition temperature though the changes are considerably smaller. The curve for the \( T_y[100] \) mode clearly shows a small variation in velocity at \( T_c \) (132 K), while for the \( T_z[100] \) mode, it shows a slight increase in slope. Except in the vicinity of the transition, the velocity variations for both modes are typical. From 300 K to 4 K, the sound velocities \( V_{T_y[100]} \) and \( V_{T_z[100]} \) only increase by 3.8% and 4.7%, respectively. Again, let's mention that our sound velocity measurements for both modes are in good agreement with those obtained by Breczewski et al. [21].

Finally, we present in Fig. 4.4 the temperature dependence of the velocity of longitudinal modes propagating along [110] and [011], respectively. Again, both curves show a considerable jump at \( T_c \). For the \( L[011] \) mode, the drop in velocity is about 3.3% while for the \( L[110] \) mode it is estimated to be no less than 2.4%. Above \( T_c \), the velocities along both directions increase monotonically with cooling from room temperature. However, in the low temperature phase we could not obtain reproducible results for the \( L[110] \) mode. That explains why only the results obtained at temperatures above \( T_c \) are presented. Comparatively, the measurements for the \( L[011] \) mode are much better though the curve shows that the velocity for this mode reaches its
Figure 4.3: Temperature dependence of the sound velocity of transverse modes propagating along the x-axis with their polarizations along the y and z-axis, respectively ($V_{Ty[100]}$ and $V_{Tz[100]}$).
Figure 4.4: Temperature dependence of the sound velocities for longitudinal waves propagating along [110] and [011] directions, respectively ($V_{L[110]}$ and $V_{L[011]}$).
minimum at $127 \, K$, well below $T_c$. Both of these two phenomena might be caused by twinning and domain stress effects in the monoclinic phase.

In order to confirm the nature of the transition, we compared in Fig. 4.5 the temperature dependence of the velocity $V_{L[100]}$ obtained during a cooling-heating cycle. As shown in Fig.4.5, we observe no thermal hysteresis. This observation confirms that the transition is indeed second order, consistent with the conclusion based on pyroelectric [18], dielectric [18] and specific heat measurements [12, 18].

It is well known that for crystals that have a tetragonal structure, the lattice parameter $a$ and $b$ are indistinguishable, i.e. the $x$-axis and the $y$-axis are equivalent. However, for crystals with a monoclinic structure, $a$ is no longer equivalent to $b$, in another word, the $x$-axis is different from the $y$-axis. As stated previously, above and
below $T_c$, $Rb_4LiH_3(SO_4)_4$ single crystals have a tetragonal and monoclinic symmetry, respectively. In order to distinguish the x and y axes in the low symmetry phase, we measured, using the same sample, the temperature dependence of the velocity of longitudinal waves propagating along two orthogonal directions in the $a - b$ plane. The results presented in Fig. 4.6 show that both measurements coincide above $T_c$, which is consistent with the fact that the high temperature phase has a tetragonal symmetry. For the monoclinic phase, we expect to see a significant difference between both curves. On the contrary, the difference turns out to be trivially small. As we see from Fig. 4.6, even at a temperature 45 degrees below $T_c$, the velocities along both directions deviate by only 0.3%. According to optical studies [9], in the monoclinic phase two kinds of birefringent domains are observed. Moreover, these domains are separated by perpendicular walls lying in the (100) and (010) planes. If we assume that the two kinds of domains fill the crystal volume at the same ratio, we can understand why the sound velocity measurements along the x and y-directions remain almost identical. The same conclusion has been reached by Piskunowicz et al. [19] based on thermal expansion measurements.

4.1.2 Temperature Dependence of the Elastic Constants

Using the sound velocity measurements presented in section 4.1.1, the temperature dependence of five of the seven independent elastic constants of $Rb_4LiH_3(SO_4)_4$ have been determined. Making use of the temperature dependence of the sound velocities, we can, in principle, solve the set of equations listed in Table 4.1. From Table 4.1, we see that the elastic constants $C_{33}$ and $C_{44}$ can be obtained directly from their corresponding velocities. However, deriving $C_{11}$, $C_{66}$ and $C_{12}$ is much more difficult. However, as $C_{16}$ is known to be almost temperature independent [14, 21], values for
Figure 4.6: Temperature dependence of the sound velocities for longitudinal waves propagating along the two crystallographic axes \(a\) and \(b\) directions. In conformity with the convention, the coordinates axes \(x\) and \(y\) are set to be along \(a\) and \(b\), respectively.
these three elastic constants can be estimated by using $V_{L[100]}$, $V_{T_y[100]}$ and $V_{T_{110}[110]}$. For instance, as $C_{16}$ is relatively small, the velocity of the $L[100]$ mode is dominated by $C_{11}$, see Table 4.1. The temperature dependence of five independent elastic constants are presented in Fig. 4.7, where $C_{16}$ has been assumed to be constant with the value of $0.33 \times 10^{10} \text{ N/m}^2$ [21]. It should be noted that the elastic constants in the monoclinic phase are calculated using the Christoffel equations derived for the tetragonal phase. Therefore, they do not necessarily correspond to the elastic constants in the monoclinic phase. The results presented in Fig. 4.7 indicate that the elastic constant $C_{33}$ increases almost linearly with cooling and shows a step-like variation of 3% at $T_c$ ($132 \text{ K}$). After that, it still increases linearly with further cooling down to 25 K. Clearly, the linear increase of $C_{33}$ with cooling is a consequence of the normal thermal behavior of the corresponding acoustic phonons. For the elastic constant $C_{11}$, we see that it becomes soft at temperatures well above $T_C$. At the transition temperature, this elastic constant shows a relative change of 9 %, the largest relative variation observed for this crystal. In contrast, the variations of the elastic constants $C_{44}$ and $C_{66}$ are quite small. At $T_c$, $C_{66}$ shows a very small variation while $C_{44}$ shows a slight change in slope. Figure 4.7 also shows that the elastic constant $C_{12}$ increases rapidly with cooling. As no good measurements can be used to calculate $C_{12}$ below $T_c$, only the results obtained at temperatures above $T_c$ are presented.

According to our sound velocity measurements, the mode that shows the largest variation in velocity above $T_c$ is associated with transverse waves propagating along the $[110]$ with a polarization normal to the z-axis ($V_{T_{[110][110]}},$ Fig. 4.2). Considering that for the tetragonal structure, we have that

\begin{equation}
\rho V_{T_{[110][110]}}^2 = \frac{1}{2} \left( C_{11} + C_{66} - \sqrt{(C_{12} + C_{66})^2 + 4C_{16}^2} \right).
\end{equation}

Using the approximation, where $C_{16} = 0$, we immediately obtained that the effective
Figure 4.7: Temperature dependence of five of the seven independent elastic constants of the tetragonal phase for $Rb_4LiH_3(SO_4)_4$. Note that the values of the elastic constants in the monoclinic phase are not accurate since they are calculated using relations derived for the tetragonal phase.
elastic constants of the soft mode can be approximated by \((C_{11} - C_{12})/2\). For that reason, we present in Fig. 4.8 the temperature dependence of this elastic combination. As shown in Fig. 4.8, this elastic constant combination shows considerable softening well above \(T_c\). From 300 \(K\) to 140 \(K\), its value decreases by about 70\%. However, this softening is incomplete because the elastic constant combination does not go to zero at the transition temperature. By extrapolating this curve to \(T_c\) (132 \(K\)), we find that the value of this elastic combination at \(T_c\) is 0.10 \(\times\) \(10^{10}\) \(N/m^2\). Furthermore, we see that the temperature dependence of this elastic constant combination is nonlinear. This last observation might be an indication that this transition cannot be described as a proper ferroelastic phase transition. As we will see in Chapter 5, that this observation will be used as the foundation for our theoretical model.

## 4.2 Pressure Dependence of the Elastic Constants measured at Room Temperature

As point out in section 3.3, external parameters that can cause the structure of a crystal to change are not limited to temperature, the application of pressure \(P\) can also be used to induce a phase transition. To our knowledge, the effect of pressure on the properties of \(Rb_4LiH_3(SO_4)_4\) have not been investigated yet. In this project, we measured the pressure dependence of the velocities using modes listed in Table 4.1. The effect of pressure on the velocities was studied using the pressure cell described in section 3.4. Using these velocity measurements realized at room temperature, we could calculate the pressure dependence of the elastic constants. Here, as well, we assume that \(C_{16}\) is constant \((C_{16} = 0.33 \times 10^{10} \text{ } N/m^2)\) [21] so that the elastic constants \(C_{11}, C_{66}\) and \(C_{12}\) can be calculated using \(V_L[100], V_T[y][100]\) and \(V_T[110][110]\). Thus, in this
Figure 4.8: Temperature dependence of $(C_{11} - C_{12})/2$. 

$T_c = 132 \, \text{K}$
Figure 4.9: Pressure dependence of $C_{33}$ at room temperature. The dashed line represents the linear extrapolation of the results of $C_{33}$ at pressures below $P_c$.

section we present the pressure dependence of the elastic constants obtained at room temperature. Let add that the elastic constants in the monoclinic phase are calculated using the equations corresponding to the tetragonal phase. Therefore, they may not represent the elastic constants in the monoclinic phase.

We first present in Fig. 4.9 the pressure dependence of the elastic constant $C_{33}$. The curve clearly shows that $C_{33}$ drops abruptly at a critical pressure of $P_c = 8.4 \text{ kbar}$. This rapid variation of 3.5% clearly indicates the occurrence of a phase transition. Based on the sound velocity measurements realized as a function of temperature, Fig. 4.1, we can assume that the transition observed at $P_c$ corresponds to a $4 \rightarrow 2$ symmetry change. Below $P_c$, the elastic constant $C_{33}$ increases linearly with pressure at a rate of $0.08 \times 10^{10} \text{ N/m}^2 \cdot \text{kbar}$. We can consider this variation to be typical
since for most crystals the elastic constants increase linearly with pressure, at least between 0 and 10 kbar. Significant nonlinear behavior are normally observed at higher pressures. Consequently, a linear extrapolation of the low pressure results can be used to evaluate the variations in the elastic constants which are strictly associated with the incidence of the phase transition. It is those variations that have to be compared to the theoretical predictions presented in Chapter 5. Thus, in the inset of Fig. 4.9 we present the variation of $C_{33}$ produced by the phase transition. This variation is obtained by subtracting the linear extrapolation from the data presented in Fig. 4.9. As shown in the inset of Fig. 4.9, the effect of the transition on $C_{33}$ is to produce a drop of 3.5% at $P_c$. Moreover, $C_{33}$ increases with pressure at higher pressures.

The pressure dependence of $C_{11}$ and $C_{12}$ are presented in Fig. 4.10. Comparing with $C_{33}$, the elastic constant $C_{11}$ shows a more pronounced jump at $P_c$. We also see that the precursor effect of the phase transition starts to affect $C_{11}$ from pressures well below $P_c$. In this case, the linear extrapolation cannot be definitely determined using the low pressure results of $C_{11}$. For this reason, we assume that the linear extrapolation of $C_{11}$ is similar to the one observed for $C_{33}$. Thus, the variation associated with the soft mode is obtained by subtracting a linear extrapolation derived from the results obtained on $C_{33}$. As shown in the inset, $C_{11}$ gets softened at pressures well below $P_c$. At $P_c$, the phase transition causes a variation of 7% in the elastic constant. At pressures above $P_c$, the elastic constant begins to increase with pressure again. The curve for $C_{12}$ shows that this elastic constant increases rapidly with pressure. From 0 kbar to 7.6 kbar, it increases by about 37%. Unfortunately, due to the limit of our sound velocity measurements, we could not derive the values of $C_{12}$ at higher pressures. Among the elastic constants obtained in this project, two elastic constants, $C_{11}$ and $C_{33}$, show significant variations around the transition, whether it is caused by temperature or by pressure. For comparison, we list in Table 4.2 their
Figure 4.10: Pressure dependence of $C_{11}$ and $C_{12}$ at room temperature. The dashed line in the upper graph represents the linear extrapolation derived from the results obtained on $C_{33}$. 
Parameters | $C_{11}$ | $C_{33}$  
--- | --- | ---  
Temperature | 9% | 3%  
Pressure | 7% | 3.5%  

Table 4.4: The variations of $C_{11}$ and $C_{33}$ at the transition caused by temperature and by pressure.

variations corresponding to both external parameters. As shown in Table 4.2, the magnitude of the variations are comparable.

Based on our sound measurements as a function of pressure, the velocity of transverse waves propagating along [110] with a polarization normal to the z-axis shows a strong pressure dependence below $P_c$, comparable with its temperature dependence above $T_c$ (Fig. 4.2). As $C_{16}$ is quite small [14, 21], from Table 4.1 we see that the effective elastic constant associated with the soft mode is approximately equal to $(C_{11} - C_{12})/2$. Consequently, we present in Fig. 4.11 the pressure dependence of $(C_{11} - C_{12})/2$. As we lost the signal at 7.6 kbar, when measuring the velocity for the mode $T_{[110]}[110]$, our calculation of $(C_{11} - C_{12})/2$ can only be extended up to that pressure. From Fig. 4.11, we see that $(C_{11} - C_{12})/2$ shows a large softening well below $P_c$. From 0 kbar to 7.6 kbar, its value decreases by about 70%. Extrapolating the curve to the critical pressure (8.4 kbar), it is found that at the critical pressure $(C_{11} - C_{12})/2$ is equal to $0.1 \times 10^{10} \text{ N/m}^2$, which is the same as the value estimated from Fig. 4.8. This indicates that the softening of $(C_{11} - C_{12})/2$ is also incomplete in this case. Furthermore, we see that $(C_{11} - C_{12})/2$ shows a nonlinear dependence as a function of pressure. Both features further confirm that the observed transition is a pseudoproper ferroelastic phase transition.

Comparatively, the elastic constants $C_{66}$ and $C_{44}$ show a considerably weak pres-
Figure 4.11: Pressure dependence of $(C_{11} - C_{12})/2$ for $Rb_4LiH_3(SO_4)_4$. 

$P_c = 8.4$ kbar
sure dependence, see Fig. 4.12. Nevertheless, they still undergo a considerable variation at the transition. At the critical pressure, the curves for $C_{66}$ and $C_{44}$ show a variation of 1.4% and an increase in the pressure dependence. Below $P_c$, both elastic constants increase linearly with pressure. Because the results below 2 kbar are not so good, the elastic constants corresponding to that pressure range are not presented. At pressures above $P_c$, they both increase with pressure, however, $C_{66}$ increases with pressure considerably slower than $C_{44}$ does.

### 4.3 Temperature-Pressure Phase Diagram

In order to derive the temperature-pressure phase diagram of $Rb_4LiH_3(SO_4)_4$, we measured the temperature dependence of the sound velocity at different pressures. The measurements have been realized using longitudinal waves propagating along the z-axis. This configuration has been chosen principally because the acoustic attenuation is small and that the transition temperature is easily observed. The temperature dependence of the sound velocities measured at different pressures is presented in Fig. 4.13. As the pressure in the cell decreases with cooling due to the thermal contractions, two pressures are given for each curve, the pressure measured at the room temperature and the pressure measured at the transition temperatures. The uncertainty on the pressure determination is estimated to be ±0.2 kbar. The main feature of this figure is that the transition temperature shifts toward higher temperatures as the pressure increases. The curve at the bottom of the figure shows that at 6.6 kbar the transition temperature has been shifted to a value well above room temperature. Except for this one, all curves show a drop in velocity at the transition temperature. Though the magnitude of these drops differ a little from one to the other, no sign show that it has been damped by increasing the pressure. However, the shape of
Figure 4.12: Pressure dependence of \( C_{66} \) and \( C_{44} \) for \( \text{Rb}_4 \text{LiH}_3(\text{SO}_4)_4 \).
Figure 4.13: Temperature dependence of the sound velocity of longitudinal waves propagating along the z-axis at different pressures.
the curves around the minimum of the velocity does change with pressure. As this phase transition is a ferroelastic transition, that means that domains form in the low temperature phase. Consequently, the change in the shape of the curves in this phase might indicate that the domains pattern near the transition temperature is modified by pressure. The figure also shows that in the high temperature phase the slopes of the curves obtained at pressures larger than 1 bar are different from that corresponding to the ambient pressure. This is due to the fact that those measurements are not realized at constant pressure.

In Fig. 4.13, we present the critical temperatures obtained using cooling processes. Considering that the temperature sensor is mounted on the outside wall of the pressure cell, the transition temperatures obtained from these measurements are smaller than the real ones due to the temperature gradient. However, the difference is estimated to be less than 0.5 K. Using the results presented in Fig. 4.13, we can easily derive the temperature-pressure phase diagram, which is shown in Fig. 4.14. We identify two phases between 4 K and 300 K with pressure extending to 7 kbar. As shown in Fig. 4.14, the region above the curve corresponds to the monoclinic phase while the region below the curve corresponds to the tetragonal phase. The boundary of these two phases can be well represented by a linear relation. It shows that the transition temperature, $T_c$, increases rapidly with pressure at a rate of $19 \pm 1 \, K/kbar$. 
Figure 4.14: Temperature-pressure phase diagram for $Rb_4LiH_3(SO_4)_4$ crystals.
Chapter 5

Theoretical Model

Phase transitions can be analyzed using various types of theoretical methods. One of them, the Landau mean field theory, is a simple but powerful thermodynamic model by which many features associated with a phase transition can be described. So far, several Landau models [10, 12, 14, 19, 21] have been put forward intending to explain the phase transition observed for $Rb_4LiH_3(SO_4)_4$, however, none of them seem to be fully compatible with the experimental observations. For this reason, we dedicate this chapter to the elaboration of a Landau model consistent with the experimental results. In order to test our model, we compared the theoretical predictions with the elastic constants obtained as a function of temperature and pressure. Naturally, we begin this chapter by given a rudimentary description of the Landau mean field theory. A detailed development can be found in “The Landau Theory of Phase Transitions” written by J.C. Tolédanno et al. [65].
5.1 Phase Transition and Landau Theory

5.1.1 Phase Transition

A phase is characterized by thermodynamic quantities that include the volume $V$, pressure $P$, temperature $T$, and the Gibbs free energy $G$. When the free energy corresponds to a minimum, under some specified thermodynamic conditions, the phase associated with those conditions is normally stable. As temperature, pressure or any other external variable acting on a system is changed, the free energy of the system also changes. Whenever such variation in the free energy is associated with structural modifications, a phase transition is said to occur [63]. Depending on the type of modifications, the phase transition is normally classified as first, second, or higher order. This classification scheme is, in fact, based on which of the thermodynamic properties undergo a discontinuous variation at the critical temperature or pressure. In general, a transition is said to be of the same order as the lowest derivative of the Gibbs free energy that shows a discontinuous change at the critical temperature or pressure. From Thermodynamics, we know that the total derivative of the Gibbs free energy takes the form

$$dG = VdP - SDT.$$  \hspace{1cm} (5.1)

Thus, from Eq. 5.1 we immediately obtain that the partial derivatives of the Gibbs energy give the volume

$$V = \left( \frac{\partial G}{\partial P} \right)_T$$ \hspace{1cm} (5.2)

and the entropy

$$S = -\left( \frac{\partial G}{\partial T} \right)_P.$$ \hspace{1cm} (5.3)

Hence, a phase transition is first order if a discontinuous change in the volume $V$ or the entropy $S$ is observed during the transition. From equation 5.2, we see that the
volume thermal expansivity $\alpha$ can be expressed in terms of the second derivatives of the Gibbs energy as

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \frac{\partial^2 G}{\partial P \partial T}. \quad (5.4)$$

Moreover, making use of $dQ = TdS$, the specific heat capacity at constant pressure $C_P$ can be expressed as

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p. \quad (5.5)$$

Thus, a phase transition is said to be second order if a discontinuity in the specific heat capacity $C_P$ or the volume thermal expansivity $\alpha$ is observed [63]. Actually, many transitions are truly mixed order, exhibiting features of both first and second order.

**5.1.2 Landau Theory**

Landau theory is a macroscopic, thermodynamic theory which is extensively used to describe phase transitions without giving any information about the microscopic causes of the transition. It is applicable to phase transitions in which a symmetry change occurs whenever the point group of the low symmetry phase is a subgroup of the high symmetry phase. The theory is based on the introduction of an order parameter which is some quantity that differentiates both phases. When the order parameter takes on a value equal to zero, the crystal symmetry is that of the high symmetry phase. As soon as the order parameter takes on a nonzero value, the symmetry is reduced to that of the low symmetry phase [52]. What differentiates a first and a second order transition is that the order parameter varies continuously across the transition for a second order transition, while for the first order transition the order parameter jumps discontinuously at the critical temperature or pressure. Landau
assumes that the excess free energy $G_e$ of the low temperature phase relative to the high temperature phase can be expanded in a power series of this order parameter $Q$, such that

$$G_e = \alpha_1 Q + \frac{1}{2} \alpha_2 Q^2 + \frac{1}{3} \alpha_3 Q^3 + \frac{1}{4} \alpha_4 Q^4 + \cdots$$

(5.6)

where the coefficients may depend on parameters such as temperature, pressure, etc.

The order parameter $Q$ is zero in the high symmetry phase and scaled to unity in the low symmetry phase well below the transition temperature or pressure. Therefore, in the vicinity of the transition, the contribution of the higher degree terms to the free energy are considerably small. Depending on the nature of the phase transition, the expansion is sometime extended up to the sixth order term. Moreover, as we will see later, some terms in the power series should vanish as required by symmetry considerations.

As the transition studied in this project belongs to the second order type, our discussion about the application of Landau theory is limited to this type of transition. Since the order parameter varies continuously through the transition for this class of phase transitions, terms with the powers of $Q$ greater than four in the expansion of the excess free energy can be neglected for conventional second order phase transitions. Moreover, considering that changing the sign of $Q$ does not change the state of the body [63], the excess free energy $G_e$ must also be invariant under that operation. Thus, all coefficients associated with an odd power in $Q$ must be set to zero, such that the excess free energy reduces to

$$G_e = \frac{1}{2} \alpha_2 Q^2 + \frac{1}{4} \alpha_4 Q^4 .$$

(5.7)

As stated previously, a phase is stable only if the free energy corresponds to a minimum. Therefore, in order to have global stability, the coefficient $\alpha_4$ must be positive. This ensures that as we increase $Q$ to large values, the free energy increases. Using
that the free energy corresponds to a minimum, the conditions

\[
\frac{\partial G_e}{\partial Q} = \alpha_2 Q + \alpha_4 Q^3 = 0 \quad (5.8)
\]

\[
\frac{\partial^2 G_e}{\partial Q^2} = \alpha_2 + 3\alpha_4 Q^2 > 0 \quad (5.9)
\]

must be satisfied. As \( Q = 0 \) in the high symmetry phase, it follows from Eq. 5.9 that \( \alpha_2 > 0 \) in this phase. While in the low symmetry phase, owing that \( Q > 0 \) and \( \alpha_4 > 0 \), Eq. 5.8 leads to \( \alpha_2 < 0 \). Since \( \alpha_2 \) changes sign across the transition point, Landau made the assumption that

\[
\alpha_2 = a \left( T - T_0 \right) \quad (5.10)
\]

where \( a \) and \( T_0 \) are positive constants. Thus, the excess free energy takes the form

\[
G_e = \frac{1}{2} a(T - T_0)Q^2 + \frac{1}{4} \alpha_4 Q^4 . \quad (5.11)
\]

A plot of \( G_e \) as a function of \( Q \) for various temperatures is given in Fig. 5.1. As shown in this graph, for \( T \geq T_0 \) the excess free energy is minimum at \( Q = 0 \), while for \( T < T_0 \) it reaches its minimum at \( Q > 0 \). Differentiating Eq. 5.11 with respect to \( Q \) and setting the derivative equal to zero shows that, at equilibrium

\[
Q = 0, \quad T > T_0 \quad (5.12)
\]

\[
Q = \sqrt{\frac{a}{\alpha_4} (T_0 - T)}, \quad T < T_0 \quad (5.13)
\]

The first solution corresponds to the high symmetry phase, while the second solution corresponds to the low symmetry phase. From the second solution, we see that \( T_0 \) corresponds to a critical temperature \( (T_c) \) at which the order parameter appears. Therefore, in the low temperature phase the order parameter are often expressed as

\[
Q = \sqrt{\frac{a}{\alpha_4} (T_c - T)} \quad (5.14)
\]
Figure 5.1: A schematic plot of the free energy $G$ as a function of the order parameter $Q$ for various temperatures (Eq. 5.11).
A typical curve of the order parameter against temperature is given in Fig. 5.2. From this figure, we see that the order appears at $T = T_c$ and its magnitude varies as the temperature further deceases.

### 5.1.3 Expansion of the Landau Model

So far, we have presented the free energy expansion in terms of the order parameter $Q$. Such an expansion is useful in order to derive a phase diagram, however, our goal is to derive the elastic constants from the free energy. Therefore, the free energy should include the elastic energy which arises from the appearance of spontaneous strains in the low temperature phase. These spontaneous strains can be obtained by considering the coupling between the strains and the order parameter. In that
case, the appropriate Landau free energy expansion can be expressed in the form of a convergent power series including several distinct contributions due to particular physical mechanisms, such that

$$F(Q, e_i, P) = F_1(Q) + F_2(e_i) + F_3(Q, e_j) + F_4(P, e_{kk}).$$  \hspace{1cm} (5.15)

The first term $F_1(Q)$ is the usual Landau free energy which depends on the Landau order parameter corresponding to Eq. 5.11. The second term $F_2(e_i)$ is the elastic energy while the third term $F_3(Q, e_j)$ takes into account the coupling between the order parameter and the strains. The last term $F_4(P, e_{kk})$ is related to the work done on the crystal by an external pressure $P$. Using this free energy, the elastic constants can be calculated using \[33\]

$$C_{mn} = \frac{\partial^2 F}{\partial e_m \partial e_n} - \frac{\partial^2 F}{\partial Q \partial e_m} \left( \frac{\partial^2 F}{\partial Q^2} \right)^{-1} \frac{\partial^2 F}{\partial e_n \partial Q}. \hspace{1cm} (5.16)$$

### 5.2 Landau Analysis of the Experimental Results

As mentioned in chapter 1, the phase transition we observed for $Rb_4LiH_3(SO_4)_4$ belongs to second order and the symmetry change through the transition is $4 \rightarrow 2$ [11]. As the point groups satisfy the group-subgroup relation, a Landau model can be used to describe the observed phase transition. Actually, several Landau models for this phase transition have already been presented by other groups [10, 12, 14, 19, 21]. However, none of them can satisfactorily explain the observed results. According to group theory, for a $4 \rightarrow 2$ type transition, the order parameter should have the same symmetry as the strain components ($e_1 - e_2$) and $e_6$ [24]. If the order parameter coincides with the strains, the transition should be classified as a proper ferroelastic
transition, otherwise it corresponds to a pseudoproper ferroelastic transition. Among the models mentioned in this paragraph, those presented by the groups [12, 14, 19] are based on the assumption that the phase transition is a proper ferroelastic phase transition. These models cannot explain the variation of $C_{11}$ observed at $T_c$. The models presented by the groups [10, 21] are based on the assumption that the phase transition has a pseudoproper character. These two models are not fully compatible with experimental observations either. The one proposed by [10] predicts that $C_{66}$ gets softened (which is inconsistent with the experimental results, see Fig. 4.7). The other [21] does not consider the coupling terms involving $e_3$ and, therefore, cannot explain the variations observed on $C_{33}$.

During a proper ferroelastic transition, one normally observes a substantial elastic anomaly on one of the elastic constants, or a combination of elastic constants (soft elastic mode), which goes to zero as the transition point is approached from either side. Typically, for proper ferroelastic transitions this soft elastic mode varies linearly with temperature over a wide temperature range. However, our measurements indicate that the temperature dependence of $(C_{11} - C_{12})/2$ (see figure 4.8), which shows incomplete softening, does not display a well defined linear dependence. Consequently, based on this last observation, we will assume that the transition corresponds to a pseudoproper ferroelastic transition. Thus, the order parameter is a physical quantity that is different from the strains, however it must have the same symmetry as $(e_1 - e_2)$ and $e_6$ in order to describe a $4 \rightarrow 2$ symmetry change.

In writing the explicit form of the Landau free energy, we must take into account the symmetry properties of the crystal. As the atomic configuration of the crystal remains unaltered under a symmetry operation of the high symmetry phase, the free energy must also be invariant under the same symmetry operation. Thus, all terms considered in the free energy must be invariant under the symmetry operations of the
CHAPTER 5. THEORETICAL MODEL

Table 5.1: Transformations of the strains under the operation of the elements of point group 4.

<table>
<thead>
<tr>
<th>Strains</th>
<th>$e_1$ ($e_{xx}$)</th>
<th>$e_2$ ($e_{yy}$)</th>
<th>$e_3$ ($e_{zz}$)</th>
<th>$e_4$ ($e_{yx}$)</th>
<th>$e_5$ ($e_{zx}$)</th>
<th>$e_6$ ($e_{xy}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4^1$</td>
<td>$e_2$</td>
<td>$e_1$</td>
<td>$e_3$</td>
<td>$-e_5$</td>
<td>$e_4$</td>
<td>$-e_6$</td>
</tr>
</tbody>
</table>

high symmetry phase. In the case of $Rb_4LiH_3(SO_4)_4$, the point group for the high symmetry phase is 4 [11]. One of the symmetry operation that must be considered is $C_4^1$, which corresponds to a rotation of $90^\circ$ relative to the z-axis. The symmetry properties of the spontaneous strains under the operation of $C_4^1$ are given in Table 5.1. As $e_{11}$ transforms as a $x^2$ function, $e_{22}$ as $y^2$, $e_{33}$ as $z^2$, $e_{44}$ as $yz$, $e_{55}$ as $xz$ and $e_{66}$ as $xy$, the strains are sometimes written as $e_{xx}$, $e_{yy}$, $e_{zz}$, $e_{yz}$, $e_{xz}$, $e_{xy}$, respectively. Moreover, we know that the transformation of the order parameter $Q$ under the operation of $C_4^1$ must be the same as $e_6$ or $(e_1 - e_2)$. Thus, the symmetry invariant form of the free energy associated with the order parameter is

$$F_1(Q) = \frac{1}{2} \alpha_2 Q^2 + \frac{1}{4} \alpha_4 Q^4$$

(5.17)

where $\alpha_2 = a (T - T_0)$, as given previously. It is worthwhile to mention that the quadratic and quartic terms are always allowed by symmetry. From Eq. 2.1.3, we have that the elastic energy for the tetragonal phase (4) is

$$F_2(e_i) = \frac{1}{2} C_{11} (e_1^2 + e_2^2) + \frac{1}{2} C_{44} (e_4^2 + e_5^2) + \frac{1}{2} C_{33} e_3^2 + \frac{1}{2} C_{66} e_6^2 + C_{12} e_1 e_2 + C_{13} (e_1 + e_2) e_3 + C_{16} (e_1 - e_2) e_6$$

(5.18)

where the elastic constants refer to their values at temperatures above $T_c$. It is easy to check that all terms in Eq. 5.18 are invariant with respect to $C_4^1$. The lower coupling terms must at least include

$$F_3(Q, e_j) = \beta Q (e_1 - e_2) + \gamma Q e_6 + \delta Q^2 e_3 + \lambda Q^2 (e_1 + e_2)$$

(5.19)
where the coefficients $\beta$, $\gamma$, $\delta$, and $\lambda$ are constants, whose values will be determined later. In this model, we only consider the dominant coupling terms. Based on the fact that $C_{44}$ (or $C_{55}$) is slightly affected by the phase transition, we know that the coupling between the order parameter and the strain $e_4$ (or $e_5$) is negligible. That explains why $e_4$ and $e_5$ do not appear in the above expression. Since the order parameter $Q$ has the same symmetry as the strains $e_6$ and $e_1 - e_2$, the two linear-linear coupling terms ($\beta Q (e_1 - e_2)$ and $\gamma Q e_6$) automatically transform like $Q^2$, and therefore are allowed by symmetry. From Table 5.1, we see that $e_3$ and $e_1 + e_2$ are invariant under the symmetry operation, so the last two quadratic-linear terms are also allowed. Finally, the work associated with an external pressure can be expressed as

$$F_4(P, e_{kk}) = P (e_1 + e_2 + e_3)$$

(5.20)

where $P$ is the pressure and $e_1, e_2, e_3$ are strains affected by the hydrostatic pressure. It is easy to check that this expression is invariant under the symmetry operation as well. Combining these four expressions, we obtain the free energy,

$$F = \frac{1}{2} \alpha_2 Q^2 + \frac{1}{4} \alpha_4 Q^4$$

$$+ \frac{1}{2} C_{11} (e_1^2 + e_2^2) + \frac{1}{2} C_{44} (e_4^2 + e_5^2) + \frac{1}{2} C_{33} e_3^2 + \frac{1}{2} C_{66} e_6^2$$

$$+ C_{12} e_1 e_2 + C_{13} (e_1 + e_2) e_3 + C_{16} (e_1 - e_2) e_6$$

$$+ \beta Q (e_1 - e_2) + \gamma Q e_6 + \delta Q^2 e_3 + \lambda Q^2 (e_1 + e_2)$$

$$+ P (e_1 + e_2 + e_3).$$

(5.21)

which can be used to calculate the elastic constants and the strains associated with the phase transition. Under equilibrium conditions, we know that the free energy must correspond to a minimum. Therefore, we have that

$$\frac{\partial F}{\partial e_i} = 0$$

(5.22)

where $i$ ranges from 1 to 6. From these equations, we find that the strains in the low temperature phase can be expressed in terms of the order parameter $Q$ and pressure
Table 5.2: Expressions for the parameters used in the equations of the strains as a function of Q and P.

\[
\begin{array}{|c|c|}
\hline
\zeta & C_{11} + C_{12} \\
\epsilon & C_{11} - C_{12} \\
b_1 & \beta C_{66}(2 C_{13}^2 - \zeta C_{33}) + \gamma C_{16}(\zeta C_{33} - 2 C_{13}^2) \\
b_2 & \delta C_{13}(\epsilon C_{66} - 2 C_{16}^2) + \lambda C_{33}(2 C_{16}^2 - \epsilon C_{66}) \\
b_3 & \epsilon C_{13} - C_{66} - \epsilon C_{33} - C_{66} - 2 C_{16}^2(C_{13} - C_{33}) \\
\hline
\end{array}
\]

where the parameters \( \zeta, \epsilon, b_1, b_2 \) and \( b_3 \) are given in Table 5.2. From the first two equations, we see that

\[
e_1(Q, P) = \frac{b_1 Q + b_2 Q^2 + b_3 P}{(2C_{13}^2 - \zeta C_{33})(2C_{16}^2 - \epsilon C_{66})}
\]

\[
e_2(Q, P) = \frac{-b_1 Q + b_2 Q^2 + b_3 P}{(2C_{13}^2 - \zeta C_{33})(2C_{16}^2 - \epsilon C_{66})}
\]

\[
e_3(Q, P) = \frac{(\delta \zeta - 2\lambda C_{13})Q^2 + (\zeta - 2C_{13})P}{2C_{13}^2 - \zeta C_{33}}
\]

\[e_4(Q, P) = 0\]

\[e_5(Q, P) = 0\]

\[e_6(Q, P) = \frac{(2\beta C_{16} - \epsilon \gamma)Q}{\epsilon C_{66} - 2C_{16}^2}\]

is indeed proportional to the order parameter as well as \( e_6 \) (see Eq. 5.28). This is consistent with the statement that the order parameter has the same symmetry as \( e_1 - e_2 \) and \( e_6 \). Minimizing the free energy with respect to \( Q \), we obtain that

\[
\alpha_2 Q + \alpha_4 Q^3 + \beta (e_1 - e_2) + \gamma e_6 + 2 \delta e_3 Q + 2 \lambda (e_1 + e_2) Q = 0.
\]
Combining equations 5.23-5.28 with Eq. 5.30 and making use the relation $a_2 = a (T - T_0)$, it is not difficult to find the critical temperature at which the order parameter vanishes. Since this expression is too long, it is not shown here. However, taking the derivative of $T_c$ with respect to $P$, we find that the rate at which the critical temperature changes with pressure is given by

$$\frac{dT_c}{dP} = \frac{2\gamma(C_{11} + C_{12} - 2C_{13}) - 4\delta(C_{13} - C_{33})}{a(C_{11} + C_{12})C_{33} - 2aC_{13}^2}. \tag{5.31}$$

As the value of $dT_c/dP$ has been measured ($dT_c/dP = 19 \, K/kbar$), we can use Eq. 5.31 to fix the value of one of the adjustable coefficients. Though the expression for $T_c$ with $P \neq 0$ is complicated, the expression under normal pressure condition is given by

$$T_c = T_0 + \frac{\gamma(4\beta C_{16} - \gamma \epsilon) - 2C_{66}\beta^2}{a(2C_{16}^2 - \epsilon C_{66})}. \tag{5.32}$$

The equation above shows that due to the coupling between the order parameter and the spontaneous strains, the transition temperature has been shifted from $T_0$ to $T_c$. As $T_c$ is already known, this expression can be used to solve for another coefficient.

As shown in section 5.1.2, in the low temperature phase the order parameter depends on temperature. For simplicity, we only consider its temperature dependence at $P = 0 \, kbar$. Thus, combining Eq. 5.23-5.28 with Eq. 5.30, we obtain that

$$Q(T) = \sqrt{\frac{a(2C_{13}^2 - \zeta C_{33})(\epsilon C_{66} - 2C_{16}^2)}{(\epsilon C_{66} - 2C_{16}^2)[a_4(\zeta C_{33}^2 - 2C_{13}^2) - 2(\zeta \delta^2 - 4C_{13} \delta \lambda + 2C_{33} \lambda^2)]}(T - T_c)}. \tag{5.33}$$

where we have made use of Eq. 5.10 and Eq. 5.32. Comparing Eq. 5.33 with the second equation in 5.12, we see that the only difference is in their coefficients. Therefore, the temperature dependence of the order parameter in this model is described by a curve similar to that given in Fig. 5.2 and corresponds to a mean field order parameter. Inserting Eq. 5.33 into Eq. 5.23 - 5.28 for $P = 0$, we easily obtain the temperature
Figure 5.3: Temperature dependence of the strains $e_1$ and $e_2$ for $Rb_4LiH_3(SO_4)_4$. The circle and square symbols represent the data obtained by B. Mróz et al. [6], while the solid line are the fits of these data.

dependence of the strains. By fitting the experimental data for the strains using these later relations, all adjustable coefficients can be determined. Our fits and the experimental data reported by B. Mróz et al. [6] are presented in Fig. 5.3-5.4. In the process, we have made use of Eq. 5.31 and Eq. 5.32 as well as the convention that $Q = 1$ at 0 K. The coefficients obtained that way are given in Table 5.2. Let add that in the low temperature phase, Landau models are expected to describe the features of a phase transition close to $T_c$. Therefore, the deviations between theory and experiment at low temperatures ($T/T_c < 0.4$) for $e_1$ and $e_6$ are not significant. As for $e_3$, considering the poor experimental data, no good agreement between theory and experiment is expected.
Figure 5.4: Temperature dependence of the strain $e_6$. Again the symbols and solid lines stand for the experimental data [6] and the fits, respectively.

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$\lambda$</th>
<th>$a$</th>
<th>$a_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.43</td>
<td>0.92</td>
<td>1.5</td>
<td>0.00068</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 5.3: The values of the coefficients for this model. Each coefficient shown in this Table should be multiplied by $10^8$. 
Figure 5.5: The fit of the temperature dependence of the strain $e_3$. The data is obtained by B.Mróz et al. [6].
5.2.1 Soft Mode

Now that the free energy has been totally determined, the elastic constants can be obtained by using Eq. 5.1.3. The calculation is straight forward, but the results are often represented by long expressions. However, at \( P = 0 \) kbar, the elastic tensor corresponding to the tetragonal phase is given by

\[
\begin{pmatrix}
C_{11}^0 - \frac{\beta^2}{a(T-T_k)} & C_{12}^0 + \frac{\beta^2}{a(T-T_k)} & C_{13}^0 & 0 & 0 & C_{16}^0 - \frac{\beta\gamma}{a(T-T_k)} \\
C_{12}^0 + \frac{\beta^2}{a(T-T_k)} & C_{11}^0 - \frac{\beta^2}{a(T-T_k)} & C_{13}^0 & 0 & 0 & -C_{16}^0 + \frac{\beta\gamma}{a(T-T_k)} \\
C_{13}^0 & C_{13}^0 & C_{33}^0 & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44}^0 & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44}^0 & 0 \\
C_{16}^0 - \frac{\beta\gamma}{a(T-T_k)} & -C_{16}^0 + \frac{\beta\gamma}{a(T-T_k)} & 0 & 0 & 0 & C_{66}^0 - \frac{\gamma^2}{a(T-T_k)}
\end{pmatrix}
\]

with \( T_k = T_c - (\gamma^2 (C_{12}^0 - C_{11}^0) + 4\beta\gamma C_{16}^0 - 2\beta^2 C_{66}^0)/a (2(C_{16}^0)^2 + (C_{12}^0 - C_{11}^0) C_{66}^0) \). Here the elastic constants \( C_{ij}^0 \) refer to their values at temperatures well above \( T_c \) and are given in Table 5.4. Our model predicts that the elastic constants \( C_{11}, C_{12}, C_{16} \) and \( C_{66} \) more or less depend on temperature. The expressions for these elements can be used to fit the measured elastic constants presented in Chapter 4. Moreover, they are also used to calculate the temperature dependence of the effective elastic constant associated with the soft mode. The expression for this effective elastic constant can

<table>
<thead>
<tr>
<th>( C_{11}^0 )</th>
<th>( C_{12}^0 )</th>
<th>( C_{13}^0 )</th>
<th>( C_{16}^0 )</th>
<th>( C_{33}^0 )</th>
<th>( C_{44}^0 )</th>
<th>( C_{66}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.65</td>
<td>2.05</td>
<td>0.50</td>
<td>0.20</td>
<td>4.30</td>
<td>0.68</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table 5.4: The values of the elastic constants used in this model as that corresponding to temperatures well above \( T_c \). Each coefficient shown in this Table is in unit \( N/m^2 \) and its value should be multiplied by \( 10^{10} \).
be obtained by considering the strain components which have the same symmetry as
the the order parameter, i.e. \( \varepsilon_1 - \varepsilon_2 \) and \( \varepsilon_6 \). As their corresponding elastic constants
are \( (C_{11} - C_{12})/2 \) and \( C_{66} \) respectively, the elastic constant submatrix associated with
these strains takes the form

\[
\begin{pmatrix}
\frac{1}{2}(C_{11} - C_{12}) & C_{16} \\
C_{16} & C_{66}
\end{pmatrix}
\]  

(5.35)

The eigenvalues of this matrix give us the effective elastic constant of the soft mode,
which is found to be

\[
\rho V_s^2 = \frac{1}{2} \left( \frac{C_{11} - C_{12}}{2} + C_{66} - \sqrt{\left( \frac{C_{11} - C_{12}}{2} - C_{66} \right)^2 + 4C_{16}^2} \right)
\]  

(5.36)

where \( V_s \) stands for the sound velocity of the soft mode. Comparing with Eq. 4.2,

\[
\rho V_{T[110][110]}^2 = \frac{1}{2} \left( C_{11} + C_{66} - \sqrt{(C_{12} + C_{66})^2 + 4C_{16}^2} \right)
\]  

(5.37)

we see that though the transverse waves propagating along [110] and polarized perpendicularly to the z-axis shows the largest variations in velocity above \( T_c \), its effective elastic constant is not equivalent to the soft mode (Eq. 5.36). This explains why the velocity of the transverse waves propagating along the [110] direction and polarized perpendicularly to the z-axis does not decrease to zero at \( T_c \). In order to see if this soft mode does indeed show complete softening at \( T_c \), we calculated its temperature dependence using the relevant elements of the matrix 5.34. The plot of the effective elastic constant of the soft mode as a function of temperature is presented in Fig. 5.6 along with the experimental data. Our calculations clearly show that the effective elastic constant for this soft mode goes to zero at \( T_c \). Extrapolating the data to \( T_c \), we find that the soft effective elastic constant takes the value \( 0.07 \times 10^{10} \, \text{N/m}^2 \) at the transition temperature. As the uncertainty of the experimental result for this effective elastic constant is estimated between \( 0.05 \times 10^{10} \, \text{N/m}^2 \) and \( 0.1 \times 10^{10} \, \text{N/m}^2 \),
Figure 5.6: The temperature dependence of the effective elastic constant associated with the soft mode. The solid line represents the calculations using our model. The squares represent our experimental data. The vertical line segment represents the error bar.
our data can be considered in agreement with our calculations. However, this result contradicts the calculation given by Mróz et al. [14]. A close inspection reveals that their calculation is based on an inappropriate equation. In their paper, they used an asymmetric elastic constant submatrix

\[
\begin{pmatrix}
(C_{11} - C_{12}) & C_{16} \\
2C_{16} & C_{66}
\end{pmatrix}
\] (5.38)

which is obvious wrong because the elastic constant matrix is always symmetric (see Eq. 2.19). Based on this submatrix, they obtained an expression for the effective elastic constant of the soft mode

\[
\rho V_s^2 = \frac{1}{2} \left( \frac{C_{11} - C_{12}}{2} + C_{66} - \sqrt{\left( \frac{C_{11} - C_{12}}{2} - C_{66} \right)^2 + 8C_{16}^2} \right)
\] (5.39)

which is naturally incorrect. Thus, we believe, that in the case of \(Rb_4LiH_3(SO_4)_4\), the soft mode should show complete softening at \(T_c\). According to Dieulesaint [60], for crystals that have the symmetry of point group 4, the propagating direction of the sound waves associated with the soft mode can be found in the (001) plane. Based on the slowness curves in the (001) plane, it is found that this direction can be calculated using equation [60]

\[
tan 4\phi_0 = \frac{4C_{16}}{C_{11} - C_{12} - 2C_{66}}
\] (5.40)

where \(\phi_0\) refers to the angle between the propagating direction and the [110] direction. Based on our model, \(\phi_0\) is found to be equal to \(-5^0\) at \(T_c\). In another word, complete softening of the soft mode should be observed only along that direction.

### 5.2.2 Comparison of the Calculations with Experimental Data

As the elastic constants can be calculated from the Landau free energy, their experimental counterparts presented in Chapter 4 provide an appropriate data set for
testing our model. Due to the fact that the data are obtained using the equations corresponding to the tetragonal phase, the results for the monoclinic phase may not be accurate. For that reason, we focus our attention to the comparison relative to the tetragonal phase. In this section, we analyze only those elastic constants which are significantly affected by the phase transition, i.e. \( C_{11}, \ C_{33} \) and \( (C_{11} - C_{12})/2 \). The variations in the elastic constant is a consequence of anharmonic effects. Some of the anharmonic effect is associated with the soft mode, the rest is not. As the theoretical model only predicts the variations associated with the soft mode, before conducting the comparison, the variations caused by anharmonic effects (the normal anharmonic effect) not related to the soft mode need to be subtracted from the experimental data.

In the case where the external variable is the temperature, our model predicts that \( C_{33} \) is constant above \( T_c \), see Fig. 5.7. That means that, for the tetragonal phase, there is no contribution of the soft mode on \( C_{33} \). Therefore, the linear temperature dependence of \( C_{33} \) is obviously a result of the normal anharmonic effect (see Fig. 4.7). Subtracting the linear extrapolation, we obtain the variation associated with the soft mode for \( C_{33} \). For \( C_{11} \), Fig. 4.7 shows that it gets softened at temperatures well above \( T_c \). Thus, in this case, the contribution of the normal anharmonic effect can only be derived from data obtained well above room temperature. Since those data is unavailable, we assume that the contribution of the normal anharmonic effect is the same as the one observed on \( C_{33} \). Thus, we estimate the effect of the soft mode on \( C_{11} \) by subtracting a linear extrapolation similar to the one observed for \( C_{33} \). The data obtained this way for \( C_{33} \) and \( C_{11} \) are shown in Fig. 5.7 along with the calculations based on our theoretical model. Both graphs show that our model agrees well with the experimental results for the high temperature phase. However, in the low temperature phase the predictions of the model deviate from the measurements significantly. The appearance of domains in this phase may explain, at least partially, the disagreement.
Figure 5.7: Temperature dependence of $C_{33}$ and $C_{11}$ at 0 kbar. The solid lines represent the fits obtained using our model. The squares represent data deduced from our measurements.
regarding the magnitude of the variation close to the transition. Besides, we should also keep in mind that the data for $C_{11}$ is not accurate in this phase, so no full agreement is expected for this elastic constant. However, the disagreement for $C_{33}$ may be also due to the fact that only lower coupling terms are considered in this model. As higher coupling terms involving $e_3$ are included, the fit might be improved.

As stated previously, the elastic constant combination $(C_{11} - C_{12})/2$ shows significant softening above $T_c$. It shows a nonlinear temperature dependence that convinces us that the observed transition belongs to a pseudoproper ferroelastic phase transition. For this reason, the calculated temperature dependence of $(C_{11} - C_{12})/2$ is compared with the experimental data. Considering that the data for the monoclinic phase is unavailable, the comparison is confined to the tetragonal phase. For this phase, the temperature dependence of $(C_{11} - C_{12})/2$ can be easily calculated using the elements of matrix 5.34, such that

$$
\frac{1}{2}(C_{11}(T) - C_{12}(T)) = \frac{1}{2}(C_{11}^0 - C_{12}^0) - \frac{\beta^2}{a (T - T_k)} .
$$

The plot of our calculation and the corresponding experimental data are presented in Fig. 5.8. In this case, as the normal anharmonic effect is not significant relative to the strong softening, we do not subtract any linear temperature dependence from the data. The figure shows that the model can roughly describe the temperature dependence of this elastic constant combination in the tetragonal phase. In principle, the fit can be improved by including high order coupling terms in our model. In the meantime, the normal anharmonic effect should be eliminated if we want to obtain a better agreement.

At constant temperature, the pressure dependence of the elastic constants can also be calculated from the free energy using Eq. 5.1.3. Thus, the experimental results of the elastic constants as a function of pressure provide supplementary data for testing
Figure 5.8: Temperature dependence of $(C_{11} - C_{12})/2$ at 0 kbar. Again, the solid line represents the fit using Eq. 5.41, while the square symbols represent the experimental data. The vertical line segment represents the error bar.
our model. In this case, the variations associated with the normal anharmonic effect is expected to be linear. Thus, the variations which are strictly associated with the soft mode can be obtained more rigorously by subtracting a proper linear extrapolation. In this sense, these data is more suitable for comparison. Actually, the variations associated with the soft mode for $C_{33}$ and $C_{11}$ have already been derived, see the insets of Fig. 4.9 and Fig. 4.10. Here, in Fig. 5.9, they are reproduced and compared with our calculations. Again, our model can adequately describe the pressure dependence of both $C_{33}$ and $C_{11}$ in the low pressure phase. We also see that in this case the fit for $C_{11}$ agrees fully with the data except at pressures close to $P_c$. On the other hand, the predictions of our model disagree with the experimental results considerably in the monoclinic phase. The reason may still be that we only consider the lower coupling terms in our model. Besides, the appearance of the domains as well as the modifications of domains patterns with pressure may also account for part of the disagreements in this phase. For $C_{11}$, we should note that the data for the high pressure phase is not accurate. Thus, no full agreement is expected.

This simple model can explain the pressure behavior of $(C_{11} - C_{12})/2$ considerably well, see Fig. 5.10. Due to the limit of our data, the comparison has not been extended to higher pressure. In this case, we did not subtract any linear pressure dependence. Nevertheless, our calculation agrees fully with the data. This may indicate that the results of the normal anharmonic effect on $C_{11}$ and $C_{12}$ are the same, so they are cancelled out in the combination of $(C_{11} - C_{12})/2$. Our calculation clearly shows that this elastic constant combination exhibits incomplete softening at $P_c$. At this critical pressure, the calculated value is $0.08 \times 10^{10} \text{ N/m}^2$, which is very close to the value obtained by extrapolating the experimental results obtained as a function of temperature. Our calculation also shows that $(C_{11} - C_{12})/2$ exhibits a nonlinear pressure dependence in the low pressure phase.
Figure 5.9: Pressure dependence of $C_{33}$ and $C_{11}$ at room temperature. The solid lines represent the fit. The squares represent the data obtained from our measurements.
Figure 5.10: Pressure dependence of \((C_{11} - C_{12})/2\) at room temperature. Again, the solid line stands for the fit, while the squares represent the experimental data. The vertical line segment represents the error bar.
All these comparisons show that our model can appropriately describe the properties of $Rb_4LiH_3(SO_4)_4$. As we have seen, it can describe the temperature and pressure dependence of the elastic constants of this crystal though, for the monoclinic phase, due to the appearance of domains, the experimental results deviate from the calculations significantly. Of course, this is just a simple model. For better agreement, we need to elaborate the model a bit more. In particular, higher coupling terms $Q^2 e_3^2$, $Q^2 (e_1 - e_2)^2$ and $Q^2 e_6^2$ can be added to the model. More importantly, we need to extract the intrinsic elastic constants for the monoclinic phase so that the validity of our model can be further tested in this phase.
Chapter 6

Conclusions

In this project, the temperature and pressure effect on the elastic properties of $Rb_4LiH_3(SO_4)_4$ has been investigated using an acoustic interferometer. The temperature and pressure ranges in our investigation were 4 K-300 K and 0 kbar-10 kbar, respectively. Our high resolution sound velocity measurements show that at ambient pressure $Rb_4LiH_3(SO_4)_4$ undergoes a phase transition at $T_c = 132 \pm 0.3$ K. This phase transition shows no thermal hysteresis on successive heating and cooling processes, confirming that it is a second order phase transition. In addition, at constant temperature $T = 300$ K, the occurrence of a phase transition is observed at a pressure of $P_c = 8.4 \pm 0.2$ kbar. Even in the absence of X-ray scattering measurements, in analogy to results obtained as a function of temperature, we can safely assume that the transition observed at $P_c$ corresponds to $4 \rightarrow 2$ symmetry change.

It is well established that the monoclinic phase of $Rb_4LiH_3(SO_4)_4$ is ferroelastic. It is also known that two kinds of birefringent domains separated by mutually perpendicular walls exist in this phase [9]. However, the ratio of these two kinds of domains is not clearly demonstrated. Our results show that in the monoclinic phase the temperature dependence of the velocities of longitudinal waves propagating along $x$ and
y directions are still equivalent. Based on this fact, we believe that the domains are roughly half and half in this phase. In order to derive the elastic constants, we need to measure the sound velocities along the crystal axes. However, if domains exist, the sound waves do not propagate along the same crystal axes in the different domains. In this case, the measured sound velocity cannot be used to accurately determine the elastic constants. Therefore, the elastic constants obtained for the monoclinic phase of \( \text{Rb}_4\text{LiH}_3(\text{SO}_4)_4 \) cannot be used to test the proposed theoretical model. In order to obtain appropriate data in this phase, we would need to measure the sound velocity using a single domain crystal.

In the range between 4 \( K \) and 300 \( K \), we observed only one phase transition. The high and low temperature phase are known to have the tetragonal and monoclinic symmetry, respectively. Using the sound velocity measurements as a function of temperature under different pressures, the temperature-pressure phase diagram of \( \text{Rb}_4\text{LiH}_3(\text{SO}_4)_4 \) is obtained. The diagram covers the temperature range between 4 \( K \) and 300 \( K \) for pressures up to 7 \( kbar \). The phase boundary is well described by a linear function. It is found that the transition temperature \( T_c \) increases rapidly with pressure at a rate of \( dT_c/dP = 19 \pm 1 \ K/kbar \).

The temperature and pressure dependence of five of the seven independent elastic constants of \( \text{Rb}_4\text{LiH}_3(\text{SO}_4)_4 \) are obtained. Our results regarding the temperature behavior of the elastic constants agree well with those reported by groups [14, 21]. The pressure dependence of the five elastic constants are obtained using the sound velocity measurements realized as a function of pressure at room temperature. Unfortunately, our sound velocity measurements could not go to high pressure (\( P \geq 10 \ kbar \)), so the pressure dependence of the elastic constants at pressures well above \( P_c \) are not well defined. To our knowledge, we are the first to investigate the elastic constants as a function of pressure. It is found that the pressure behavior of the elastic constants
is similar to their temperature behavior. In spite of that, these results provide complementary data that can be used to test the Landau model. The variations in the elastic constant is a consequence of the anharmonic effect. Some of the anharmonic effect is associated with the soft mode, the rest is not. In the case where the external variable is the pressure, the variations associated with the anharmonic effect which is not related to the soft mode is expected to be linear. Therefore, the variations in the elastic constant which are strictly associated with the phase transition can be obtained more rigorously. For this reason, the data as a function of pressure is more useful for testing a model.

So far, experimental results about the properties of the elastic constants associated with the soft mode are not consistent. While some experiments [9, 14, 21] show that the elastic constant associated with the strain $e_1 - e_2$, i.e. $(C_{11} - C_{12})/2$, gets softened, other groups [10, 12] observed that $C_{66}$ (associated with $e_6$) gets softened. Our results indicate that it is elastic constant $(C_{11} - C_{12})/2$ which exhibits incomplete softening at $T_c$ (or $P_c$). Above $T_c$ (or below $P_c$), it shows a nonlinear temperature (or pressure) dependence. In contrast, $C_{66}$ shows a small temperature (or pressure) dependence. These results are consistent with a pseudoproper ferroelastic mechanism for the point group symmetry change $4 \rightarrow 2$. The stronger softening of $(C_{11} - C_{12})/2$ can be explained in terms of a stronger coupling with the order parameter of the $e_1 - e_2$ mode.

In order to explain the experimental features observed in this project, we have presented a Landau model involving both temperature and pressure as external parameters. This model is based on the assumption that the observed phase transition has a pseudoproper character. In another word, we suppose that the order parameter for this phase transition is a physical quantity, but not $e_1 - e_2$ or $e_6$. Unfortunately, present information about this phase transition does not allow us to identify this
physical quantity. However, as far as the expansion of the Landau free energy is concerned, what is relevant is the symmetry of the order symmetry. A Landau model can be developed as long as the symmetry of the order parameter is known. According to group theory, for a $4 \rightarrow 2$ phase transition the symmetry of the order parameter should have the same symmetry as the strain components $e_1 - e_2$ or $e_6$. Our model has been derived using this information. Landau models contain adjustable parameters. It should be emphasized that all the parameters used in our model has been fixed in the process of fitting the temperature dependence of the strains and the shift of the transition temperature $dT_c/dP$. With the same parameters, our model can consistently accounts not only for the temperature dependence of the strains but also for the temperature and pressure dependence of the elastic constants as well. As we have demonstrated, our model can quantitatively describe both the temperature and the pressure behaviors of the elastic constants for the tetragonal phase of $Rb_4 Li H_3 (SO_4)_4$. In particular, our model describes quite well the pressure behavior of $(C_{11} - C_{12})/2$. For this elastic combination, due to its strong softening, the variations caused by anharmonic effects not related to the soft mode are insignificant. Therefore, any valid model for this phase transition is expected to be able to explain the behavior of this elastic combination even without subtracting any variations. Thus, the good agreement of our model with the experimental results of $(C_{11} - C_{12})/2$ is a strong argument for our model. For the monoclinic phase, due to the fact that the experimental values of the elastic constants are obtained using the equations corresponding to the tetragonal phase and that domains appear, it is no longer possible for us to carry on a quantitative comparison in the low temperature phase. Therefore, the validity of the model in this phase has not been fully proved. Nevertheless, we still see that our model can qualitatively describe the behavior of the elastic constants in this phase. All these evidences show that our model can appropriately describe the properties of
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$Rb_4LiH_3(SO_4)_4$. Considering that only the lowest coupling terms are considered in this model, no better agreement is expected.

According to our sound velocity measurements, the acoustic mode associated with the transverse waves propagating along $[110]$ and polarized perpendicularly to the $z$-axis shows the largest variations in velocity above $T_c$. However, this mode is not the actual soft acoustic mode accompanying a $4 \rightarrow 2$ transition. The actual soft acoustic mode does not propagate along one of the investigated directions. According to our model, the actual soft acoustic mode should be observed in a direction corresponding to $-5^0$ relative to the $[110]$ direction. Moreover, in contradiction with the calculation reported by Mróz et al. [14], our model predicts that the effective elastic constant associated with the soft mode shows complete softening at $T_c$. Our prediction is consistent with our experimental results. To our knowledge, no one has directly investigated the actual soft acoustic mode of $Rb_4LiH_3(SO_4)_4$ using sound waves propagating along the proper direction. Mróz et al. [14] did measure the velocities of transverse phonon propagating along two directions away from $[110]$ by 5 and 9 degree, respectively. Their results show that the softening becomes less pronounced as the angle of deviation is increased. Based on our calculation, we believe that they investigated along the wrong directions. The actual soft acoustic mode can be observed only by turning the investigation direction the other way around.

As mentioned above, velocity measurements using transverse waves propagating along the direction deviating $[110]$ by $-5^0$ angle should reveal complete acoustic phonon softening at $T_c$. Thus, a series of measurements in the $xy$-plane are needed in order to clarify if the soft acoustic soft mode shows complete softening. For this investigation, Brillouin scattering technique is recommended. Using that technique, measurements along different directions can be easily realized.

In order to obtain accurate elastic constants in the monoclinic phase, measure-
ments using single domain crystal are needed. According to Wolejko et al. [9], the single domain crystal can be obtained by applying normal stress along [100] or [010] directions. With the appropriate velocity measurements, the elastic constants in this ferroelastic phase can be derived using Christoffel equations corresponding to the monoclinic phase. Subsequently, the validity of the proposed Landau model could be tested further.

According to group theory, for a $4 \rightarrow 2$ phase transition, the driving mechanism may be the instability of the B symmetry optic mode in the prototype phase 4. In order to determine whether the order parameter for the phase transition observed in this project is identified with a soft Raman mode, further Raman scattering investigations are recommended.
Bibliography


