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The soft optic mode in ferroelastic $Rb_4LiH_3(SO_4)_4$

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Abstract

Raman scattering measurements were performed on the ferroelastic compound $Rb_4LiH_3(SO_4)_4$ to determine the nature of the structural transition observed at $T_c = 134$ K. A double-grating spectrometer was used to obtain the Raman active B modes of $Rb_4LiH_3(SO_4)_4$. Back-scattering measurements, as a function of temperature, reveal that the 31 cm^{-1} mode shows softening consistent with that of an order parameter. As a result, our investigation indicates that the structural transition in $Rb_4LiH_3(SO_4)_4$ should be cataloged as a pseudo-proper ferroelastic transition rather than a proper ferroelastic one.

1. Introduction

The compound $Rb_4LiH_3(SO_4)_4$ belongs to a family of $A_4LiH_3(BO_4)_4$ crystals, where A = Rb, NH_4, K, and B = S, Se [1–5]. Apart from $K_4LiH_3(SO_4)_4$ and $K_4LiH_3(SeO_4)_4$ [3], these compounds are known to undergo a ferroelastic phase transition from the tetragonal point group 4 to the monoclinic point group 2. In most cases ferroelastic transitions are determined by the observation of an acoustic mode that displays complete softening at the critical temperature, accompanied by the appearance of structure domains in the low temperature phase. Thus, as proper and pseudo-proper ferroelastic [6] materials have many similar thermodynamic features, it is not rare to find conflicting interpretations regarding the driving mechanism of ferroelastic transitions.

In the case of $Rb_4LiH_3(SO_4)_4$, the ferroelastic character of the phase transition observed at $T_c = 134$ K has been clearly established by Brillouin scattering [3] and ultrasonic [7] measurements. While both techniques showed large softening of the effective elastic constant $(C_{11} - C_{12})/2$ as the temperature is decreased down to T_c, the proposed mechanisms leading to softening are significantly different. On the one hand, the Brillouin scattering [3] data have been analyzed using a proper ferroelastic model assuming that the strain combination $e_s = \alpha_1(e_1 - e_2) + \alpha_6 e_6$ is the order parameter. On the other hand, the ultrasonic velocity measurements [7] have been interpreted within the framework of a pseudo-proper ferroelastic model driven by another type of order parameter. To resolve this issue, we recently published a detailed analysis of the elastic properties of $Rb_4LiH_3(SO_4)_4$ measured as a function of temperature and pressure [8]. On the basis of this numerical analysis, it has been proposed that the order parameter Q, which must belong to the same irreducible representation as the spontaneous strain, e_s [6] could be a low frequency Raman active B mode. Thus, motivated by this hypothesis and existing Raman scattering data [9], we present a new Raman scattering investigation of $Rb_4LiH_3(SO_4)_4$ between 60 and 285 K. These measurements enable us to clearly establish the pseudo-proper character of the ferroelastic phase transition.

The remainder of the paper is organized as follows. In section 2 we briefly describe the experimental method used for this investigation, while the experimental results are presented in section 3. Section 4 is devoted to the analysis of the temperature dependence of the soft Raman mode in the context of a pseudo-proper ferroelastic transition. Finally, a summary of the principal findings is presented in section 5.

2. Experimental procedure

Crystals used in the experiments were grown in the Crystal Physics Division, Faculty of Physics, at Adam Mickiewicz University, Poland [3]. Laue x-ray diffraction was used to determine the crystal orientation. Prior to Raman scattering experiments, samples were ground with abrasive slurry using a mixture of glycerin and silicon carbide grain and then polished with a soft piece of cloth in order to minimize surface scattering. The sample dimensions were typically $3 \times 5 \times 0.35$ mm^3.

The laser light for Raman scattering measurements was generated by an argon-ion laser (Spectra Physics, series 2000) whose wavelength output was set to 514.5 nm. The power of

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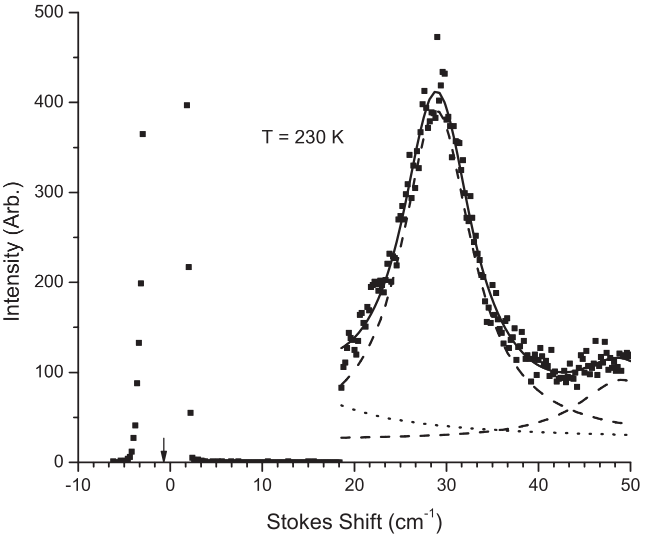

Figure 1. Polarized Raman spectrum at 230 K with back-scattering geometry for $Rb_4LiH_3(SO_4)_4$. The spectra are fitted using a Gaussian profile for the Rayleigh line contribution (dotted line) and two Lorentzian functions (dashed lines) for the observed Raman modes centered at ∼29 and ∼49 cm^{-1}. Here, the arrow indicates the position of the Rayleigh line.

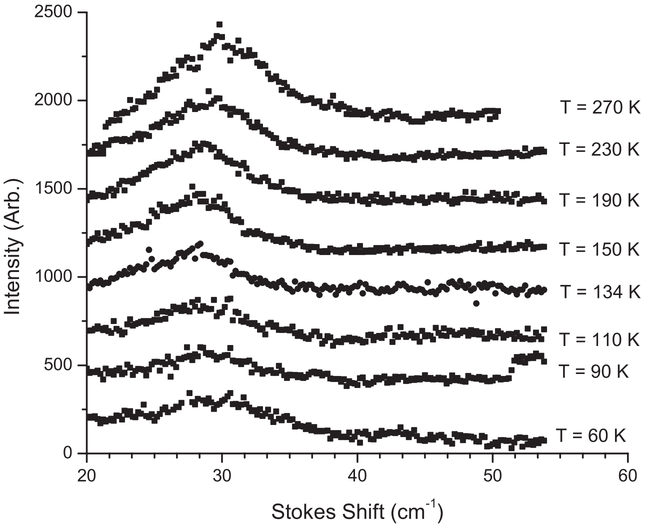

Figure 2. Raman spectra of the B symmetry mode at ∼30 cm^{-1} for $Rb_4LiH_3(SO_4)_4$ from 20 to 295 K. The frequency of the B mode decreases as the temperature is decreased down to $T_c = 134$ K and increases with further decrease in temperature.

the incident light was approximately 100 mW. The scattered light was detected using a data collection and acquisition system consisting of a double-grating spectrometer (Spex Industries Inc., model 1401), a cooled-photomultiplier tube (RCA, model 31034), an amplifier–discriminator (Princeton Applied Research, model 1120), and a photon counter (Princeton Applied Research, model 1109).

To perform experiments under vacuum in the temperature range from 60 to 285 K, a two-stage closed cycle helium refrigerator system (APD Cryogenics Inc., model HC2) was used. The temperature of the sample was regulated using a cryogenic temperature controller (LakeShore Cryotronics, model DTC 500) to a stability of 0.03 K.

3. Results

Raman measurements on $Rb_4LiH_3(SO_4)_4$, as a function of temperature, have already been reported [9]. In particular, this study provides the classification of the observed Raman modes into their symmetries (A, B, and E). The authors also present data which indicate that the B mode at 31 cm^{-1} shows slight softening in the paraelastic phase, while other modes are temperature independent. Thus, in order to determine whether the observed softening is consistent with a pseudo-proper ferroelastic phase transition, we present a series of Raman measurements obtained between 60 and 285 K. As the Raman tensor B mode associated with point group 4 is [10]

$$\begin{bmatrix} c & d & \cdot \\ d & -c & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}, \tag{1}$$

back-scattering geometry, with polarizations along [110] and [$\bar{1}$10] for incident and scattered light, was used to measure the low frequency vibrational B mode around ∼30 cm^{-1}. In order to accurately determine the frequency shift of the B mode relative to the laser line, an attenuator was used to permit recording of the laser spectral profile without saturating the detector. This explains why the Raman spectrum shown in figure 1, for $T = 230\ K$, displays almost no amplitude between 2 and 18 cm^{-1}. The frequency of the B mode was then determined by fitting the spectra using a Gaussian profile for the Rayleigh line and two Lorentzian functions for the modes observed at ∼29 and ∼49 cm^{-1}.

The Raman spectra between 60 and 285 K are presented in figure 2. As shown, the frequency of the B mode slightly decreases as the temperature is decreased down to T_c, while it increases with further decrease in temperature. Typically, the frequency of the B mode is 30.6 cm^{-1} at 285 K, going down to 28.3 cm^{-1} at $T = 134$ K, and back up to 30.3 cm^{-1} at 60 K.

4. Pseudo-proper ferroelastic Landau model

As pointed out, different models (proper and pseudo-proper) have been proposed in order to account for the elastic properties of $Rb_4LiH_3(SO_4)_4$ [3, 7]. Since then, the numerical analysis of the temperature dependence of the soft acoustic mode, presented in [8] (see figure 7), has given further evidence that $Rb_4LiH_3(SO_4)_4$ displays the characteristics of a pseudo-proper ferroelastic compound. Thus, according to group theory [6], the transition could be driven by the softening of a B-symmetric mode belonging to the point group 4. In that context, the expansion of the Landau Gibbs free energy, in terms of the normal vibration coordinates u of the B mode, can be written as

$$G_L = \tfrac{1}{2} m \omega_o^2 u^2 + \tfrac{1}{4} B u^4. \tag{2}$$

Here, the first term represents the energy of uncoupled oscillators of mass m and frequency ω_o. As usual, the only temperature-dependent coefficient, in this case $m w_{\mathrm{o}}{}^{2}$, is given by

$$m w_{\mathrm{o}}{}^{2} = a(T - T_{\mathrm{o}}). \qquad (3)$$

In order to account for the temperature dependence of the soft acoustic mode, other contributions such as elastic energy G_{el} and terms for coupling between acoustic and optical modes must also be considered. For simplicity, dealing with only one effective strain e_{s}, the elastic energy G_{el} reduces to

$$G_{\mathrm{el}} = \tfrac{1}{2} C_{\mathrm{s}} e_{\mathrm{s}}^{2} \qquad (4)$$

with C_{s} representing the elastic constant of the soft acoustic mode. Considering that, for a pseudo-proper ferroelastic transition [6], e_{s} and u must belong to the same irreducible representation, the dominant coupling energy term corresponds to the bilinear combination

$$G_{\mathrm{c}} = \gamma e_{\mathrm{s}} u. \qquad (5)$$

As we now show, the total free energy

$$G_{\mathrm{t}} = G_{\mathrm{L}} + G_{\mathrm{el}} + G_{\mathrm{c}} \qquad (6)$$

can be used to account for the temperature dependence of the order parameter u, the strain e_{s}, the soft optical mode, and the soft acoustic mode. Minimization of the total free energy with respect to u and e_{s} yields the relation

$$e_{\mathrm{s}} = -\frac{\gamma}{C_{\mathrm{s}}} u \qquad (7)$$

with

$$u = \sqrt{\frac{a(T_{\mathrm{o}} - T)}{B} + \frac{\gamma^{2}}{B C_{\mathrm{s}}}}. \qquad (8)$$

Due to the bilinear coupling term, the transition temperature

$$T_{\mathrm{c}} = T_{\mathrm{o}} + \frac{\gamma^{2}}{a C_{\mathrm{s}}} \qquad (9)$$

is renormalized relative to the uncoupled value T_{o}. Equation (7) also indicates that the temperature dependence of the strain e_{s} is identical to that of the order parameter u. For that reason, the distinction between a proper and a pseudo-proper phase transition, based on elastic measurements alone, is sometimes subtle. The solution for the elastic constant is obtained using [11]

$$C_{\mathrm{s}}^{*} = \frac{\partial^{2} G_{\mathrm{t}}}{\partial^{2} e_{\mathrm{s}}} - \left(\frac{\partial^{2} G_{\mathrm{t}}}{\partial e_{\mathrm{s}} \partial u}\right)^{2} \left(\frac{\partial^{2} G_{\mathrm{t}}}{\partial^{2} u}\right)^{-1} \qquad (10)$$

and, hence,

$$C_{\mathrm{s}}^{*}(T) = \begin{cases} C_{\mathrm{s}} - \dfrac{\gamma^{2}}{a(T - T_{\mathrm{c}}) + \frac{\gamma^{2}}{C_{\mathrm{s}}}}, & T > T_{\mathrm{c}}, \\ C_{\mathrm{s}} - \dfrac{\gamma^{2}}{2a(T_{\mathrm{c}} - T) + \frac{\gamma^{2}}{C_{\mathrm{s}}}}, & T < T_{\mathrm{c}}. \end{cases} \qquad (11)$$

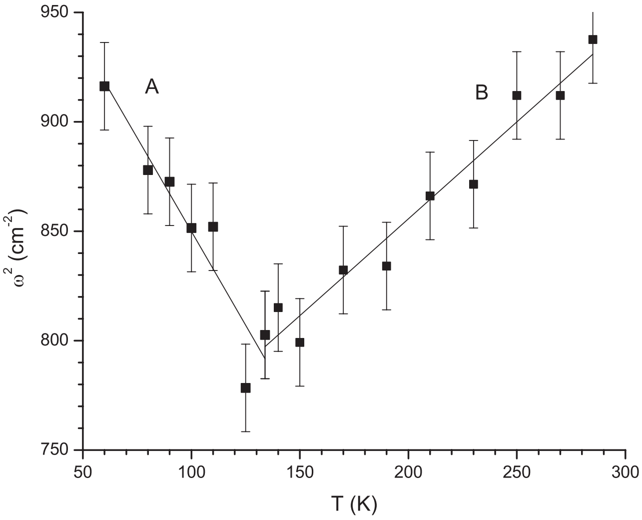

Figure 3. Temperature dependence of the frequency squared of the B/A active Raman modes of $Rb_4LiH_3(SO_4)_4$. Symbols correspond to data with continuous lines representing linear fits (see equation (13)).

We notice that, contrary to the case for a proper ferroelastic transition [8], the temperature dependence of the elastic constant associated with the soft acoustic mode is non-linear. However, in both cases complete softening at T_{c} is to be expected for a continuous phase transition. Finally, the frequency of the optical mode, associated with the order parameter, can be calculated using [12]

$$m\omega^{2} = \frac{\partial^{2} G_{e}}{\partial u^{2}} \qquad (12)$$

leading to

$$\omega^{2}(T) = \begin{cases} \dfrac{a(T - T_{\mathrm{o}})}{m}, & T > T_{\mathrm{c}} \\ \dfrac{2a(-T + T_{\mathrm{o}})}{m} + \dfrac{3\gamma^{2}}{m C_{\mathrm{s}}}, & T < T_{\mathrm{c}}. \end{cases} \qquad (13)$$

According to this simple model, the frequency square of the soft optical mode should change linearly with temperature. Thus, in order to confirm the pseudo-proper character of the ferroelastic transition, we present in figure 3 the square of the frequency of the B mode as a function of temperature. The slopes shown in figure 3 (continuous lines) correspond to 0.9 ± 0.1 cm^{-2} K^{-1} above T_{c} and -1.9 ± 0.3 cm^{-2} K^{-1} below the critical temperature. From the slope ratio, we find -2.1 which agrees well with the Landau prediction of equation (13). By extrapolating the high temperature fit down to the temperature at which the frequency goes to zero, we find $T_{\mathrm{o}} = -868$ K. As T_{o} represents the transition temperature in the absence of coupling, the temperature difference $T_{\mathrm{c}} - T_{\mathrm{o}}$ can be used to estimate the strength of coupling between the soft acoustic and optic modes. In comparison with those of other pseudo-proper ferroelastics, the coupling strength obtained for $Rb_4LiH_3(SO_4)_4$, $T_{\mathrm{c}} - T_{\mathrm{o}} = 1002$ K, is significantly larger than $T_{\mathrm{c}} - T_{\mathrm{o}} = 163$ K for $BiVO_4$ [13], $T_{\mathrm{c}} - T_{\mathrm{o}} = 161$ K for LaP_5O_{14} [14], and $T_{\mathrm{c}} - T_{\mathrm{o}} = 137$ K for $KH_3(SeO_3)_2$ [15].

5. Conclusion

Our Raman scattering measurements reveal that the B mode at 31 cm^{-1} shows softening. As shown, the square of the frequency of the soft mode changes linearly as a function of temperature, both below and above T_c. Moreover, the ratio of the slopes for ω^2 versus temperature is found to be -2.1, consistent with the prediction from a Landau model for a pseudo-proper ferroelastic transition. These measurements indicate that the phase transition at $T_c = 134$ K is indeed driven by the softening of this B mode. Coupling between vibrations associated with this soft optical mode u with the strain deformation e_s, belonging to the same irreducible representation, simultaneously leads to complete softening of the elastic constant C_s coupled to e_s. However, as pointed out in this paper and in [8], contrary to the case for a proper ferroelastic transition, the temperature dependence of the soft elastic constant should be non-linear.

It should be noted that the ferroelastic compound $(NH_4)_4LiH_3(SO_4)_4$, just like $Rb_4LiH_3(SO_4)_4$, has also been analyzed within the framework of a proper ferroelastic model [17, 16]. However, considering that this isomorphic compound shows elastic properties very similar to those of $Rb_4LiH_3(SO_4)_4$, it is possible that the character of the transition is also pseudo-proper. Thus, in order to identify the true nature of the transition at $T_c = 232$ K, Raman measurements are required.

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