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Brillouin spectra of the solid electrolyte Li_2SO_4

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Brillouin spectra of single crystals of the solid electrolyte Li_2SO_4 were obtained for various crystal orientations in the temperature range 899–1120 K. The spectra contained one longitudinal component and at least one and sometimes both transverse components. The frequency shifts varied between 14.5 and 17.4 GHz for the longitudinal and between 4.1 and 9.0 GHz for the transverse component, the shift being strongly dependent on crystal orientation. The observed frequency shifts correspond to values of the elastic constants typical for plastic materials.

For many years, there has been considerable theoretical and experimental interest in the dynamics of superionic conductors, also called solid electrolytes.¹ The dynamics of ionic motion in superionic materials are similar to those of both liquids and solids; the non-conducting species form a rigid lattice in which the highly mobile ions can move and the transition to the superionic phase is often described as a sublattice melting. This high conducting disordered phase has been investigated by inelastic light scattering by many groups.² Raman scattering has been used to study the ionic motions, whereas Brillouin scattering gives the elastic constants which will reveal the strength of the structure and give information on how plastic the material is. Details of lattice structure have an important role to play in a complete theory of fast-ion behavior in any particular system.^{3,4} The present report is devoted to a Brillouin scattering study of Li_2SO_4 , which is an excellent superionic conductor with a conductivity⁵ very close to that of AgI ,⁶ i.e., about ten times as large as that of most superionic conductors. The phase transition occurs at 848 K and involves an extremely high heat of transformation⁷ and a large volume change.⁸ Below this temperature it is monoclinic, above, it is face centered cubic up to the melting point at 1133 K.⁹ In this region, it shows a plastic behavior¹⁰ and a high mobility of the Li ions.

Brillouin spectroscopy has previously been used in this laboratory to investigate the hypersonic velocity of the longitudinal mode through the liquid–plastic phase transition.¹¹ The velocity increased abruptly when going from the liquid to the plastic phase. In both phases, the velocity decreased linearly with temperature, however, with different temperature coefficients. The plastic phase was reached simply by lowering the temperature and no attempts were made to grow single crystals. Nevertheless, in the plastic phase, some of the spectra revealed one transverse mode in addition to the studied longitudinal one. The transverse component was, however, too weak in intensity and too close to the Rayleigh line to be accurately resolved with the equipment used at that time.

The aim of the present study of the plastic phase of Li_2SO_4 is to determine the frequency shift and its temperature dependence for the transverse mode and to investigate both the transverse and longitudinal shift for different crystal orientations. This required some significant modifications of the experimental equipment;

the novel aspects derive from using a recently installed high resolution interferometer and using single crystals. The high resolution allows for a separation of the transverse line from the central one and single crystals with a known orientation are necessary for a proper analysis of the spectra. The shift in wave number of the Brillouin scattered light is

$$\Delta\nu = (2nv/\lambda_0) \sin \theta/2, \quad (1)$$

where v is the velocity of the sound waves causing the scattering, n is the refractive index of the crystal, λ_0 is the wavelength of the incident light in vacuum, and θ is the scattering angle. Hence, if the refractive index is known it is possible to determine the sound velocity from the measured frequency shift $\Delta\nu$. The elastic moduli may then be obtained from the hypersonic velocities and from a knowledge of the corresponding crystal orientation.

The apparatus used includes a stabilized single mode Ar^+ laser (Spectra Physics model 165) operating at 488.0 nm. Light scattered at about 90° was analyzed by a triple-passed piezoelectrically scanned Fabry–Perot interferometer system (Burleigh Instruments Inc. DAS 10). The Fabry–Perot was adjusted for a spectral free range of 27.27 GHz and kept at a high resolution by an advanced feedback system. The detector system includes a cooled ITT-FW 130 photomultiplier and photon counting equipment coupled to a multichannel analyzer for storage of the data. For each temperature and crystal orientation the spectrum is the result of thousands of sweeps.

A small thermostat was constructed to fit the scattering cell and to allow the x-ray beam to pass in the horizontal direction for determination of the orientation of the crystal. The laser beam passed through the sample cell in a vertical direction through a light port at the bottom of the thermostat. The sample cell was made from a quartz capillary tube having a 3.0 mm bore and a wall thickness of 0.5 mm. Thin walls were necessary in order to minimize absorption of the x-ray beam while passing the sample cell. A quartz plug with a polished upper end was fused to the bottom of the capillary, and a good quality optical window for the laser beam was obtained by finally polishing the bottom of the cell. The sample cell was fused to a long quartz tube suspended to a rotatable table at the top of the thermostat which made measurements at different crystal orientations possible.

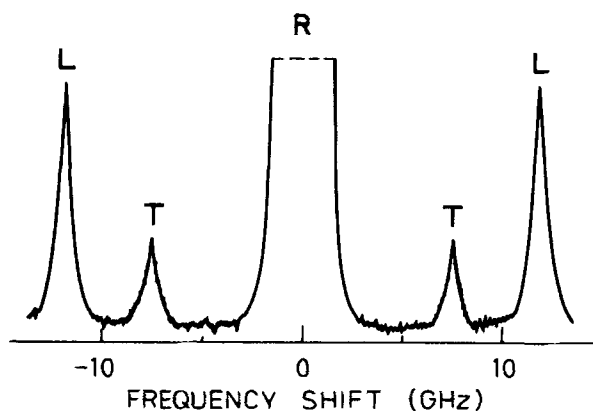


FIG. 1. Brillouin spectrum of Li_2SO_4 at a temperature of 996 K and a rotation angle of 40° . R: Rayleigh component, L: longitudinal and T: transverse Brillouin component.

One of the major difficulties was to grow and orient the crystals at the scattering point inside the thermostat. Single crystals were grown from the liquid by cooling in a temperature gradient until a small seed crystal formed at the bottom of the cell. Then cooling was continued until the crystal filled the cell. Laue x-ray transmission photographs were taken to check that the samples were single crystals, and to establish their orientation. When the temperature was lowered the crystal, once formed, was transparent all over the fcc region but when passing the first order transition at 848 K cracks made further measurements impossible.

The Brillouin spectrum was recorded for seven to eight different crystal orientations with the rotation angle changing in increments of 10° by rotating the sample cell about its vertical axis. Also, for each crystal orientation, the frequency shift was measured at several temperatures in the range 900–1120 K. The spectrum obtained at a temperature of 996 K is shown in Fig. 1. The central component is very intense because of stray light from the small scattering cell. However, this did not affect the position of the Brillouin lines due to the high resolution of the triple-passed Fabry-Perot interferometer. For all orientations the spectra consisted of one pair of longitudinal components (L) and one pair of transverse components (T). The

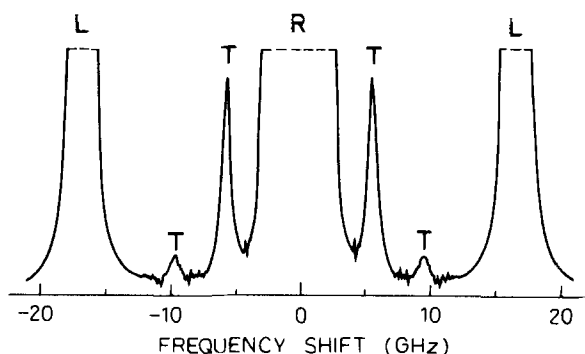


FIG. 2. Brillouin spectrum of Li_2SO_4 at a temperature of 938 K and a rotation angle of 140° .

second pair of transverse components were of extremely weak intensity and only in four of the spectra all three components were recorded (see Fig. 2). In order to get a high resolution spectrum of the transverse components the free spectral range of the interferometer was chosen to give overlapping orders of the longitudinal modes.

The frequency shifts for the longitudinal and transverse components for different rotational angles and temperatures are summarized in Tables I and II. No frequency shifts are given for the second transverse mode since there are only a few recordings and the signal-to-noise ratio is too low to give accurate results. Furthermore, the results for some of the crystal orientations (60° , 70° , 80°) are excluded as the longitudinal Brillouin lines then overlapped and it was therefore difficult to determine their proper position. The frequency shifts for both the longitudinal and transverse components showed a linear temperature dependence, which can be seen in Fig. 3. The solid lines represent linear regression lines with a correlation factor better than 0.99 for all measurements except three. The standard deviations of the frequency shift were less than 0.6% for the longitudinal mode and less than 2% for the transverse mode, the difference in accuracy being due to a large intensity difference for the two lines. From the figure, it is obvious that there is a large difference between the values of the frequency of the transverse and longitudinal mode which is in accordance with other

TABLE I. Frequency shift for the longitudinal component at different temperatures and crystal orientations.

Temperature (K)	Rotation angle (deg.)							
	40	50	60	90	100	110	120	140
899	16.41	15.93		15.78	16.36	16.82	17.20	17.41
915	16.26	15.80		15.66	16.12	16.66	17.01	17.18
947	15.97	15.58		15.39	15.89	16.40	16.77	16.96
966	15.84	15.45	15.13	15.29	15.78	16.20	16.54	16.83
988	15.75	15.35		15.10	15.54	16.02	16.38	16.69
1007	15.49	15.08	14.76	15.01	15.51	15.94	16.30	16.50
1021	15.32	15.13		14.91	15.42	15.85	16.24	16.41
1043	15.45	14.94		14.72		15.69	16.04	16.30
1078	15.16	14.72		14.50	14.94	15.44	15.86	16.06
1099	14.94				14.98	15.39	15.74	15.92
1120	14.93				14.84	15.22	15.57	15.80

TABLE II. Frequency shift for the transverse component at different temperatures and crystal orientations.

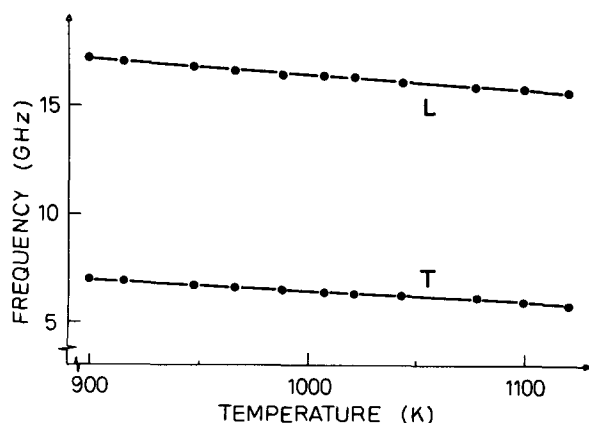
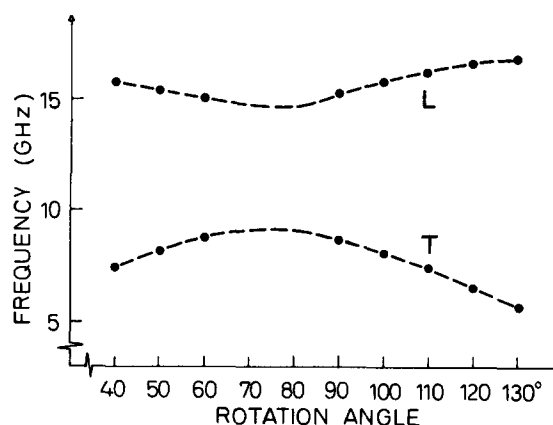
Temperature (K)	Rotation angle (deg.)							
	40	50	60	90	100	110	120	140
899	7.61	8.51		8.95	8.54	7.84	7.03	6.13
915	7.70	8.46		8.88	8.40	7.78	6.94	6.02
947	7.44	8.19		8.74	8.31	7.54	6.70	5.82
966	7.42	8.24	8.84	8.66	8.13	7.49	6.59	5.68
988	7.19	7.92		8.46	7.93	7.39	6.52	5.65
1007	7.45	8.08	8.80	8.46	7.89	7.21	6.35	5.60
1021	7.38	7.84		8.37	7.84	7.16	6.30	5.41
1043	6.90	7.66		8.21		7.13	6.26	5.33
1078	6.74	7.55		8.09	7.58	6.95	6.13	5.25
1099	6.74	7.53		7.96	7.45	6.76	5.88	5.00
1120	6.57				7.39	6.63	5.75	4.87
							4.87	4.14

light scattering studies in solid electrolytes.¹² The variation of the frequency shifts for different rotation angles is shown in Fig. 4 for both modes and, characteristically, the variation is more pronounced for the transverse than for the longitudinal mode.^{13,14}

Values of the elastic moduli can be calculated directly from values of the transverse and longitudinal velocity for wave vector transfer along a direction of high symmetry in a cubic crystal. For instance, the velocity of a longitudinal wave in the [100] direction is related to the elastic constant C_{11} according to $v_L = (C_{11}/\rho)^{1/2}$. For a transverse wave in the same direction, the corresponding equation is $v_T = (C_{44}/\rho)^{1/2}$. For an arbitrary direction in the crystal, there is a coupling between the different modes, the dynamical equations become more complicated, and a computer is needed to determine the elastic constants. However, an estimation of C_{11} and C_{44} can be directly obtained from the experimental data for arbitrary directions by observing the variation of v_L and v_T with crystal orientation. In the present study, the crystal orientation at a rotation angle $\sim 75^\circ$ (see Fig. 4) is very close to the [100] direction for the wave vector transfer, since a minimum of the longitudinal frequency variation occurs at a maximum of the transverse frequency.¹⁵ The corresponding frequencies at a

temperature of 966 K are $v_L = 14.6$ GHz and $v_T = 9.2$ GHz which give a longitudinal and transverse velocity of 3436 and 2165 ms^{-1} , respectively. In calculating the velocities, Eq. (1) was used together with refractive index data from Aronsson *et al.*¹¹ The density data used when calculating the elastic constants were obtained from structure parameters.⁹ The value of C_{11} and C_{44} corresponding to the longitudinal and transverse velocities were calculated to 24×10^9 and $10 \times 10^9 \text{ nm}^{-2}$, respectively. From x-ray studies, the wave vector transfer used in the calculations was determined to deviate from the [100] direction by less than 12° . The deviation from the high symmetry direction introduces an error in the elastic constant in such a way that it will decrease the C_{11} and increase the C_{44} values. We estimate that, in the present case, C_{11} should be smaller by less than 15% and C_{44} larger by less than 20%.

For a correct calculation of the elastic constants, the dynamical equation of the cubic crystal, i.e., a 3×3 eigenvalue problem, has to be solved. Work is in progress to solve the equation for an arbitrary crystal orientation, by a computer program using a least-squares fitting routine, starting with a set of trial values for the elastic constants. This method has been used to determine the elastic constants of rare-gas

FIG. 3. Temperature dependence of acoustic mode frequencies in Li₂SO₄ at a rotation angle of 120° .FIG. 4. Acoustic mode frequencies of Li₂SO₄ at 966 K as a function of rotation angle.

solids,¹⁴ where the same problem had to be faced; to grow and orient single crystals at the scattering point and use the obtained crystal orientation for the measurements. However, the rare gases were studied at low temperature, whereas the present work is, to our knowledge, the only work reported where this method has been used at high temperatures.

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