Ordering and symmetry effects in RbLiSO$_4$: A Raman study

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Abstract. Ordering effects in RbLiSO$_4$ have been studied using Raman scattering. The Raman spectra obey monoclinic selection rules below 439 K only, suggesting that a complete monoclinic order appears in this temperature range (in connection with birefringence results), while above 439 K the various existing phases (even when monoclinic) behave, from a Raman point of view, as if they were subjected to an orthorhombic disorder. Nevertheless, precursor effects in the high temperature phases have been detected through weak, broad and theoretically forbidden lines which are tentatively interpreted as arising from a pseudo-second-order Raman effect.

1. Introduction

Structural phase transitions in AA′BX$_4$ compounds deriving from tridymite structure seem to involve mainly rotations of the BX$_4$ tetrahedra. However, contrary to K$_2$SeO$_4$ for which the displacive character of the transitions has been clearly established [1], the dynamics of other members of this family, such as K$_2$ZnCl$_4$ [2] or KLiSO$_4$ [3, 4] are not well understood and a unified view of AA′BX$_4$ compounds is still missing.

Rubidium Lithium Sulphate (RLS) undergoes many structural transitions between 439 and 477 K. It belongs to the monoclinic point group $P112_1/n$ (C_{2h}^5; $Z = 4$) at room temperature (phase V) and is orthorhombic ($Pmcn$–D_{2h}^{16}; $Z = 4$) above 477 K (phase I). Phases IV ($439 < T < 458$ K) and III ($458 < T < 475$ K) are known to be monoclinic (respectively $P11n$–C_s^2; $Z = 20$ and $P2_1/c11$–C_{2h}^5; $Z = 8$) and phase II ($475 < T < 477$ K) exhibits an incommensurate modulation [5, 6]. Nevertheless, it should be noticed that even in the monoclinic phases, the distortion of the lattice from the orthorhombic structure is small since the monoclinic angles are very close to 90° [5]. Moreover, the b/a ratio of the lattice parameters is about 1.73 in all phases, i.e. the Bravais lattice is almost hexagonal. Indeed, like many compounds of the AA′BX$_4$ family, RbLiSO$_4$ has been described by some authors as a pseudo-hexagonal network of six-membered rings of SO$_4$ and LiO$_4$ tetrahedra [6].

The incommensurate (II), twofold (III) and fivefold (IV) superstructures of RLS have been recently interpreted [6, 7] as resulting from an ordering along the z direction of the SO$_4$ tetrahedra involving mainly a rotation of these ions about the c axis. In the high temperature disordered phase I, these ions occupy with an equal probability two positions related by the mirror of the $Pmcn$ structure. Furthermore, precursor effects have

Table 1. Detailed Raman selection rules for phases I and V of $RbLiSO_4$. T and R hold for translation and rotation external modes respectively, and the ν's for the internal modes of the SO_4^- ion.

Phase Polarisation	$P112_1/n$ (V)	$Pmcn$ (I)
xx, yy, zz	A_g modes: $3T_{Rb} + 3T_{Li} + 3T_{SO_4} + 3R_{SO_4}$ $+ \nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4$	A_g modes: $2T_{Rb} + 2T_{Li} + 2T_{SO_4} + R_{SO_4}$ $+ \nu_1 + \nu_2 + 2\nu_3 + 2\nu_4$
xy		B_{1g} modes: $T_{Rb} + T_{Li} + T_{SO_4} + 2R_{SO_4}$ $+ \nu_2 + \nu_3 + \nu_4$
zy	B_g modes: $3T_{Rb} + 3T_{Li} + 3T_{SO_4} + 3R_{SO_4}$ $+ \nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4$	B_{3g} modes: $2T_{Rb} + 2T_{Li} + 2T_{SO_4} + R_{SO_4}$ $+ \nu_1 + \nu_2 + 2\nu_3 + 2\nu_4$
zx		B_{2g} modes: $T_{Rb} + T_{Li} + T_{SO_4} + 2R_{SO_4}$ $+ \nu_2 + \nu_3 + \nu_4$

been observed in phase I through neutron diffuse scattering [8] and mono-Laüe experiments [9]. It could be expected these order–disorder precursor effects to appear in other experiments such as specific heat measurements or Raman scattering.

Only a few papers have been devoted to calorimetric [10, 11] or Raman [12, 13] studies. No precursor effect has been detected in the DSC study by Kurihama *et al* [10], and the work of Abello *et al* [11] deals with the 4 to 300 K temperature region, which is out of the scope of this study. A calorimetric investigation from 300 to 600 K has been recently undertaken in our group. The only Raman study on single crystals of RLS has been performed by Raghunata Chary *et al* [13]. These authors have found and attributed a small increase in the linewidth of the ν_2 mode within the phase II to the incommensurate modulation wave. The aim of this work is to report and discuss some aspects of the Raman spectra which are related to the distortion in the monoclinic phases, and to order–disorder effects through the successive phase transitions of RLS.

Crystals of $RbLiSO_4$ have been grown by slow evaporation at 35 °C of an aqueous solution of Rb_2SO_4 and Li_2SO_4, H_2O in stoichiometric proportions. Single domain parts have been selected using a polarising microscope, and samples of about $0.5 \times 1.5 \times 2$ mm^3 have been prepared from them. Raman experiments were performed using a Coderg T 800 triple monochromator. A spectral resolution of 3 cm^{-1} was chosen. The 5145 Å line of an argon laser was used as the excitation source, and the light power was monitored at a constant and rather small value (140 mW) during the experiments in order to allow reliable intensity measurements and to prevent any excessive heating of the sample from the laser beam. The temperature of the crystal was monitored at ± 0.1 K and the static dielectric susceptibility ε_a was recorded simultaneously as a signature of the phase transitions. Spectra in the geometrics $y(xx)z$, $y(xy)z$, $y(zx)z$ and $y(zy)z$ have been obtained for temperatures ranging from 297 to 530 K.

2. Symmetry effects

The Raman selection rules in the various phases of $RbLiSO_4$ have been previously established [13]. Those for phases I and V are detailed in table 1. It appears from this

Intensity (arbitrary units)

(a)

xx

xy
zy
zx

0   220

(b)

xx

xy
zy
zx

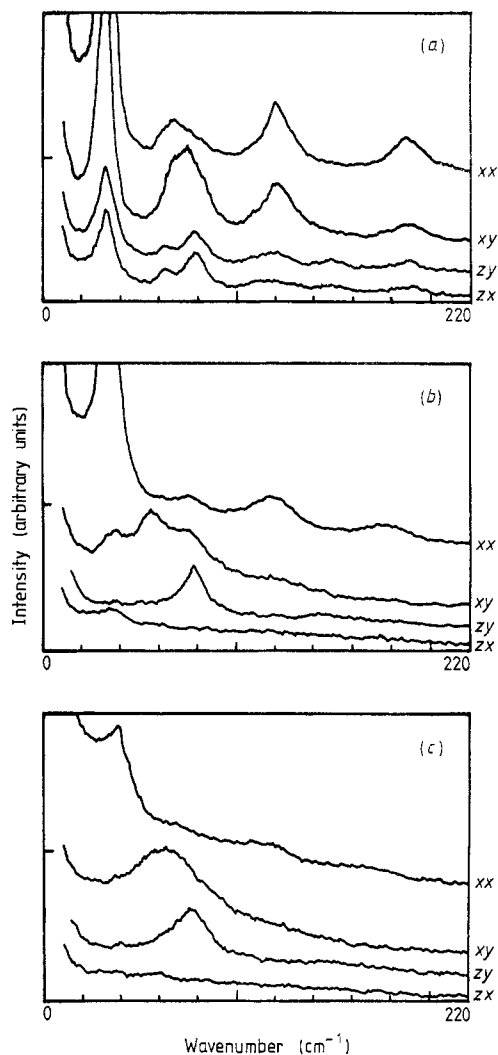0   220

(c)

xx

xy
zy
zx

0   220

Wavenumber (cm⁻¹)

Figure 1. Comparison of the Raman spectra obtained in the low frequency region for the four different geometries studied: (a) 297 K (phase V); (b) 451 K (phase IV); (c) 530 K (phase I).

table that xx and xy spectra should be different in the orthorhombic structure, while they should give rise to the same frequencies in phase V. The same remark holds for zy and zx geometries. More particularly, 3 ν_3 modes of $A_g(C_{2h})$ symmetry should be expected in phase V, splitting in two $A_g(D_{2h})$ modes for xx polarisation and one $B_{1g}(D_{2h})$ mode in the xy geometry in the orthorhombic phase. B_g modes of phase V behave in the same way, dividing into two ν_3–B_{3g} and one ν_3–B_{2g} modes in phase I. We have represented in figure 1 the low frequency spectra obtained in phases V, IV and I. It can be seen from figure 1(a) that monoclinic selection rules are obeyed in phase V, as expected and already reported by Raghunata Chary *et al* [13]. At higher temperatures, orthorhombic selection rules are followed, not only in phase I, but also in phase IV (figure 1(b)) which is known as monoclinic, and in which selection rules should have led to similarities between xx and xy spectra on one hand, and zx and zy spectra on the other hand.

The lattice modes of the sulphate ions have been analysed as a function of the temperature in the xx geometry. One of the translation modes shows a drastic increase in
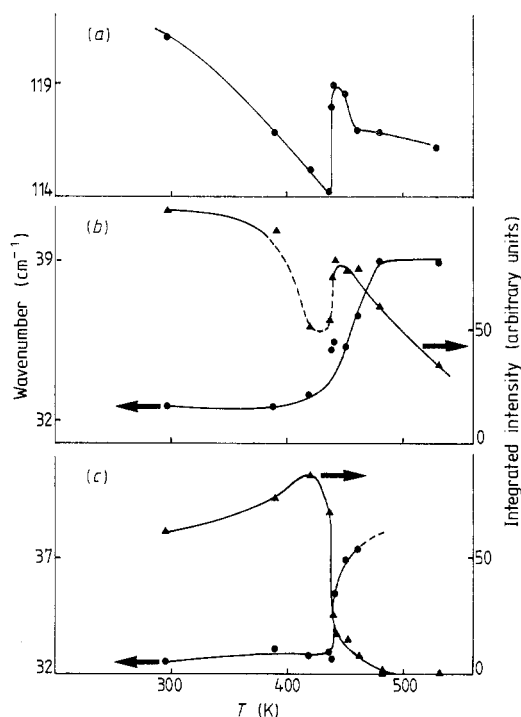
Figure 2. Frequency and integrated intensity variations with the temperature of low frequency modes: (a) T_{SO_4} in xx polarisation (frequency variation only); (b) T_{Rb} in xx polarisation; (c) T_{Rb} in xy polarisation.

frequency at 439 K (figure 2(a)), while the frequency of the libration mode decreases continuously from 187.5 to about 173 cm^{-1} as the temperature increases from 297 to 530 K.

Concerning Rb ions, their translation frequency in xx polarisation increases smoothly, contrary to what is usually observed (figure 2(b)). As far as the intensity of the rubidium translation mode is concerned, it must be kept in mind that the structure of these AA'BX$_4$ compounds derive from $P6_3/mmc$ (D_{6h}). This phase is only virtual for RbLiSO$_4$ (i.e. the melting of the crystal occurs before any transition to D_{6h} symmetry), but its pseudo-hexagonal character has been already underlined. If it were hexagonal, the Rb ions, situated on the inversion centre, should not give rise to any Raman line. These considerations could be a tentative explanation of the decreasing intensity of the Rb translation mode as the temperature is raised.

The behaviour of the corresponding mode in xy geometry is more interesting, as its intensity as well as its frequency exhibit an abrupt variation at 439 K (figure 2(c)). A fall in the intensity is obviously expected if this mode is assumed to be of A_g symmetry in the D_{2h} phase (see table 1). But it should happen at a temperature of 475 K rather than 439 K.

A quite similar aspect is presented by the variations of the integrated intensities of the ν_3 modes as a function of the temperature in the zx and zy geometries (figure 3). Table 1 shows that among the three ν_3 internal modes of B_g symmetry existing in phase V, one (B_{2g}) is predicted to appear in zx polarisation and the two other (B_{3g}) in zy polarisation as soon as the crystal structure becomes orthorhombic. It can be seen from figure 3 that for the lowest frequency mode (figure 3(a)), the intensity of the zx Raman line is about 3 or 4 times that of zy line at 530 K, while they were of equal intensities at room temperature. The same behaviour can be observed for the two other ν_3 modes, provided to reverse zx and zy (figure 3(b) and (c)). Selection rules are thus rather well
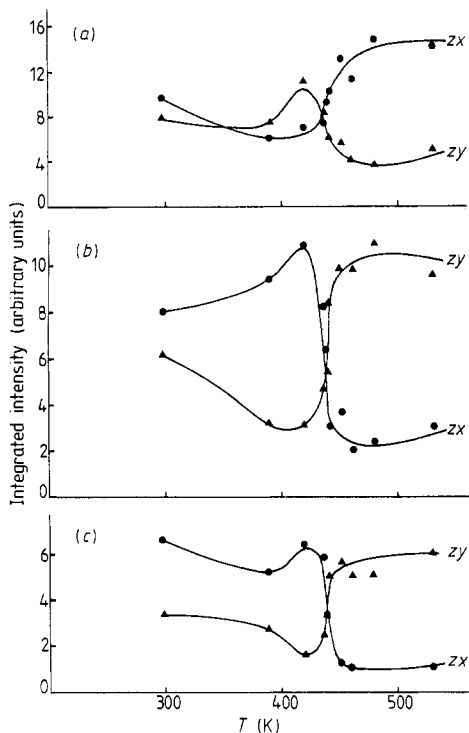
Figure 3. Temperature dependence of the integrated intensity of the ν_3 modes in zx and zy polarisation: (a) 1110 cm^{-1} mode; (b) 1150 cm^{-1} mode; (c) 1190 cm^{-1} mode.

obeyed if we put aside the partial character of the cancellation of the forbidden modes in D_{2h} symmetry which will be the subject of the next section. Nevertheless, the main event takes place at 439 K, as reported above for the lattice external modes.

It can be clearly concluded from what precedes that Raman spectra are sensitive to the V–IV transition only. Below 439 K, RbLiSO₄ follows monoclinic selection rules, while from 439 K to the highest temperature investigated (530 K), it looks as if it belonged to an orthorhombic point group. This transition in the optical Raman properties should be closely related to the abrupt variation of the angle of rotation of the optical index ellipsoid with respect to the crystallographic axes (a, b), which has been observed in a birefringence study of RbLiSO₄ [14]. The main discontinuity is observed at 439 K, and phase V exhibits a very strong monoclinic character from an optical point of view, when compared with the other phases, including phases IV and III which are also monoclinic (the rotation of the indicatrix with respect to the (b, c) axes is $0 \pm 0.3°$ in phase III where the monoclinic axis is a). For lack of any microscopic model, it is not possible to connect quantitatively the terms of the Raman tensor with those of the optical permittivity tensor.

3. Ordering effects

It has been reported in the previous section that the integrated intensities of the forbidden ν_3 modes in the D_{2h} phase do not fall to zero, contrary to what is normally expected. Furthermore, the linewidth of these forbidden lines is subjected to a steep increase at
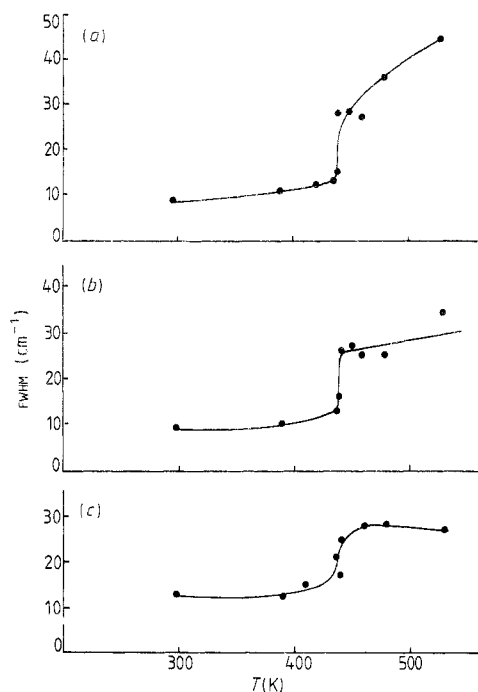
Figure 4. Temperature dependence of the full width at half maximum of the 'D_{2h}-forbidden' ν_3 modes: (a) $1110\,cm^{-1}$ mode; (b) $1150\,cm^{-1}$ mode; (c) $1190\,cm^{-1}$ mode.

439 K (figure 4). Conversely, the permitted lines do not exhibit any irregular behaviour: their full width at half maximum (FWHM) is about 10 to 15 cm^{-1} from 297 to 530 K, compared with the 25 to 45 cm^{-1} of the forbidden lines in D_{2h} phase. This excludes the possibility for the latter to be polarisation leaks of the former. It should be noticed once more that the structural transition at 439 K takes the prominent part as far as the broadening of the lines is concerned, since nothing seems to happen above this temperature, and more particularly within the III $\rightarrow$ II $\rightarrow$ I sequence of transitions.

Very recently, Kunishige and Mashiyama [6], in an extensive x-ray structural study, have estimated the mean-square amplitudes of the atoms in RbLiSO$_4$ from the relevant thermal parameters. In phase V, these amplitudes are proportional to the temperature. A strong departure from this linear behaviour is observed above 443 K, following these authors, and this deviation is much more pronounced for the oxygen atoms than for the others, suggesting that SO$_4$ tetrahedra are subjected to disorder from phase IV up to phase I.

In their neutron scattering study, Frey *et al* [8] have pointed out the existence of an '*l*-independent' diffuse scattering in phases III to I, with a maximum intensity coinciding with phase II. Furthermore, very broad maxima have been detected well above the II $\rightarrow$ I transition at positions $l = 1 \pm 0.4$. These observations have been tentatively interpreted in terms of a static ordering along the c direction.

Finally, very large precursor order effects have been detected in phase I during our birefringence study [14]. The deviation from the normal linear variation of Δn_{cb} as a function of the temperature has been interpreted as arising from order–disorder fluctuations which would persist at lower temperatures if the 477 K transition did not occur.

The following interpretation may be given of our light scattering experiments. The monoclinic order is definitively achieved in phase V only. From a Raman point of view,

the crystal behaves as if it were orthorhombic above 439 K. Nevertheless, a monoclinic ordering subsists in this temperature range and it is expressed through remanent Raman lines, the apparent damping constants of which are very large compared with those of the permitted lines for the orthorhombic phase. The microscopic nature of this ordering is mainly related to the rotation of the SO_4 tetrahedra about the c axis, as already stated by many authors. But the problem of its spatial extension seems to be more complicated if the experiments of Frey *et al* [8] and the present Raman study are taken into account.

The cluster approach has been very often used to explain precursor effects in the vicinity of order–disorder transitions. In our case, we should have to consider that the clusters involved are representative of phase V. Futhermore, they should exist not only in phase I, but also within the 439 to 477 K temperature interval since, according to our Raman observations, complete monoclinic ordering settles down only below 439 K.

Diffuse scattering experiments [8, 9] have shown that, in addition to localised maxima in the reciprocal space, a diffuse streak is observed in phases III to I, involving a continuous set of wavevectors along the c^* direction. It can be thought that superstructures are obtained when a particular value of this set becomes the main component of the long-range ordering within a defined temperature range. Our Raman experiments should be thus understood more realistically in terms of spatial and/or temporal correlations of the polarisability. Such an analysis has been developed and applied to the cubic-tetragonal transitions in $KMnF_3$ and $RbCaF_3$ by Bruce *et al* [15]. However, it should be emphasised that their treatment is relevant only when a soft mode is associated to the structural transition, as it is the case for the two aforementioned fluorides. In spite of this limitation, the temperature variations of the intensity and width of the hard E_g-modes in $RbCaF_3$ and $KMnF_3$ are quite similar to those reported in this paper for $RbLiSO_4$. The question of the validity of such a model when hard modes are coupled with a non-displacive order parameter, the wavevector of which extends over a wide range of q values, rather than with a soft mode of well defined wavevector q_s is still open. Nevertheless, the main qualitative results obtained by Bruce *et al* [15] may be, in many ways, applied to our Raman experiments. The spectra obtained at $T > 439$ K for the ν_3 modes can be tentatively interpreted as pseudo second-order Raman lines superimposed on the permitted first-order lines of the mean quasi-orthorhombic structure. The broadening of these pseudo second-order lines has to be attributed, following Bruce *et al* [15], simultaneously to the ν_3 modes dispersion and the non-zero q-width of the spatial correlation of the order parameter.

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