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2008 J. Phys.: Condens. Matter 20 224004

(http://iopscience.iop.org/0953-8984/20/22/224004)

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **20** (2008) 224004 (5pp) doi:10.1088/0953-8984/20/22/224004

Surface phonons in LiCsSO$_4$ crystal studied by high-resolution Brillouin scattering

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Received 8 November 2007, in final form 14 December 2007
Published 13 May 2008
Online at stacks.iop.org/JPhysCM/20/224004

Abstract
In crystals of lithium–caesium sulfate some anomalies in the behaviour of certain surface phonons have been detected by surface Brillouin scattering. The anomalies of the first type have been interpreted as being related to a change in crystal symmetry at a phase transition, while the second type of anomalies has been found to be related to surface phonon interactions with a soft bulk mode.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Lithium–caesium sulfate crystal of the molecular formula LiCsSO$_4$ (LCS) belongs to the family of crystals with the general formula Me$^{\mathrm{I}}$Me$^{\mathrm{II}}$BX$_4$ [1]. This crystal undergoes a ferroelastic phase transition of second order at 202 K. In the high-temperature phase the crystal symmetry belongs to the orthorhombic $D_{2h}^{15} = Pmmm$ group, while in the low-temperature phase it belongs to the monoclinic $C_{2h}^{5} = P112/m$ group [2, 3]. The elastic properties of LiCsSO$_4$ have been studied by ultrasound spectroscopy [4, 5] and Brillouin spectroscopy [6, 7]. LCS crystal shows a soft acoustic bulk mode, which is characteristic of ferroelastic phase transitions. For this crystal the soft mode is determined by the c_{66} component of the elasticity tensor. The softening, almost to zero, of the bulk component c_{66} has been reported [5–7].

Brillouin spectroscopy permits determination of the elastic properties on the basis of the behaviour of bulk phonons propagating in a given material [8], while the surface phonons provide information on the near-surface layers of the material [9, 10]. The method that is applied also permits investigation of the behaviour of surface phonons in the material in which the bulk ferroelastic phase transition takes place.

This paper reports the velocities of the surface phonons propagating in the principal planes. Anisotropy of the phonons that are observed has been determined.

The aim of this paper was to characterize the behaviour of the surface phonons in the vicinity of the bulk phase transition in LCS crystal. Of particular interest was to determine the effect of the soft bulk phonon on the propagation of the surface phonons in the near-surface layer of a few hundred nanometres. The thickness of the near-surface region that was studied varied from 300 to 570 nm. By studying near-surface layers of different thicknesses, we aimed to answer the question whether the strong ferroelastic bulk phase transition is manifested on the crystal surface.

2. Experimental procedure

Single crystals of LiCsSO$_4$ of the size of a few 10 cm^3 and good optical quality were grown by the isothermal method at 315 K from a stoichiometric water solution. The crystal density was $\rho = 3.442 \times 10^3$ kg m^{-3} at room temperature [2]. The samples to be studied were in the size range of a few cm^3. LCS crystals are transparent, so to get reliable Brillouin data on their surface it was necessary to improve their reflectivity. This was achieved by deposition of a metallic film of about 40 nm in thickness. The film the permitted observation of surface phonons from the near-surface layer and did not disturb the frequency of the modes observed in the spectra for the crystal without the film [11, 12].

The behaviour of the surface phonons propagating in the LCS crystal was studied by high-resolution Brillouin spectroscopy. The working of the relevant spectrometer in a tandem system and made by JR Sandercock is described in [13, 14]. The arrangement of the experimental setup permits

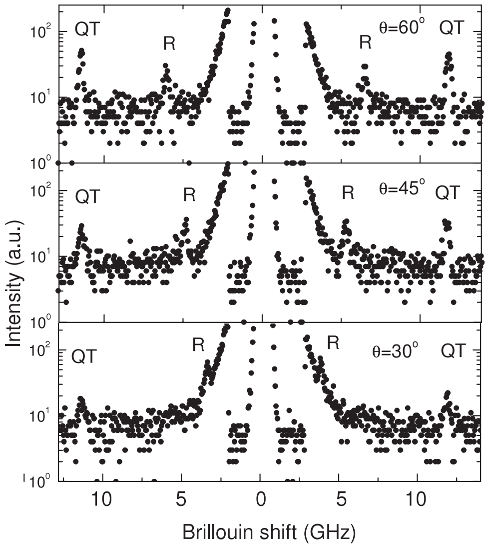

Figure 1. Brillouin scattering spectrum of the surface phonon propagating in the direction [001] in the plane (100) of the LCS crystal.

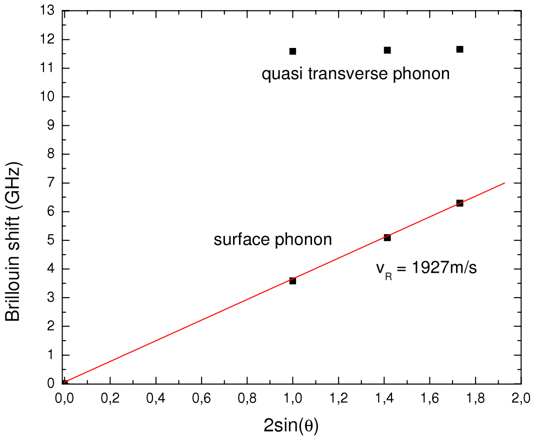

Figure 2. The Brillouin shift versus $2\sin(\theta)$ for the modes propagating in the direction [001] in the plane (100) in the LCS crystal.

Table 1. Velocities of surface phonons for LCS at RT.

Direction of propagation	Propagation plane	Velocity (m s^{-1})
[100]	(010)	2100 ± 10
[100]	(001)	1910 ± 10
[010]	(100)	2180 ± 10
[010]	(001)	1750 ± 10
[001]	(100)	1930 ± 10
[001]	(010)	1760 ± 10

simultaneous measurements in two geometries of scattering: 180° and 90° [15]. In our measurements the 180° geometry was used. The light source was an Nd:YAG single-mode diode-pumped laser with a power of 200 mW, emitting the second harmonic of the wavelength $\lambda = 532$ nm (Coherent Laser Group, Model 532). The samples were placed in a flooded nitrogen cryostat made by Janis Research Company, with temperature stability of 0.01 K.

3. Results and discussion

The elastic properties of crystals can be characterized by the bulk and surface Brillouin scattering spectra. On the basis of the Brillouin frequency shift the propagation rate of the surface phonons was found, which is typical of a given material [16]. The velocity of surface phonons, υ_R, can be found from the following expression:

$$\Delta\nu_R = \frac{2\sin\theta}{\lambda}\upsilon_R \qquad (1)$$

where $\Delta\nu_R$ is the Brillouin frequency shift of surface phonons, θ is the angle made by the incident beam to the normal to the surface, and λ is the laser wavelength.

Observations at different angles of the incident beam allowed us to get information on near-surface layers of different thicknesses. In our study the angle of beam incidence, θ, was varied in the range 20°–70°, so the thickness of the near-surface layer examined was 300–700 nm (from the crystal surface). By changing the beam incidence angle it was possible to study the effect of bulk modes on the behaviour of the surface phonons. Exemplary Brillouin scattering spectra of the surface phonon (R) propagating in the direction [001] in the plane (100) of the LCS crystal are shown in figure 1.

The position of the quasi-transverse (QT) mode does not change with the angle of beam incidence, which is typical of bulk modes. According to equation (1), the surface phonon velocity was determined on the basis of the linear dependence of the Brillouin shift on $2\sin(\theta)$; see figure 2.

The surface phonon velocities determined at room temperature (RT) in the principal directions in the three principal planes of the LCS crystal are given in table 1.

The phonon propagating in the [010] direction in the (100) plane has the greatest velocity, while the lowest velocity characterizes the phonon propagating in the [010] direction in the (001) plane.

The phonon propagation velocity determined from the Brillouin frequency shift is anisotropic. The distributions of the Brillouin frequency shift for the modes appearing in the spectra in the (001) plane in near-surface layers of 380 nm and 310 nm thickness are shown in figures 3(a) and (b), respectively.

The ferroelastic phase transition in $LiCsSO_4$ crystal takes place at about 202 K [2, 3]. The behaviour of particular surface phonons as a function of temperature was studied for different thicknesses of the near-surface layer. The Brillouin frequency shift of the phonon [100] propagating in the plane (010) in LCS is shown in figure 4.

The behaviour of the [100] phonon in the (010) plane in the vicinity of the phase transition point was found to depend on the thickness of the near-surface layer that was considered. In the layer with a thickness of 310 nm, a small increase in the Brillouin frequency shift was observed in the vicinity of the phase transition point. A distinct anomaly of a 7% decrease in the Brillouin shift was observed for a near-surface layer of 530 nm. The Brillouin shift determined from the

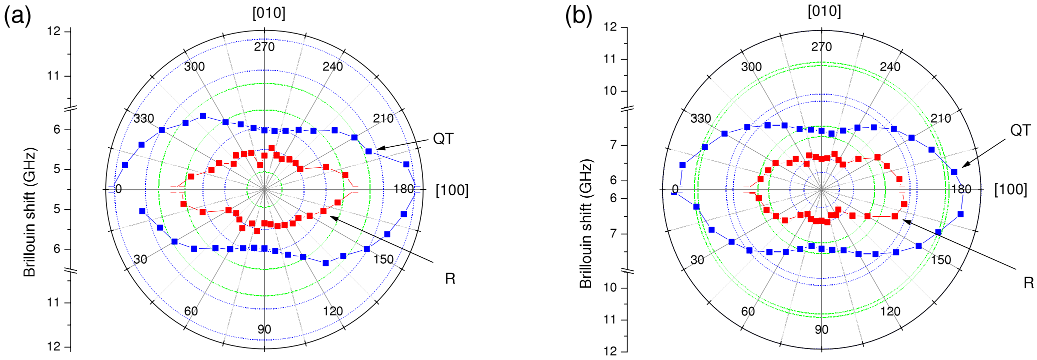

Figure 3. Anisotropy of the quasi-transverse (QT) mode and surface (R) mode in the (001) plane of the LCS crystal in the near-surface layer of (a) 380 nm, (b) 310 nm thickness.

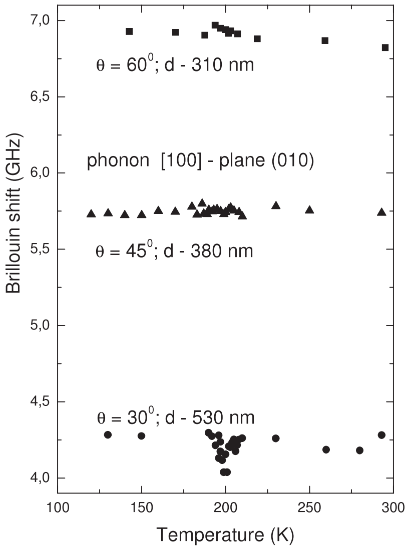

Figure 4. Temperature dependence of the Brillouin frequency shift of a surface phonon propagating in the [100] direction in the (010) plane in near-surface layers of different thicknesses.

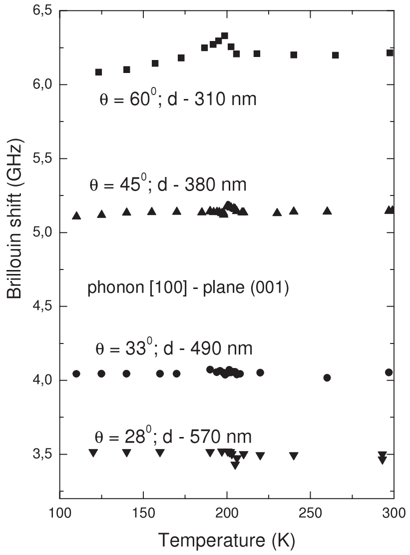

Figure 5. Temperature dependence of the Brillouin frequency shift for a surface phonon propagating in the [100] direction in the (001) plane in near-surface layers of different thicknesses.

scattering spectrum recorded for a near-surface layer of 380 nm suggests that, for a certain thickness of this layer, the effect of the positive anomaly (like that observed for 310 nm) can be cancelled by the effect of the negative anomaly (like that observed for 530 nm). In order to find out for which thickness of the near-surface layer these two effects cancel out, a series of measurements was performed for layers of intermediate thicknesses. The results for thicknesses of 310, 380, 490 and 570 nm are presented in figure 5 for the [100] phonon propagating in the (001) plane. In the 490 nm thick layer the positive anomaly in the Brillouin shift was no longer observed, while in the 570 nm thick layer a small softening of the phonon was observed.

The appearances of the two types of anomalies were not observed for all surface phonons. Different behaviour was detected for phonons propagating in the direction [001] in the two principal planes; see figure 6.

Surface phonons propagating in the [001] direction revealed a distinct positive anomaly for the thinnest near-surface layer, and this was also detected for the layer about 380 nm thick. For layers of greater thicknesses, no anomalies in surface phonon propagation were noted. As follows from the above results presented in figures 5 and 6, the surface phonons do not show the same type of behaviour in the near-surface layer in the vicinity of the phase transition point. Their behaviour is related to the direction of phonon propagation and the plane in which they are observed. The differences in the behaviour of the surface phonons are supposed to stem from the presence of a soft bulk mode in the LCS crystal and a change in the crystal symmetry at the phase transition.

In the direction of propagation of the soft bulk mode in the LCS crystal, in the two principal planes (010) and (001) a local displacement of the atomic planes takes place. The behaviour of the surface phonon propagating in the [100] direction in the two principal planes correlates with the bulk displacement of the soft mode; see more details in *Ferroelectrics* [17]. Therefore, surface phonons in near-surface layers of increasing thickness are increasingly disturbed by the soft bulk mode. This effect is clearly seen when the near-surface layer is of the order of 530 nm. This disturbance is responsible for

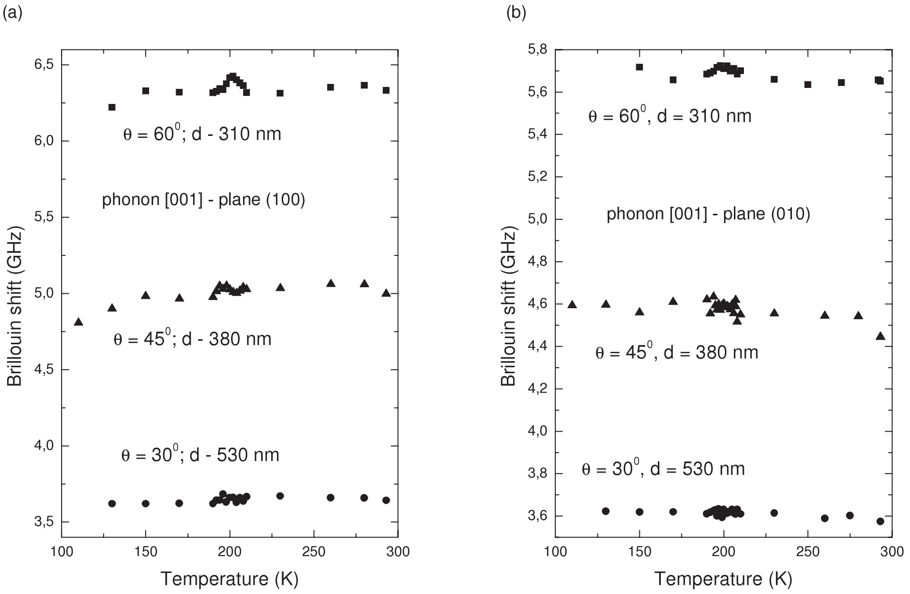

Figure 6. Temperature dependences of Brillouin shift of the surface phonon propagating in the [001] direction in the planes (a) (100) and (b) (010) in near-surface layers of different thicknesses.

the softening of the surface phonon. For surface phonons propagating in the directions [010] and [001] in the principal planes (not related to the bulk soft mode propagation), no negative anomaly was observed in the vicinity of the phase transition point, in near-surface layers up to about 500 nm in thickness.

On the other hand, the positive anomaly was observed for near-surface layers with a thickness of the order of 300 nm. Taking into regard the fact that the phase transition in the LCS crystal is accompanied by a change in the symmetry of the crystal, the relevant stress in the system related to this change has an essential influence on the behaviour of the surface phonons. The appearance of the positive anomaly in the near-surface layers is distinct for all surface phonons studied, which suggests that the effect must be related to the symmetry change in the entire crystal and not to the soft mode propagating in a certain direction. As follows from the study of the surface and quasi-bulk phonons' anisotropy (figure 3), the symmetry of both modes is comparable. This implies that the structure of the near-surface layer does not differ significantly from that of the bulk of the crystal studied, therefore defects in the near-surface layers—unavoidable in the sample preparation—are not a source of the positive anomaly that is observed.

4. Conclusions

The study of LCS crystal by Brillouin spectroscopy has revealed the anomalous behaviour of near-surface phonons in the temperature range covering the bulk ferroelastic phase transition in this crystal. The behaviour of surface phonons in the vicinity of the phase transition point in the LCS crystal has been studied versus the thickness of the near-surface layer thickness. To our great surprise it has been found that surface phonons have shown different types of frequency anomalies depending on the direction of phonon propagation and the thickness of the near-surface layer that was studied. The appearance of the positive anomaly in near-surface layers of the smallest thicknesses that were considered has been interpreted as being due to the change in crystal symmetry at the phase transition and the accompanying stress effects. The appearance of the negative anomaly, i.e. surface phonon softening, in a near-surface layer of about 530 nm in thickness has been attributed to the disturbance caused by the soft bulk mode propagating in the crystal.

Acknowledgment

This work has been supported partially by grant no 1 P03B 066 30 from the Ministry of Science and Higher Education.

References

[1] Aleksandrov K S, Szerebszczowa L I, Iskoriev I M, Krulik A I and Rozanov O W 1980 *Fiz. Tverd. Tela* **22** 3673
[2] Kruglik A I, Simonov M A, Zhelezin E P and Belov N V 1979 *Dokl. Akad. Nauk. SSSR* **247** 1384
[3] Pakulski G, Mroz B and Krajewski T 1983 *Ferroelectrics* **48** 259
[4] Radzhabov A K and Charnaya E V 2001 *Fiz. Tverd. Tela* **43** 732
[5] Ozeki H and Sawada A 1982 *J. Phys. Soc. Japan* **51** 2047
[6] Drozdowski M and Hołuj F 1987 *Ferroelectrics* **76** 113
[7] Mroz B, Kiefte H, Clouter M J and Tuszyński J A 1987 *Phys. Rev.* B **36** 3745
[8] Sandercock J R 1982 Trends in Brillouin scattering *Topics in Applied Physics* vol 51 (Berlin: Springer)
[9] Sandercock J R 1978 *Solid State Commun.* **26** 547
[10] Every A G 2002 *Meas. Sci. Technol.* **13** R21
[11] Sussner H, Pelous J, Schmidt M and Vacher R 1980 *Solid State Commun.* **36** 123
[12] Pang W, Every A G, Comins J D, Stoddart P R and Zhang X 1999 *J. Appl. Phys.* **86** 311

[13] Sandercock J R 1970 *Opt. Commun.* **2** 73
[14] Sandercock J R 1976 *J. Phys. E: Sci. Instrum.* **9** 566
[15] Mroz B and Mielcarek S 2001 *J. Phys. D: Appl. Phys.* **34** 395
[16] Farnell C W 1970 *Physical Acoustic* vol 6 (New York: Academic)
[17] Trzaskowska A, Mielcarek S, Mroz B and Andrews T 2008 *Ferroelectrics* at press