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Raman studies of lattice vibrations in $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ and $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$ single crystals

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Abstract. The Raman scattering technique was used to study lattice vibrations in single crystals of $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$, from 100 to 295 K, covering their 4→2 structural phase transitions. All of the Raman modes of $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$ were found not to be affected by the transition. In the case of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ a slight softening of the B mode (at 31 cm^{-1}) was observed in the paraelastic phase.

1. Introduction

Recently a number of papers have been published on investigations of crystals of the general formula $\text{A}_4\text{LiH}_3(\text{BO}_4)_4$ where $\text{A} = \text{Rb}$ or K and $\text{BO}_4 = \text{SO}_4$ or SeO_4 [1-9]. In several of these materials an interesting phase sequence, leading to the appearance of ferroelastic phases, was reported to occur [1, 3, 5-7].

The present authors [6] have reported Brillouin scattering studies of $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ and $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$ (abbreviated henceforth as RLHS and KLHS, respectively). Both crystals are known to exhibit structural phase transitions from the tetragonal point group 4 to the monoclinic point group 2. From x-ray investigations [10, 11], it was found that RLHS and KLHS are isomorphic and belong to the space group $P4_1$ or $P4_3$ with $Z = 4$, $a = 7.623, 7.403\text{ \AA}$ and $c = 29.483, 28.725\text{ \AA}$, respectively.

For a phase transition to be ferroelastic, the necessary condition is a change of the crystallographic system [12]. This is usually accompanied by the onset of an elastic order parameter (spontaneous strain) which, in turn, leads to anomalous temperature behaviour of the elastic properties. Such changes have been observed, for RLHS, in various different kinds of experiments such as: observation of ferroelastic domain structure [7] sensitive to the mechanical stress, and investigations of elastic properties using the series impedance method [7], ultrasonic [13, 14] and Brillouin scattering [5, 6] techniques.

The characteristic feature of RLHS, as observed by the Brillouin technique, was incomplete softening of the soft elastic constant c_{25} [5, 6]. A theoretical model, given by Mroz *et al* [6], was based on the Landau expansion of the primary (e_1-e_2) and secondary (e_6) order parameters with additional coupling to the spontaneous polarization P_5 . This model explains both (1) the crossover behaviour of the function

$P_s(T)$ characterized by a change from linear dependence, in the ferroelastic phase, to quadratic in the paraelastic phase, and (2) the incomplete softening of c_{2s} at $T_c \simeq 130$ K.

In the case of KLHS, ferroelasticity was not confirmed and the only indication of a phase transition was a slight change in slope of the velocity of L phonons versus temperature at $T_c \simeq 115$ K [4,6].

As is well known, coupling between the soft acoustic and optic phonons may involve a temperature anomaly, around T_c , for the optical mode of the same symmetry as predicted by group theory [15]. Such behaviour was observed for several ferroelastic phase transitions [16–21].

The present investigation was undertaken to: (i) determine whether the transition in RLHS is the proper one according to the classification proposed by Toledano *et al* [22] or whether an order parameter other than spontaneous strain is involved, as well as (ii) compare the polarized Raman spectra of KLHS and RLHS in a wide temperature range and study the differences in lattice dynamics leading to 'hard' behaviour of KLHS.

2. Experimental procedure

Single crystals of KLHS and RLHS were grown, at about 315 K, from the appropriate acid aqueous solutions. The samples were prepared in the form of cubes ($4 \times 4 \times 4$ mm³). The edges of the cubes corresponded to the crystallographic axes a , b , c respectively.

The room temperature Raman spectra of the lattice vibrations were recorded in the frequency range from 0 to 250 cm⁻¹, using a JEOL JRS-S1 Raman spectrometer with 2 cm⁻¹ spectral slit width. The spectra were excited by 488 nm radiation from an argon-ion laser at powers not exceeding 200 mW.

The temperature changes of the lattice vibrations were measured, using a Spex 14018 Raman spectrometer with an instrumental resolution of about 1.5 cm⁻¹ at 514.5 nm. The scattered light was detected by a cooled phototube (RCA 31034) and processed by a photon-counting system (PAR 1120 Amplifier Discriminator and PAR 1109 Photon Counter). The measurements were performed, from 100 to 295 K, using a liquid-nitrogen cryostat as described in a previous paper [23]. The sample temperature was regulated with a THOR Cryogenics (3010 II) controller to a stability of ± 0.03 K.

3. Results and discussion

3.1. Room temperature spectra

The Raman tensors for the tetragonal point group 4 are

$$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix} \quad \begin{pmatrix} c & d & . \\ d & -c & . \\ . & . & . \end{pmatrix} \quad \begin{pmatrix} . & . & e \\ . & . & f \\ e & f & . \end{pmatrix} \quad \begin{pmatrix} . & . & -f \\ . & . & e \\ -f & e & . \end{pmatrix} .$$

$A(z)$
 B
 $E(x)$
 $E(y)$

Thus a combination of three scattering geometries allows for classification of all Raman lattice vibrations into the symmetry species A, B and E. These sets of polarized Raman spectra for both KLHS and RLHS are given in figure 1. The Porto notation $k_i(e_i, e_s)k_s$ was used, where k_i and k_s are the wave vectors and e_i and e_s are the unit vectors in the polarization directions of the incident and scattered light, respectively.

The isomorphism of the materials, as postulated from the x-ray studies, is reflected in the Raman spectra. The spectra presented in figure 1 differ from each other, sometimes considerably so, especially for those of E symmetry. These differences are, however, not of primary importance and for the most part involve changes in the intensity ratios of the neighbouring peaks of the same symmetry. A general tendency is a 10–20% increase in the frequency of all lattice vibrations observed for KLHS relative to RLHS. This is reasonable when taking into account the difference in masses of K and Rb atoms. Additional Raman bands appear at 181 cm^{-1} for KLHS and 170 cm^{-1} for RLHS in the $Z(YY)X$ and $Y(XX)Z$ geometries indicating that they may belong to A or B symmetry species.

Pairs of corresponding modes of the A, B and E symmetries for KLHS and RLHS have been collected in table 1. Table 1 also contains the ratios of the frequency pairs $\nu_{\text{RLHS}}/\nu_{\text{KLHS}}$. This ratio varies from 0.74 to 0.92 and may be understood as a measure of the contribution of the K or Rb sublattice vibration to a given normal vibration.

Table 1. Frequencies (in cm^{-1}) and symmetry species of the Raman lattice vibrations in $\text{K}_4\text{LiH}_3(\text{SO}_4)_4$ and $\text{Rb}_4\text{LiH}_3(\text{SO}_4)_4$ at room temperature: $\beta = \nu_{\text{RLHS}}/\nu_{\text{KLHS}}$.

Mode	A			B			E		
	KLHS	RLHS	β	KLHS	RLHS	β	KLHS	RLHS	β
ν_1	25	19	0.76	21	17	0.81	37	28	0.76
ν_2	38			42	31	0.74	48	38	0.79
ν_3	57	52	0.91	60	49	0.82	66	50	0.76
ν_4	77	63	0.82	78	63	0.81	78	60	0.77
ν_5	88	74	0.84	104	94	0.90	115	98	0.85
ν_6	117	99	0.85	123	107	0.87	165	151	0.92
ν_7	181 ^a	170 ^a	0.94	150	124	0.83			
ν_8				181 ^a	170 ^a	0.94			

A or B symmetry species.

It is worth noticing that for KLHS the polar modes of A and E symmetries are better separated than those of RLHS. This may be due to the higher dispersion of the TO and LO mode frequencies, which occurs when long-range forces are favoured over short-range ones [24]. Such dominance of the long-range forces may well be the lattice-stabilizing factor, making the formation of the ferroelastic phase in KLHS difficult or even impossible.

3.2. Temperature dependence investigations

Temperature investigations of the lattice vibrations of RLHS and KLHS were carried out from 100 to 295 K. Most of the observed modes, including all of those of E symmetry, were found to be independent of temperature, over the entire temperature range. For a few modes, namely, A (ν_5, ν_6) of RLHS and A (ν_5, ν_6) and B (ν_5, ν_6) of KLHS, a linear increase in frequency (6 to 9 cm^{-1}) was found, while lowering the temperature from 295 to 100 K. No frequency changes were noted at T_c .

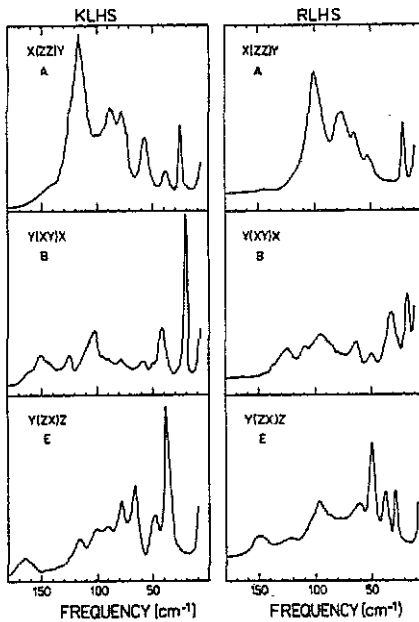


Figure 1. Polarized Raman spectra of $K_4LiH_3(SO_4)_4$ and $Rb_4LiH_3(SO_4)_4$ single crystals ($T = 295$ K).

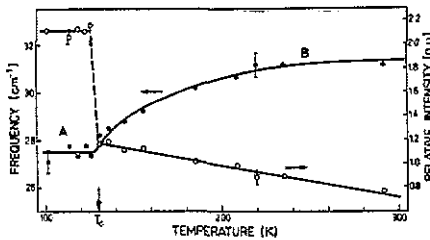


Figure 2. Temperature dependences of frequency ν_2 of the B mode in $Rb_4LiH_3(SO_4)_4$ (closed dots) and the relative integrated intensity (open dots).

The symmetries of the Raman modes, however, change at T_c according to the correlation diagram of the $4 \rightarrow 2$ phase transition. The A and B modes of the tetragonal phase become those of A symmetry of the monoclinic phase, whereas the doubly degenerate E modes become those of B symmetry.

By applying group theory, it was shown [15, 26] that the $4 \rightarrow 2$ transition may be driven by the instability of the B symmetry optic mode in the prototype phase 4. In fact, in the case of RLHS it was found that ν_2 (B mode at 31 cm^{-1}) was dependent on temperature. The frequency of this vibration changes very little between 295 and 230 K but then falls to 27 cm^{-1} at $T_c = 130$ K. Below T_c this mode becomes a vibration of A symmetry with its frequency constant down to 100 K. Moreover, it was found that the relative integrated intensity (with respect to that of ν_1 of the same symmetry) of this mode was strongly dependent on temperature, showing a step-like increase at 130 K upon lowering the temperature. This was accompanied with an approximately 20% decrease of the full-width-at-half-maximum FWHM linewidth at T_c . Both the frequency and relative intensity of this mode versus temperature are

shown in figure 2. The observed softening of the ν_2 mode is relatively weak when compared to the temperature dependence of soft Raman modes in other ferroelastic materials. For example, the soft optic mode in BiVO_4 decreases from 45 to about 30 cm^{-1} at T_c , in the temperature range of the paraelastic phase [17] corresponding to the softening of RLHS.

Another Raman mode of RLHS affected by the transition is ν_5 of symmetry B (at 94 cm^{-1}). The frequency of this mode is linearly temperature dependent in the paraelastic phase and then abruptly increases from 97 cm^{-1} , at T_c , to about 100 cm^{-1} at 100 K. Because of high inaccuracy in the measurements, due to low intensity and large linewidth at low temperatures, ν_5 versus temperature was not plotted here.

4. Summary

Preliminary Raman studies of the low-frequency optic phonons in KLHS and RLHS are reported. From room temperature spectra of different geometries, it may be concluded that the crystal lattice of KLHS is dominated by long-range forces and may be a reason for its 'hard' optical and acoustical behaviour. The phase transition did not appear to exhibit any effects on the KLHS Raman modes.

In the case of RLHS, it was found that two modes of B symmetry in the paraelastic phase showed some critical behaviour. The most interesting is the band at 31 cm^{-1} , which showed slight softening while approaching T_c from above. In addition, the relatively low value of the $\nu_{\text{RLHS}}/\nu_{\text{KLHS}}$ frequency ratio for this mode (see table 1) may indicate a contribution of the Rb sublattice in the formation of ferroelasticity.

From the results obtained, the phase transition in RLHS, which is characterized by incomplete softening of the acoustic and slight softening of the optic modes, may be classified as intermediate between BiVO_4 , on the one hand, and LaNbO_4 [27] on the other. In the former case, Pinczuk *et al* [17] observed very strong coupling between a distinctly soft optic and a completely soft acoustic mode, whereas the latter case is an example of a ferroelastic phase transition with no soft optic mode.

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