Ferroelastic LiCsSO4 Crystal. A Study of Structural Phase Transitions from Raman Phonon Spectra

Conference Paper · January 1991

DOI: 10.13140/RG.2.1.1315.6001

3 authors:

Devanarayanan Sankaranarayanan
University of Kerala
200 PUBLICATIONS **456** CITATIONS
SEE PROFILE

Gerardo Morell
University of Puerto Rico at Rio Piedras
238 PUBLICATIONS **2,395** CITATIONS
SEE PROFILE

Ram. S. Katiyar
University of Puerto Rico at Rio Piedras
901 PUBLICATIONS **17,949** CITATIONS
SEE PROFILE

Dr. S. Devanarayanan
30/7/1992

PROCEEDINGS OF THE KERALA ACADEMY OF SCIENCES

Vol. II

Editor
T.K.S. UNNITHAN

Associate Editors

Dr. V. P. BALAGANGADHARAN

Dr. G. M. NAIR

Thiruvananthapuram
1991

Proceedings of Kerala Academy of Sciences Vol. II. 1991

CONTENTS

FERROELASTIC $LiCsSO_4$ CRYSTAL : A STUDY ON STRUCTURAL PHASE TRANSITIONS FROM RAMAN PHONON SPECTRA

S.Devanarayanan*; Gerardo Morell ; R.S.Katiyar
Department of Physics, University of Puerto Rico,
San Juan, PR-00931, USA

*Permanent address:

Department of Physics,
University of Kerala
Thiruvananthapuam-695 581, INDIA

ABSTRACT

Temperature dependent first-order Raman Spectra were recorded on lithium cesium sulphate ($LiCsSo_4$) single crystal to study phase transitions. The Z(XX)Y and Z(XZ)Y geometries of scattering were examined in the temperature range 30 to 290 K at 25 different temperatures. Both low and high frequency Raman modes exhibited variations in either frequency or intensity of both with temperature. We observed the crystal to change its D_{2h}^{16} Normal (N-) phase at 202 K (T_I) and again at around 160 K (T_C) to the C-phase (Commensurate) belonging to the C_{2h}^5 symmetry of the crystal. The present study could identify the I-phase (incommensurate phase) to occur between T_I and T_C; and that this phase "locks-in" at the T_C. The lattice phonon at 44 cm^{-1} appearing below the T_C was found to soften with temperature till 30 K. This strongly suggests an "unlocking" type third phase transformation in the crystal at a still lower temperature.

INTRODUCTION

During the past 15 years a growing interest in incommensurate crystal phases has developed. Besides structural investigations, a lot of work has been devoted to the study of lattice dynamics of crystals by means of light scattering. When a given crystal has two or more phase transitions, these transitions should be investigated (not individually) collectively or in recognition of them as a system of inter-related events (AIZU, 1978). A phase transition that results from the appearance of either the occurrence of a soft mode behaviour or the appearance of new modes as one passes through it can be probed by means of Raman Spectroscopy (SCOTT, 1974; BALKANSKIT, LEITE & PORTO, 1976). However, study on the re-distribution of Raman intensity of degenerate polar modes

among different polarization configurations is another approach (which is not limited to the observation of mode frequency variation) has been utilized by some authors.

As is experimentally known L C S undergoes two phase transitions at 202 K and 160 K. At room temperature (N-phase) it belongs to orthorhombic with space group Pcmn a = 9.456 (1), b = 5.456 (1), c = 8.820 (3), A° and Z = (ALEKSANDROV, The N-phase undergoes a transition to the I-phase at the T_I of 202 K. Below the T_C (160K), in the monoclinic C-phase a = 9.379 (2), b = 5.423 (1), c = 8.834 (3) A°, r = 89^{0}d5 (1), Z = 4, p $112_1/n$ (C^{n}_{2h}). Analysis of the structure data indicates that the phase transitions involve ordering of tetrahedral SO_4 groups. A 'negative' anomaly in thermal expansion along the C-axis at the T_I was detected in the crystal. The absence of a latent heat of transition, the nature of the specific heat anomaly (discontinuity), and the structure data indicate the transition at the T_I to be a second order. The I-phase is ferroelastic. A temperature variation of Lithium ions in the nmr spectrum established further the transition at the T_I (HOLUJ, 1985). Some preliminary results herein have already been presented by us elsewhere. DEVANARAYANAN, 1991 b, c). So far only one work on the vibrational study in LCS has been reported (REGHUNATHA CHARY, et al 1985).

EXPERIMENTAL

Single crystals of LCS of optical quality were grown at 303K in a constant temperature bath by evaporation of an aqueous solution prepared in the stoichiometric ratio of AR quality $Li_2SO_4.H_2O$ and Cs_2SO_4. X-ray diffraction was used to identify the crystal axes.

stokes-shifted polarized first-order Raman spectra were obtained with an Argon 164 - ion laser working at 514.5 nm as the source and a Spex Industries double-grating monochromater which is locally modified by holographic gratings.

Spectra were recorded in the range 30-290K at 25 different values. Frequency calibration was achieved by measuring the attenuated Rayleigh line for each spectrum. A spectral resolution of 1.5 cm^{-1} was used. The sample was mounted in a DMX-1E Vacuum Shroud and using a Displex Model ^4He closed-cycle refrigeration system (CSA - 202 E). The temperature was monitored in the range by

a digital temperature controller unit, and the stability in temperature was at 0.5 K.

SPECTRAL DATA ANALYSIS AND RESULTS

The spectra of the crystal were obtained for the Z(XX)Y and Z(XZ)Y configurations of scattering at the various temperatures. The spectra and the relationship between the directions and polarizations of Ki, Ks & Kp are reproduction in Fig.1 and Fig.2,, respectively, for the Z(XX)Y and Z(XZ)Y geometries. It is known from group theory that the normal vibrational modes of a free sulphate ion (So_4^{2-}) of T_d symmetry belong to the species.

$$A_1 + E + 2F_2 :$$

with energies at 980, 450, 1104 and 620 cm^{-1}, respectively. In the N-phase of the LCS crystal the site symmetry of the So_2^{2-} ion is C_s; and all degeneracies are removed due to static field splitting, and these vibrations are called "internal" ones. In the D_{2h}^{16} phase, a factor group analysis gives a total of 84 modes of vibration. Of these, internal vibrations contribute for 36 whereas the lattice (external) modes of libratory type (of So_4) phonons give 12 and translatory phonons constitute 33 modes. In this A_g, B_{1g}, B_{2g} and B_{3g} species are expected to appear as Raman modes in the appropriate scattering geometries. In its monoclinic C_{2h}^5 phase the Raman phonons expected are A_g and B_g species.

The high energetic Raman active phonos seen in the spectra area V_1 = 1016 cm^{-1}, V_2 = 465 cm^{-1}, V_3 = 1110 cm^{-1} and V_4 = 627 cm^{-1}. These are the internal vibrations due to the relative motions of the constitutent atoms of the SO_4^{-2} ion which has strong bonding compared to the bonding between lattice points. V_1 is identified as the asymmetrical stretching mode and V_2 the symmetrical bending, whereas the totally symmetric stretching S-O vibration is V_3 and asymmetrical bending mode is V_4. This assignment which agrees well with the results reported in the literature (REGHUNATH CHARY, et al, 1985) is based on the observation that these differ not much from the free-ion values for T_d symmetry for the So_4^{2-} mentioned earlier.

Prominent among the various lattice frequencies observed in the spectra are the six modes at 455, 400, 109, 63, 50, and 44 cm^{-1}.

$$V_4^2\ (cm^{-2}) = 377856.5 \quad 41.6\ (T-T_c)$$

Of the lattice modes the one at 44 cm^{-1} (V_o) is of special interest to us. In the C-phase this mode with XX polarization obeys the equation

$$V_o(T)\ (cm^{-1}) = 31.7 + 0.0022\ (T-30) + 0.00023\ (T-30)^2.$$

The linear dependence of V_o (T) on T predicts a possible third structural phase transition of "unlock-in" type in the crystal at a temperature T_u below 20K. This mode V_o is identified as a 'soft' mode in the crystal. Fig.3 reproduces both the frequency and intensity variations with T of the soft mode V_o in its XX polarization.

CONCLUSIONS

In lithium Cesium sulphate crystal the present study on the Raman spectra revealed the lock-in of the incommensurate (I-) phase at the T_C of 160K as a change in frequency of the low energetic lattice modes at 44 cm^{-1} and 50 cm^{-1} and of the internal phonons V_1, V_2, V_3 and V_4. The phase transition at the T_{pI} of 202K is clearely observed as changed in the frequency of the phonons at 109 and 400 cm^{-1} as well as all the four internal modes. The most important result of the study is that the lowest frequency optical phonon at 44 cm^{-1} in the crystal has the features of the soft mode, and this predicts a possible phase change in the crystal at an "unlock-in" transition temperature, T_u below 20K.

ACKNOWLEDGEMENTS

This work was done with the support of the EPSCoR-NSF programme in the University of Puerto Rico. One of the authors (SD) would like to thank Prof. Alfredo Torruella, Chairman of the Physics Department for offering the post of Visiting Professor for the period 1989-'91.

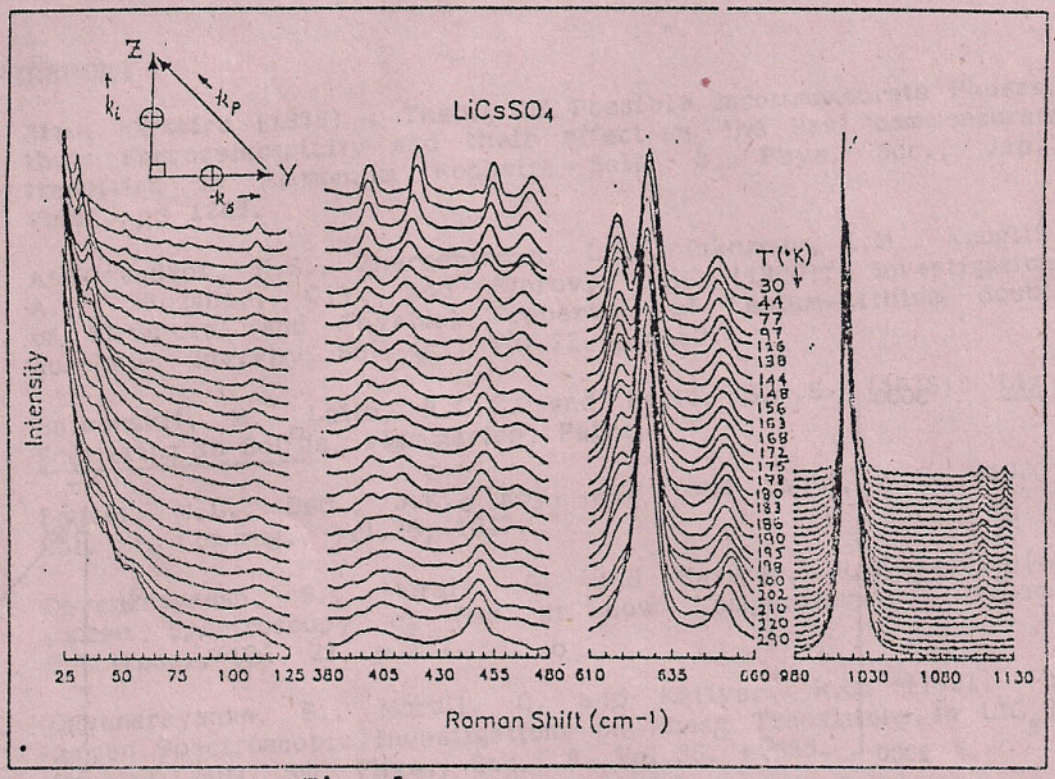
Z
Y
k_i
k_p
k_s
LiCsSO4
T(°K)
30
44
77
97
116
138
144
148
156
163
168
172
175
178
180
183
186
190
195
198
200
202
210
220
290
Intensity
25 50 75 100 125 380 405 430 455 480 610 635 660 980 1030 1080 1130
Raman Shift (cm⁻¹)

Fig. 1

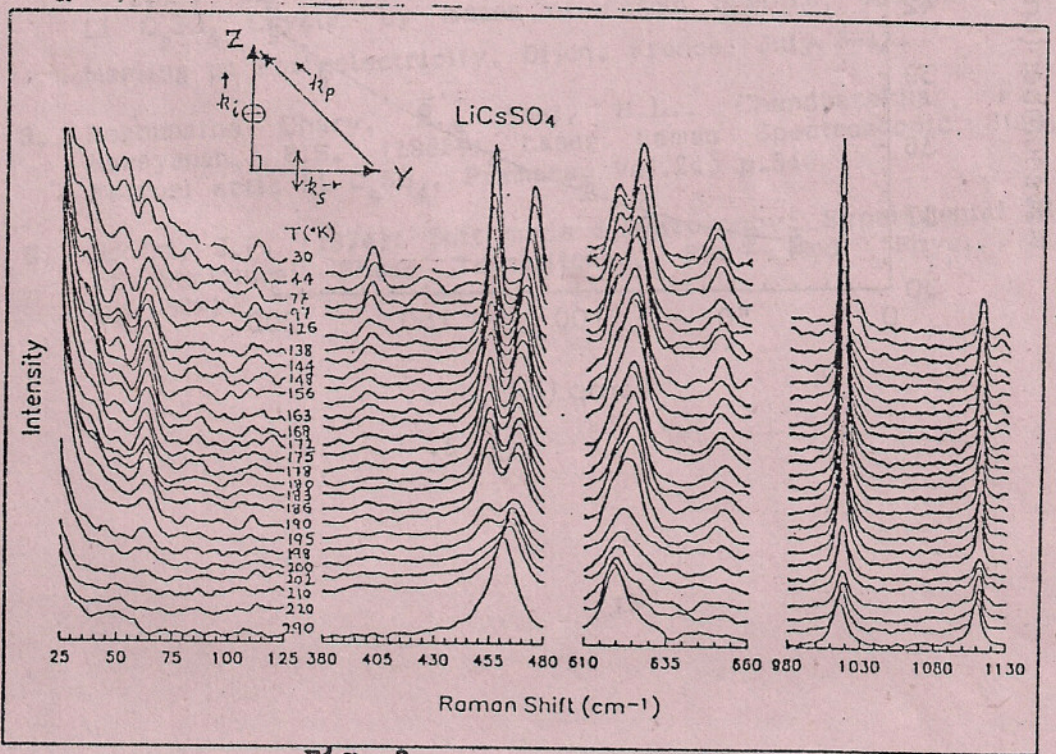
Z
Y
k_i
k_p
k_s
LiCsSO4
T(°K)
30
44
77
97
116
138
144
148
156
163
168
172
175
178
180
183
186
190
195
198
200
202
210
220
290
Intensity
25 50 75 100 125 380 405 430 455 480 610 635 660 980 1030 1080 1130
Raman Shift (cm⁻¹)

Fig. 2.

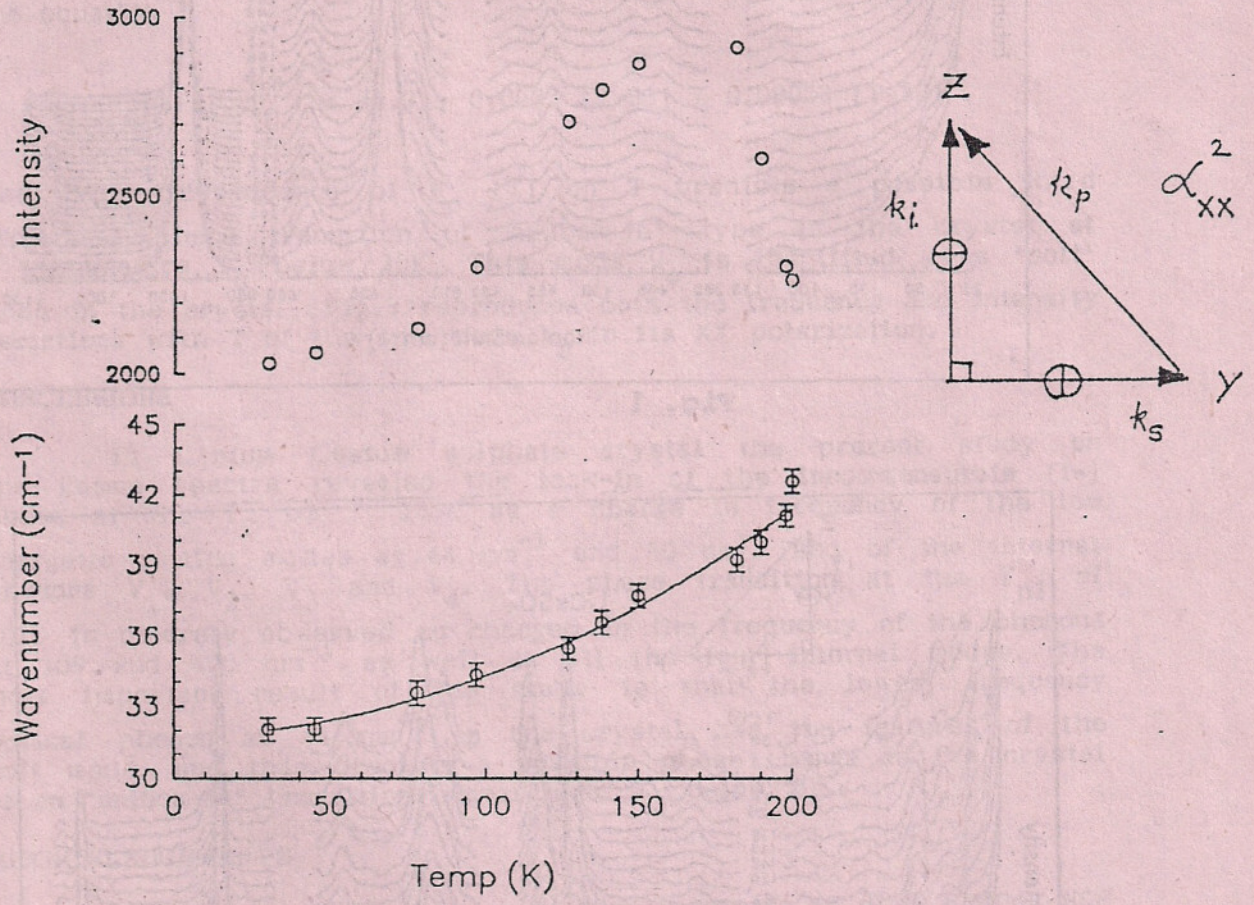
3000
2500
2000
Intensity
45
42
39
36
33
30
Wavenumber (cm−1)
0
50
100
150
200
Temp (K)
Z
k_i
k_p
α^2_{xx}
Y
k_s

Fig. 3.

REFERENCES

1. Aizu, Keitsiro (1978) : Theory of Possible Incommensurate Phases, their Ferrorelectricity and their effect on the Real commensurate transition in Ammonium Rochelle Salt, J. Phys. Soc., Jap., Vol44, pp 1248.

2. Alekisandrov, K.S., Zherrebtsova, L.I., Iskornev, I.M., Kruglik, A.I., Rozanov, O.V. and Flerov, I.N. (1980): Investigations of Structural and Physical Properties of Cesium-Lithium double sulphate, Sov.Phy. Sol. St., Vol.22, p.2150.

3. Balkanskii, M., Leite, R.C.C. and Porto, S.P.S. (1976): Light Scattering in Solids, Flammarion, Pairs.

4. Bansal, M.L., Deb., S.K., Roy, A.P. and Sahni, V.C. (1980): Sol. St. Commun., Vol.36, 1047.

5. Devanarayanan, S., Morell, G. and Katiyar, R.S. (1991)(a): Raman Spectroscopy of Beo at Low Temperatures, J. Raman Spectrosc., Vol. 22, p 312.

6. Devanarayanan, S., Morell, G. and Katiyar, R.S. (1991) (b): Raman Spectroscopic Investigations on Phase Transitions in LIC_sSO_4 Crystal, Bull. Am. Phys., Soc., 8, Vol.36, p.655.

7. Devnarayanan, S., Morell, G. and Katiyar, R.S. (1991) (c) : Study of Incommensurate to commensurate phas transition in Li C_sSO_4 Crystal by means of Raman Spectra, Seventh European Meeting on Ferroelectricity, Dijon, France, July 8-12.

8. Reghunatha Chary, B., Bhat, H.L., Chandrasekhar, P., and Narayanan, P.S. (1985): Laser Raman Spectroscopic Study of Ferroel artic Li C_sSO_4, Pramana, Vol.24, p.545.

9. Scotrt, J.F. (1974): Soft mode Spectroscopy: Experimental Studies of Structural Phase Transitions., Rev. Mod. Phys., Vol.46, pp. 83-128.

Proceedings of Kerala Academy of Sciences Vol. II. 1991

CONTENTS