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## Elastic properties of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ and $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$ crystals

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**Abstract.** High-resolution Brillouin spectroscopy was used to study the elastic properties of  $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$  and  $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$  crystals. In contrast to earlier studies of the former compound, the present results indicate that the ferroelastic phase transition, which occurs at approximately 115 K, is of the  $4 \rightarrow 2$  type rather than  $4mm \rightarrow mm2$  as previously believed. An appropriate theoretical model using a two-component order parameter free energy expansion has been presented based on the Landau theory.  $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$  does not appear to be ferroelastic in the temperature range examined and only exhibits a slight change in slope of the temperature plots for elastic constants associated with longitudinal phonons.

### 1. Introduction

Crystals with the general formula  $\text{A}_4\text{LiH}_3(\text{BO}_4)_4$ , where  $\text{A} = \text{Rb}$  or  $\text{K}$  and  $\text{BO}_4 = \text{SO}_4$  or  $\text{SeO}_4$ , show tetragonal symmetry at room temperature and in most of the cases undergo structural phase transitions (Krajewski *et al* 1988, Minge and Krajewski 1988, Mróz and Laiho 1989, Połomska and Smutny 1989).

From recent results, it is known that  $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$  (RLHS) undergoes a ferroelastic phase transition at about 130 K. The formula for this crystal was reported by Wołojko *et al* (1988) and Mróz *et al* (1988, 1989a) as  $\text{LiRb}_5(\text{SO}_4)_2 \cdot 1.5 \text{H}_2\text{SO}_4$ ; however, recent chemical analyses have led to its new formula  $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$  for which a better fit of the measured density value to that calculated from the x-ray studies has been obtained. The ferroelastic properties were manifested by the existence of a domain structure sensitive to mechanical stress and by the acoustic phonon softening observed independently in studies of the elastic properties, of this crystal, by the series impedance method (Wołojko *et al* 1988) and by the Brillouin scattering technique (Mróz *et al* 1988, 1989a). From the results of these investigations, the observed phase transition type appears to be  $4mm \rightarrow mm2$ . It was also demonstrated by Mróz *et al* (1989a) that the coupling term, involving the spontaneous strain and the polarization, appears to explain the observed incomplete softening of the  $c_{66}$  elastic constant during this pseudo-proper transition.

X-ray investigations carried out by Pietraszko and Łukaszewicz (1988), on the other hand, showed the RLHS crystal to have the symmetry of the point group 4 (space groups

$P4_1$  or  $P4_3$ ), at room temperature. For such a prototype symmetry, the theory of ferroelastic second-order phase transitions (Toledano *et al* 1983) requires that the low-temperature phase be monoclinic 2. At the same time, however, Pietraszko and Łukaszewicz (1988) suggest the presence of orthorhombic distortion in the low-temperature phase. Very recent results, from x-ray investigations (Zuniga *et al* 1990), show that RLHS is built up of layers characterized by opposite signs in optical activity and belonging to the space groups  $P4_1$  and  $P4_3$ .

Consequently, although the more reliable x-ray results are inconsistent with theory and other previous work discussed above (especially those concerning the low-temperature phase), the structural transition sequence  $4 \rightarrow 2$  will be assumed in the present paper. Such a phase transition model also applied to  $K_4LiH_3(SO_4)_4$  (KLHS) which is isomorphous to RLHS. Elastic properties of KLHS were studied using the series impedance method and the Brillouin scattering technique (Mróz and Laiho 1989). These investigations, however, did not reveal complete acoustic phonon softening. It was found that the temperature dependence of the Brillouin shifts related to the longitudinal phonons exhibited only changes in their slope at  $T_c = 115$  K. Due to a high level of noise, it was not possible to observe any temperature changes in the velocities of transverse phonons, which could be directly related to a possible soft acoustic mode.

Thus, the aim here is to reexamine the previous Brillouin scattering results (Mróz *et al* 1988, 1989a) in RLHS using the newly postulated phase sequence  $4 \rightarrow 2$ . Such a transition should be accompanied by the appearance of a soft acoustic mode of a more complicated form (Boccara 1964) in comparison with the  $c_{66}$  elastic constant (in the case of  $4mm \rightarrow mm2$ ). The  $4 \rightarrow 2$  transition also involves some changes in the theoretical model given by Mróz *et al* (1989a) and will be discussed in section 4.

Another goal of the present work is to complete the Brillouin scattering investigation of KLHS, namely the temperature-dependence of the velocities of the transverse phonons since the necessary condition for the crystal to be ferroelastic (namely a change of the crystal system) is fulfilled.

## 2. Experimental procedure

Crystals of RLHS and KLHS were grown isothermally at 310 K by the dynamic method from an acid aqueous solution ( $pH \leq 1$ ) of the appropriate initial salts (pure for analysis) in stoichiometric proportions in the Crystal Physics Laboratory (Institute of Physics, A Mickiewicz University, Poznań, Poland). The accuracy of the sample cut was better than  $0.15^\circ$ . Samples of several different orientations were prepared in the form of cubes ( $5 \times 5 \times 5$  mm<sup>3</sup>) to measure the sound velocities along the crystallographic axes and the bisectors of these axes. Samples of RLHS, for angular dependence measurements of the soft acoustic mode, were also prepared to verify the effect of incomplete softening of the transverse acoustic phonons, observed in the previous Brillouin scattering investigations (Mróz *et al* 1989b) and in the ultrasonic measurements (Hempel *et al* 1988, Bręczewski *et al* 1990).

The Brillouin spectrometer has been described in detail in previous papers (Mróz *et al* 1989b). The incident light was provided by a stabilized single-mode argon-ion laser (Spectra Physics 2020) operating at 514.5 nm. The scattered light was analysed at  $\theta = 90^\circ$  with a piezoelectrically scanned triple-pass Fabry-Perot interferometer (Burleigh RC-110). The finesse was 50 and the measured contrast ratio was about  $10^6$ .

Table 1. Some physical properties describing  $4mm \rightarrow mm2$  and  $4 \rightarrow 2$  ferroelastic transitions.

	Old	New
Transition	$4mm \rightarrow mm2$	$4 \rightarrow 2$
Orientation of crystallographic axes		
Soft elastic constant $\rho v^2$	$c_{66}$	$\frac{1}{2} \frac{c_{11} - c_{12} + c_{66} - \sqrt{(c_{11} - c_{12} - c_{66})^2 + 8c_{16}^2}}{2}$
$c_{ijk} \neq 0$ for the prototype phase	$c_{11}, c_{33}, c_{44}$ $c_{66}, c_{12}, c_{13}$	$c_{11}, c_{33}, c_{44}, c_{66}$ $c_{12}, c_{13}, c_{16}$
Spontaneous strain	$e_6$	$e_1 - e_2$ and $e_6$
Soft mode direction	$[100] = [010]$	$[110]$

The sound velocities  $v$  were found from the measured frequency shifts  $\Delta\nu$  using the Brillouin equation:

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

where  $\lambda$  is the wavelength of the incident light and  $n_i$  and  $n_s$  are the refractive indices for the incident and scattered light, respectively. Refractive indices of RLHS were found by comparing the crystal samples with several liquids (Cargille Labs) of known refractive indices. It was found that  $n_x = n_y = 1.462$  and  $n_z = 1.468$ . For KLHS it was found that  $n_x = n_y = 1.46$  and  $n_z = 1.44$  using a microscopic method. The elastic constants of the crystals were found using solutions of the equation of motion for the three acoustic waves propagating in the direction  $Q$  as given by:

$$|c_{ijkl} q_j q_k - \rho v^2| = 0 \quad (2)$$

where  $q_j, q_k$  are the direction cosines of  $Q$ ,  $\rho$  is the density of the crystal ( $2.81 \text{ g cm}^{-3}$  for RLHS and  $2.3 \text{ g cm}^{-3}$  for KLHS using the x-ray data of Pietraszko and Łukaszewicz, 1988) and  $c_{ijkl}$  are elastic stiffness tensor components.

### 3. Experimental results

#### 3.1. RLHS

In order to clarify the differences imposed by the newly postulated type of phase transition in RLHS, several properties describing the 'old' ( $4mm \rightarrow mm2$ ) and 'new' ( $4 \rightarrow 2$ ) transitions, have been collected in table 1. As is evident from this table, the soft elastic constant (for point group 4), which vanishes when  $T \rightarrow T_c$ , has a more complicated form in comparison to the  $c_{66}$  elastic constant for point group  $4mm$ . This is related to the form of spontaneous strain for the  $4 \rightarrow 2$  transition, namely  $\alpha(e_1 - e_2) + \beta e_6$  and the corresponding eigenvalues of the elastic constant matrix, given in the form (Boccaro 1964):

$$\begin{vmatrix} c_{11} - c_{12} & c_{16} \\ 2c_{16} & c_{66} \end{vmatrix}$$

The expressions for  $\rho v^2$  as a function of the elastic constants for point group 4 are

**Table 2.**  $\rho v^2$  as a function of elastic constants for the point group 4.  $A = \frac{1}{2}(c_{11} + c_{33} + 3c_{44} + c_{66})$ ;  $B = \frac{1}{2}[(c_{11} + c_{44})(c_{33} + c_{44}) + (c_{11} + c_{44})(c_{44} + c_{66}) + (c_{44} + c_{66})(c_{33} + c_{44}) - (c_{44} - c_{13})^2 - c_{16}^2]$ ;  $C = \frac{1}{8}[(c_{11} + c_{44})(c_{44} + c_{66})(c_{33} + c_{44}) - (c_{44} + c_{13})^2(c_{44} + c_{66}) - c_{16}^2(c_{33} + c_{44})]$ .

Phonon	Mode	4
[110] $\equiv$ [010]	$\begin{cases} \text{L } \gamma_1 \rightarrow \frac{1}{2}(c_{11} + c_{66} + [(c_{11} - c_{66})^2 + 4c_{16}^2]^{1/2}) \\ \text{T } \gamma_2 \rightarrow \frac{1}{2}(c_{11} + c_{66} - [(c_{11} - c_{66})^2 + 4c_{16}^2]^{1/2}) \\ \text{T } \gamma_3 \rightarrow c_{44} \end{cases}$	
[001]	$\begin{cases} \text{L } \gamma_4 \rightarrow c_{25} \\ \text{T } \gamma_5 \rightarrow c_{44} \\ \text{T } \gamma_6 \rightarrow c_{44} \end{cases}$	
[110]	$\begin{cases} \text{L } \gamma_7 \rightarrow \frac{1}{2}(c_{11} + c_{66} + [(c_{12} + c_{66})^2 + 4c_{16}^2]^{1/2}) \\ \text{T } \gamma_8 \rightarrow \frac{1}{2}(c_{11} + c_{66} - [(c_{12} + c_{66})^2 + 4c_{16}^2]^{1/2}) \\ \text{T } \gamma_9 \rightarrow c_{44} \end{cases}$	
[011] $\equiv$ [101]	$\begin{cases} \text{L } \gamma_{10} \\ \text{T } \gamma_{11} \\ \text{T } \gamma_{12} \end{cases} \rightarrow \gamma^3 - A\gamma^2 + B\gamma - C = 0$	

given in table 2. Since the transition  $4 \rightarrow 2$  may involve the onset of spontaneous strain in the  $xy$ -plane the present studies concern mainly those phonons related to the  $(e_1 - e_2)$  and  $e_6$  components of the strain tensor.

The temperature dependences of the Brillouin shifts for the quasi-longitudinal phonons (modes  $\gamma_1$  and  $\gamma_7$ ) propagating in the [100] and [110] directions are given in figure 1(a). The quasi-transverse phonons for these directions are given in figure 1(b) for the  $\gamma_2$  mode and figure 1(c) for the  $\gamma_8$  mode. The frequency shift of the  $\gamma_8$  mode falls from 5.10 GHz at 295 K to 1.95 GHz at  $T_c$  ( $\approx 115$  K).

To confirm the location and nature of the minimum, temperature dependences of the Brillouin shifts for the transverse phonons propagating in two directions deviating from [110] by 5 and 9 degree angles have been plotted in figure 1(c). As is seen from this part of the figure the observed modes  $\gamma_8$ ,  $\gamma_8'$  and  $\gamma_8''$  become more stable as the angle of deviation is increased. This stabilization effect (of the temperature behaviour) for the soft mode is also evident from the temperature dependences of the integrated intensity ( $I_{\text{tot}}$ ) as measured for the same orientations around the [110] direction (see figure 2). According to Fabelinskii (1968),  $I_{\text{tot}} \propto c_{25}^{-1}$  for the [110] direction and this relation becomes less pronounced as the angle of deviation is increased. Broadening of the Brillouin lines was observed only for phonons propagating within the limits of experimental error along the [110] direction, whereas the increase of  $I_{\text{tot}}$  for the remaining directions was related only to the increase of the mode intensity and where the full width at half maximum (FWHM) was equal to the instrumental width  $\Gamma_{\text{inst}} \approx 0.5$  GHz in the entire temperature region studied.

Using the results given in figure 1 it was possible to calculate the  $\rho v^2$  values for various temperature for phonons propagating in the  $xy$ -plane, as given in figure 3. By solving the set of four equations,  $\rho v^2 = f(c_{ijkl})$  for the  $\gamma_i$  modes (where  $i = 1, 2, 7$  and  $8$ ), the temperature dependences of the elastic constants related to the spontaneous strain were found. The values of the elastic constants  $c_{11}$ ,  $c_{66}$ ,  $c_{12}$ ,  $c_{16}$  and  $\rho v_2^2$  (where  $\rho v_2^2$  is stated for the soft elastic constant as given in table 1) for the RLHS crystal at 295 K and  $T_c$ , respectively, are given in table 3.

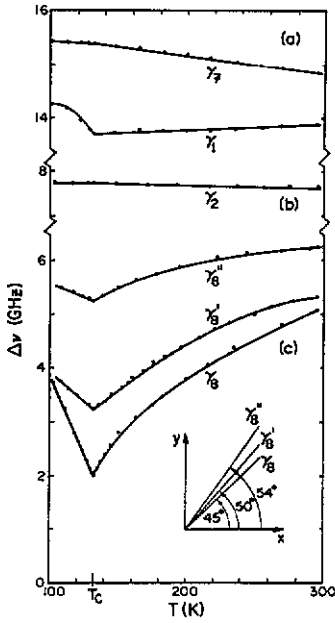


Figure 1. Temperature dependences of: (a) the Brillouin line shifts for the L-modes  $\gamma_1$  and  $\gamma_7$  of RLHS, (b) and (c) the T-modes propagating in the  $xy$ -plane.

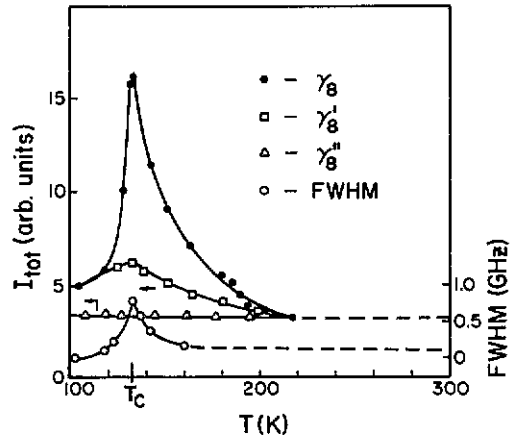


Figure 2. Temperature dependences of the total intensity  $I_{tot}$  for the  $\gamma_8$ ,  $\gamma_8'$  and  $\gamma_8''$  modes and the full width half maximum (FWHM) for  $\gamma_8$ . The instrumental width of 0.5 GHz has been subtracted.

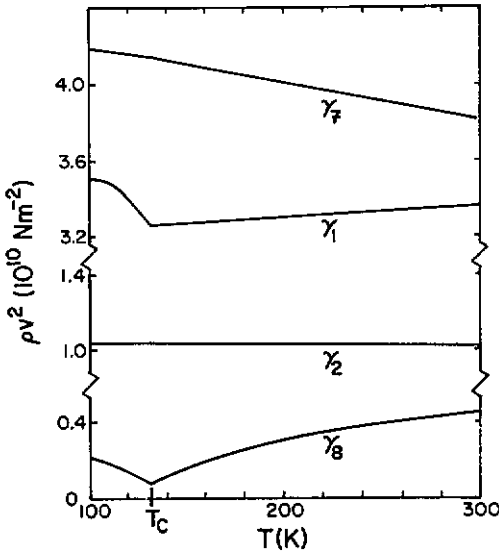


Figure 3. Temperature dependences of  $\rho\nu^2$  calculated for the  $\gamma_i$  modes ( $i = 1, 2, 7$  and  $8$ ).

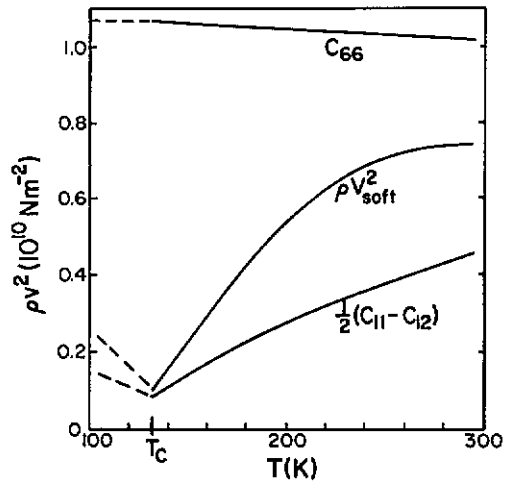


Figure 4. Temperature dependences of the  $\rho\nu_{soft}^2$ ,  $(c_{11} - c_{12})/2$  and  $c_{66}$  elastic constants calculated for the prototype phase 4 of RLHS.

Table 3. Elastic constants of RLHS at 295 K and  $T_c$ , in units of  $10^{10}$  N m<sup>-2</sup>.

Elastic constant	295 K	$T_c$
$c_{11}$	3.30	3.26
<sup>a</sup> $c_{33}$	4.17	4.65
<sup>a</sup> $c_{44}$	0.70	0.70
$c_{66}$	1.02	1.07
$c_{12}$	2.40	3.09
<sup>b</sup> $c_{16}$	-0.10	-0.20
$\rho v_s^2$	0.75	0.11

<sup>a</sup> Since the 'new' orientation of the crystal axes does not affect the [001] direction, the values of  $c_{33}$  and  $c_{44}$  are taken from a previous paper (Mróz *et al* 1989a).

<sup>b</sup> Has a large uncertainty.

The temperature dependences of elastic constants  $(c_{11} - c_{12})/2$ ,

$$\rho v_s^2 = 0.5 (c_{11} - c_{12} + c_{66}) - \sqrt{(c_{11} - c_{12} + c_{66})^2 + 8c_{16}^2}$$

and  $c_{66}$  are plotted in figure 4. As is evident from this figure neither  $(c_{11} - c_{12})/2$  nor  $\rho v_s^2$  reaches zero at  $T_c$ . Consequently, the same temperature behaviour for the soft elastic constant is noted for the  $4 \rightarrow 2$  transition as in the case of the  $4mm \rightarrow mm2$  transition, where  $c_{66}$  was found to be strongly temperature dependent but different from 0 at  $T_c$ . Such behaviour was well explained in a previous theoretical model (Mróz *et al* 1989a) through coupling between the spontaneous polarization,  $P$ , and the spontaneous strain,  $e_s$ . The transition was found to be driven by the order parameter,  $Q$ , coupled to both  $e_s$  and  $P$ . It is now necessary to verify this model according to the requirements for the newly postulated phase transition. This is done in detail in section 4.

### 3.2. KLHS

Elastic properties of KLHS have been studied using the series impedance method and the Brillouin scattering technique (Mróz and Laiho 1989). The aim of the present investigation was to complete the Brillouin scattering studies of KLHS especially regarding the temperature-dependence of the transverse phonon velocities. At room temperature, most of the Brillouin modes listed in table 2 have been observed. Table 4 contains the Brillouin shifts and the corresponding values of  $\rho v^2$  for KLHS at 295 K. Using these results, it is possible to calculate all non-zero components of the elastic constants of the point group 4. The proper values of the elastic constants were found using the requirement that the elastic energy be positive (Fedorov 1968), which for the tetragonal system takes the form:  $c_{11} > |c_{12}|$ ,  $(c_{11} + c_{12})c_{33} > 2c_{13}^2$ ,  $c_{44} > 0$  and  $c_{66} > 0$ . Table 5 contains the values of the elastic constants of KLHS at 295 K.

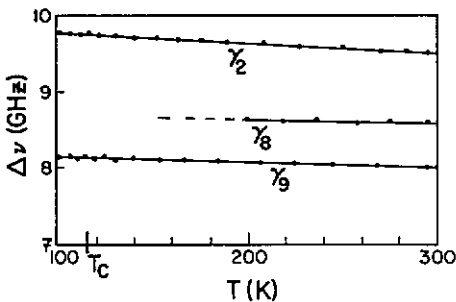
In addition, the temperature dependences of the transverse phonon velocities related to the Brillouin modes  $\gamma_2$ ,  $\gamma_8$  and  $\gamma_9$ , have been checked. The results obtained are given in figure 5. As is evident, all three frequency shifts are only linearly temperature dependent in the entire temperature region studied and show a slow increase with decreasing temperature. All modes presented in figure 5 were found to show a relatively low scattering power, which made observation of the  $\gamma_8$  mode impossible below 200 K.

**Table 4.** Brillouin scattering shifts and corresponding  $\rho v^2$  for KLHS at 295 K (as for table 2).

Mode	Brillouin shift (GHz)	$\rho v^2$ ( $10^{11} \text{ N m}^{-2}$ )
$\gamma_1$	16.81	4.04
$\gamma_2$	9.48	1.28
$\gamma_3$	—	—
$\gamma_4$	17.32	4.32
$\gamma_5$	8.00	0.91
$\gamma_6$	—	—
$\gamma_7$	17.33	4.28
$\gamma_8$	8.59	1.05
$\gamma_9$	7.98	0.91
$\gamma_{10}$	15.95	3.63
$\gamma_{11}$	10.00	1.43
$\gamma_{12}$	8.82	1.11

**Table 5.** Elastic constants for KLHS at 295 K.

$c_{11}$	$c_{33}$	$c_{44}$	$c_{66}$	$c_{12}$	$c_{13}$	$c_{16}$
4.40	4.32	0.91	1.29	1.94	-0.90	-0.063
$\pm 0.07$	$\pm 0.07$	$\pm 0.05$	$\pm 0.06$	$\pm 0.08$	$\pm 0.10$	$\pm 0.010$

**Figure 5.** Temperature dependences of the Brillouin shifts of transverse modes for KLHS.

#### 4. Theoretical model

In our earlier publication on this topic (Mróz *et al* 1989a), a Landau model was provided based on what now appears to be an incorrect assumption, namely that the transition is of the  $4mm \rightarrow mm2$  type. As argued in the present paper we now believe that the transition type is  $4 \rightarrow 2$  instead. However, both types of transition have much in common, e.g. being of second order (Boccaro 1964) and admitting very similar free energy expansions. The main difference is in the assignment of primary and secondary order parameters. It was previously argued that the transition is of improper ferroelastic character where the primary order parameter,  $Q$ , has not been identified and secondary order parameter, spontaneous strain,  $e_s$ , has been assigned to  $e_6$ . However, in view of



the more accurate measurements described in the present paper, it appears that the primary order parameter is  $\eta = e_1 - e_2$  and the secondary one is  $\sigma = e_6$ . Thus, the spontaneous strain  $e_s$  may be seen as a two-component quantity:  $e_s = \alpha(e_1 - e_2) + \beta e_6$ . This is consistent with the current identification of the transition type (Boccaro 1964). In addition, there is evidence of strong coupling to the dielectric polarization,  $P$ , (Wojtko *et al* 1988) which exhibits crossover behaviour (Mróz *et al* 1989a) in the vicinity of  $T_c$  where a square-root dependence of  $P$  on temperature for  $T > T_c$  changes to a linear dependence below  $T_c$ .

Since many of the details of the calculations of equilibrium properties of the system remain unchanged compared with those of earlier publication on this topic (Mróz *et al* 1989a), it is our intention to keep the present exposition concise and highlight only the main features of the theoretical development. The main point to note is that second-order phase transitions require a quartic Landau free energy expansion. However, a single-order parameter expansion would then inevitably lead to complete mode softening. In the present case, we deal with a two-component order parameter which is in addition coupled to other non-critical modes, namely polarization,  $P$ , and the remaining elastic strain components,  $e_i$ . In order to include only those terms in the expansion that do not violate symmetry requirements, we simply consult earlier exhaustive studies of such types of phase transitions. More specifically, following the general principles of free energy expansion published by Toledano *et al* (1983), Boccaro (1964) and Errandonea (1980), an appropriate Landau free energy expansion is postulated in the form of a convergent power series comprising several distinct contributions due to particular physical mechanisms

$$F = F_1(\eta, \sigma) + F_2(P) + F_{12}(\eta, \sigma, P) + F_{23}(\eta, e_i) \quad (3)$$

where, as mentioned above:

$$\eta = e_1 - e_2 \quad \text{and} \quad \sigma = e_6 \quad (4)$$

are the two components of the order parameter, and the various contributions to the free energy are given below. First, the free energy of the two components of the order parameter including their bilinear interaction is

$$F_1(\eta, \sigma) = \frac{1}{2}c_{2\sigma}\sigma^2 + \frac{1}{4}c_{4\sigma}\sigma^4 + \frac{1}{2}c_{2\eta}\eta^2 + \frac{1}{4}c_{4\eta}\eta^4 + \mu\eta\sigma \quad (5)$$

where  $c_{2\sigma} = a_\sigma(T - T_0)$  and  $c_{2\eta} = a_\eta(T - T_c^0)$ . This is the form required by symmetry arguments for the  $4 \rightarrow 2$  sequence of second-order transitions as demonstrated by Boccaro (1964). Then, the dielectric polarization energy  $F_2(P)$  (which corresponds to  $F_3(P)$  in Mróz *et al* 1989a) is given by

$$F_2(P) = B_2P^2 + B_4P^4 = \frac{1}{2}\chi^{-1}P^2 - E_{\text{eff}}(T)P. \quad (6)$$

Here  $\chi$  is a mean-field dielectric susceptibility of the sample and  $E_{\text{eff}}$  is the molecular effective electric field due to spontaneous polarization of the material. The approximate form on the right-hand side of (6) when minimized with respect to  $P$  yields spontaneous polarization as

$$P_s(T) = \chi E_{\text{eff}}(T) \cong \pm [b(T_p - T_c)/2B_4]^{1/2} [1 + \frac{1}{2}(T_c - T)/(T_p - T_c) + \dots] \quad (7)$$

and  $B_2 = b(T - T_p)$  with  $T_p$  denoting the transition temperature to the spontaneously polarized phase where it has been assumed that  $T$  is close to  $T_c$ , which is well below  $T_p$ .

Polarization,  $P$ , is coupled to both  $\sigma$  and  $\eta$  through biquadratic terms which are the lowest order ones allowed by symmetry principles

$$F_{12}(\eta, \sigma, P) = ((\nu/2)\sigma^2 + (\lambda/2)\eta^2)P^2. \quad (8)$$

Finally, the term  $F_{13}$  includes the energy of all other elastic modes and their predominant coupling to  $\eta$  with an additional coupling amongst the remaining modes carried out to third order as

$$F_{13}(\eta, e_i) = \sum'_i c_{ii}^0 e_i^2 + \frac{1}{2} \sum_{i \neq j} c_{ij}^0 e_i e_j + \sum'_i c_{3i}^0 e_i^3 + \eta^2 \sum'_i c_{3i\eta}^0 e_i \\ + \sum_{i,j,k} c_{ijk}^0 e_i e_j e_k + \eta^2 \sum'_{i,j} c_{4ij\eta}^0 e_i e_j. \quad (9)$$

Here,  $\Sigma'$ , denotes summation over all the remaining modes other than  $\sigma$  and  $\eta$ . Minimization of the free energy with respect to all independent thermodynamic variables is straightforward and yields the equations of state for the equilibrium values of  $\eta$ ,  $\sigma$ ,  $P$  and  $e_i$  as follows

$$\partial F / \partial \sigma = c_{2\sigma} \sigma + c_{4\sigma} \sigma^3 + \mu \eta + \nu \sigma P^2 = 0 \quad (10)$$

which implies that  $\eta = 0$  whenever  $\sigma = 0$ . Then,

$$\frac{\partial F}{\partial \eta} = c_{2\eta} \eta + c_{4\eta} \eta^3 + \mu \sigma + \lambda \eta P^2 + 2\eta \left( \sum'_i c_{3i\eta}^0 e_i + \sum'_{i,j} c_{4ij\eta}^0 e_i e_j \right) = 0. \quad (11)$$

Hence  $\sigma = 0$  if  $\eta = 0$ . Next,

$$\partial F / \partial P = \chi^{-1} P - E_{\text{eff}}(T) + \lambda \eta^2 P + \nu \sigma^2 P = 0 \quad (12)$$

implying that  $P = P_s(T)$  when  $\eta = \sigma = 0$  while

$$P = P_s(T) / (1 + \lambda \chi \eta^2 + \nu \chi \sigma^2) \quad (13)$$

otherwise. Here we have used  $B_2 = b(T - T_p)$  where  $T_p$  is the transition temperature to the polarised phase and obviously  $T_p \gg T_c$ . Finally, the other strain components satisfy

$$\frac{\partial F}{\partial e_i} = 2c_{ii}^0 e_i + \sum'_j c_{ij}^0 e_j + 3c_{3i}^0 e_i^2 + \eta^2 c_{3i\eta}^0 + 3 \sum'_{j,k} c_{ijk}^0 e_i e_k + 2\eta^2 \sum'_j c_{4ij\eta}^0 e_j = 0. \quad (14)$$

From these equations we find that:

(i) For  $T > T_c$  (the actual transition temperature):  $\eta = \sigma = 0$  (paraelastic phase) and  $P = P_s(T)$ . Equations (13) and (7) indicate a square-root dependence of polarization on temperature. From (14) the remaining strain components yield  $e_i = 0$  or  $e_i = -2c_{ii}^0 / 3c_{3i}^0 \equiv e_i^0$  which may or may not be zero (Mróz *et al* 1989a).

(ii) For  $T < T_c$  the equilibrium phase is ferroelastic and the transition at  $T = T_c$  is of second order, yielding (as in Mróz *et al* 1989a)

$$\eta \approx d_\eta (T_c - T)^{1/2} \quad \sigma \approx d_\sigma (T_c - T)^{1/2} \quad (15)$$

where  $d_\eta$  and  $d_\sigma$  are critical amplitudes depending on the various coupling constants of

the model (Mróz *et al* 1989a). Furthermore, using (15) with (13) indicates that the polarization experiences a crossover to a linear dependence on  $T$  through

$$P(T) = P_s(T_c) \{1 + [\frac{1}{2}(T_p - T_c)^{-1} - \lambda \chi d_\eta^2 - \nu \chi d_\sigma^2](T_c - T) + \dots\} \quad (16)$$

comparing favourably with experiment (Wolejko *et al* 1988). The other components of the strain tensor obey

$$e_i \approx [(e_i^0)^2 + \delta_i(T_c - T)]^{1/2} \quad (17)$$

where  $e_i^0$  is the equilibrium value above  $T_c$  and  $\delta_i$  is a parameter which depends on various coupling constants (Mróz *et al* 1989a).

It is important to calculate the second-order elastic coefficients based on this model. They are obtained as

$$c_{2\eta} = \frac{\partial^2 F}{\partial \eta^2} = c_{2\eta} + 3c_{4\eta} \eta^2 + \lambda P^2 + 2 \left( \sum_i' c_{3i\eta}^0 e_i + \sum_{i,j} c_{4ij\eta}^0 e_i e_j \right) \quad (18)$$

and

$$c_{2\sigma} = \frac{\partial^2 F}{\partial \sigma^2} = c_{2\sigma} + 3c_{4\sigma} \sigma^2 + \nu P^2 \quad (19)$$

for the two components of the order parameter and

$$c_{ij} = \frac{\partial^2 F}{\partial e_i \partial e_j} = c_{ij}^0 + 6 \sum_k' c_{ijk}^0 e_k + 2\eta^2 c_{4ij\eta}^0 \quad (20)$$

$$c_{ii} = \partial^2 F / \partial e_i^2 = 2c_{ii}^0 + 6c_{3i}^0 e_i^2 \quad (21)$$

and

$$c_{i\eta} = \frac{\partial^2 F}{\partial e_i \partial \eta} = 2\eta \left( c_{3i\eta}^0 + 2 \sum_j' c_{4ij\eta}^0 e_j \right) \quad (22)$$

for the remaining strain components. It is clear that  $c_{ij}$  and  $c_{ii}$  should not exhibit anomalous behaviour and  $c_{i\eta}$  is expected to be affected only slightly by the ferroelastic phase transition. On the other hand, both  $c_{2\eta}$  and  $c_{2\sigma}$  should be affected by it to different degrees since the terms are proportional to  $\eta^2$  and  $\sigma^2$ , respectively. Assuming that  $\eta$  is the primary order parameter during the transition, i.e. that  $T_c^0$  (the symmetry breaking temperature for the  $\eta$  component) is close to the actual transition temperature  $T_c$ , while  $T_0$  (the symmetry breaking temperature for the  $\sigma$  component) is further removed from it, it may be concluded that  $c_{2\eta}$  should exhibit a pronounced non-zero minimum at  $T_c$  and increase on either side of  $T_c$  almost linearly with  $|T - T_c|$  according to:

$$c_{2\eta} \cong c_{2\eta}(T_c) + \alpha_{2\eta}^\pm |T_c - T| + \dots \quad (23)$$

where '+' refers to  $T > T_c$  and '-' to  $T < T_c$ . From the stability analysis of the free energy (Mróz *et al* 1989a), i.e. the condition  $\delta^2 F = 0$  at  $T = T_c$  where  $\delta^2 F$  is the second variation of  $F$ , it follows that

$$c_{2\eta}(T_c) = \mu^2 / a_\sigma (T_c - T_0) > 0. \quad (24)$$

Since  $T_0 \ll T_c$ ,  $c_{2\sigma}$  is expected to be affected only by secondary effects close to  $T_c$ , i.e. through the coupling of  $\sigma$  with  $\eta$  and the coupling of  $P$  with  $\eta$ . Thus, a small change in the slope of  $c_{2\sigma}(T)$  seen experimentally and reported in this publication (see figure 4) is

consistent with the model presented here. In addition to that, the crossover behaviour of polarization agrees well with this model as discussed previously (Mróz *et al* 1989a).

## 5. Conclusions

In this paper the results of high-resolution Brillouin spectroscopy measurements were reported that were concerned with the elastic properties of two compounds:  $Rb_4LiH_3(SO_4)_4$  and  $K_4LiH_3(SO_4)_4$ . The temperature range in our investigations was from 100 to 300 K. It was found that the first crystal undergoes a second-order ferroelastic phase transition at approximately  $T_c = 115$  K and that the transition is probably of the  $4 \rightarrow 2$  type rather than the  $4mm \rightarrow mm2$  type as previously claimed (Mróz *et al* 1989a). Consistently with these results, it was assumed that the order parameter is two-component with its primary components being  $\eta = (e_1 - e_2)$  and the secondary one,  $\sigma = e_6$ . In the observed range of temperatures, the elastic constant  $\frac{1}{2}(c_{11} - c_{12})$  associated with  $\eta$  exhibits incomplete softening, while  $c_{66}$  which is associated with  $\sigma$  shows a very small dependence on temperature. The theoretical model provided in the paper was based on a Landau expansion for  $\eta$  and  $\sigma$  with additional couplings to polarization,  $P$ , and other elastic modes. The two coupling terms involving the interactions between  $P$ ,  $\eta$  and  $\sigma$  appear crucial in the qualitative description of the transition. First of all, they are indispensable in explaining the crossover behaviour of  $P(T)$ , and secondly, they provide a rationale for the incomplete softening of  $c_{2\eta}$ .

By comparing the temperature dependences of the frequencies of the longitudinal (Mróz and Laiho 1989) and transverse phonons of KLHS with those observed for RLHS it may be surmised that KLHS is not ferroelastic. The only indication of a phase transition, in KLHS, is a slight change in slope of the curves for the longitudinal phonons at  $T_c = 115$  K. None of the observed transverse modes was found to be affected by the transition.

Raman scattering investigations of both these materials are being carried out and may clarify the question of the order parameter in RLHS and the nature of the phase transition in KLHS.

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