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Elastic constants of a solid-electrolyte fcc Li_2SO_4 single crystal obtained by Brillouin scattering

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The elastic constants and their temperature dependence have been determined in the solid electrolyte Li_2SO_4 in the high-conductivity high-temperature (848–1133 K) range by using the Brillouin scattering technique. Single crystals were grown at high temperatures *in situ* in the spectrometer system and the arbitrary grown crystal orientations were used for light scattering studies; the orientation relative to the scattering configuration was established by transmission Laue x-ray diffraction. The observed Brillouin spectra exhibited one longitudinal and either one or two transverse components, depending on crystal orientation and temperature. The elastic constants were evaluated by fitting the observed Brillouin frequency shifts to the solutions of the dynamical equations for a cubic crystal. The results show low values of the elastic constants, $C_{11}=2.3$, $C_{12}=1.8$, and $C_{44}=1.2$ (in units of 10^{10} $\mathrm{N\,m^{-2}}$) at 920 K, consistent with current theories of solid electrolytes, which predict a softening of the lattice due to the liquidlike behavior of these materials. The velocity of the transverse mode in the $\langle 110 \rangle$ direction is anomalously low, which might be explained by rotational-translational coupling.

I. INTRODUCTION

The present study is devoted to an investigation of the elastic properties of Li_2SO_4, which belongs to a class of sulphate-based solids with a plastic high-temperature phase classified as superionic.[1] Superionic crystals, also called solid electrolytes, are known for their high ionic conductivity which is comparable to that of liquid electrolytes, i.e., many orders of magnitude larger than the conductivity of ordinary ionic crystals, whereas the electronic conductivity is negligible. The current interest is mainly due to the potential applications of these materials in new types of solid-state battery systems.

The ionic motions in solid electrolytes are similar to those of both liquids and solids; one ionic species is nonconducting and forms a rigid lattice in which the other highly mobile ionic species can move. The transition to the solid-electrolyte (superionic) phase is therefore often described as a sublattice melting process. Much theoretical and experimental work have been focused on the dynamics of these materials (for reviews see Ref. 2) as well as on structural properties in order to explain the high conductivity and to get a complete theory of solid electrolytes.[3–7] However, there are few reported data on the elastic constants of these highly disordered systems.[8,9] Moreover, the existing data give either relative values,[10] values with large uncertainties,[11] values from nonoriented crystals,[12] or estimated values.[13]

The traditionally method for an accurate determination of the elastic constants involves single crystals and ultrasonic techniques. However, to our knowledge there is no ultrasonic report on single crystals of solid electrolytes. The major difficulty in these experiments seems to be the requirements for large oriented single crystals. Such specimens of solid electrolytes are difficult to grow, maintain, and attach to an ultrasonic transducer, since most solid electrolytes only exist at elevated temperatures.

In the present study the Brillouin-scattering technique was chosen to obtain the elastic constants of superionic Li_2SO_4. The most important advantage in using light scattering is that only a very small specimen is required and small crystals are relatively simple to grow. However, in light scattering from single crystals, the crystals are normally cut, polished, and oriented in high-symmetry directions at room temperature. Since this is not possible for the solid electrolytes, where the conductivity phase is a higher-temperature phase, a technique has been developed to grow the crystal *in situ* at the light scattering point where also its orientation was determined by x-ray analysis. We have previously reported some preliminary results from Brillouin scattering of unoriented single crystals of Li_2SO_4.[12] In the present work arbitrary (but known) crystal orientations have been used. The analyses of the data are then not straightforward and computer programs were developed to obtain the elastic constants and the sound velocity for high-symmetry directions. The technique is essentially the same as that used by Stoicheff and coworkers,[14] developed for their light scattering investigation on rare-gas single crystals at low temperatures, however, now applied to high-temperature studies.

Superionic Li_2SO_4 was chosen for a detailed study of its elastic properties: Li_2SO_4 is interesting in itself since, in the high-conductivity phase, it is an extremely disordered plastic crystal. Also, Li_2SO_4 is the progenitor of a group of sulphate-based solid electrolytes for which the high conductivity has in fact been related to the plastic behavior.[1] The extraordinary disorder of the lattice is due to two kinds of motions; the diffusive motions of the cations which form the "molten" lattice and the rotational motions of the SO_4^{2-} ions, which form the "rigid" lattice, however, now only rigid in the sense of the center of mass. The transition into the disordered phase is a first-order transition at 848 K from a low-conductivity monoclinic phase to a cubic structure[15] of excellent conductivity.[16] The conducting phase covers a temperature range of several hundred degrees, from 848 K to the melting point at 1133 K. The high ionic conductivity ($2\ \Omega^{-1}\,\mathrm{cm}^{-1}$) is entirely due to the mobile lithium ions. Structure determination shows that the structure is fcc, described by the space group $Fm3m$.[15] The sulphate ions occupy the fcc lattice while the lithium ions occupy the tetrahedral sites $\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The lithium diffusion occurs through alternating tetrahedral and octahedral sites and is predominantly a jump diffusion.[15,17] The nonconducting sulphate ions are fixed at the lattice points. However, the oxygen atoms are rapidly reorienting around the sulphate atom.[18] The fcc phase is therefore referred to as a rotator phase or plastic crystal. It has been proposed that the reorientations of the sulphate ions in the cubic phase are coupled rotations which strongly enhance the diffusion of the cations in sulphate-based solid electrolytes.[1,18] In this laboratory we have previously investigated the ion dynamics in these materials by using Raman scattering.[17,19] We then determined the SO_4^{2-} reorientational time (~ 1 ps) and the Li^+ time of flight (~ 0.3 ps) and demonstrated similar activation energies for the two processes in favor of the proposed coupling model. In the present study we focus on the elastic properties of Li_2SO_4.

II. EXPERIMENT

The Brillouin-scattering apparatus and the experimental technique have already been described in detail in a separate paper from this laboratory concerning Brillouin measurements in another solid electrolyte, namely α-AgI.[20] Therefore, only those features which are significantly different will be discussed below.

In the analysis of the Brillouin-scattering data to obtain values of the elastic constants, it is necessary to know the refractive index of the scattering medium. A value of the refractive index of fcc-Li_2SO_4 is not, so far, available in the literature and it has therefore been measured in the present work, both as a function of wavelength and temperature.

A. Refractive-index measurements

The experimental procedure is a modified thermooptical method based on interferometry. It has been developed for very accurate determinations of refractive index ($\Delta n < \pm 10^{-6}$) from room temperature to about 1200 K and is described in detail in Ref. 21. The measurements are accomplished in two steps. First the absolute value of the refractive index is measured at a constant temperature by recording the change in the interference order between two light beams, one passing through the sample and the other passing through a reference medium (air), as the sample is rotated and thereby the optical path is changed. In the second step the temperature dependence of the refractive index is determined by recording the change in interference order as the temperature is changed for a fixed sample position. The changes of the interference pattern were recorded with a photomultiplier and immediately processed in a desk-top computer which calculated the refractive index and its temperature dependence automatically. The Li_2SO_4 sample was of suprapure quality (Merck). The refractive index of the solid fcc phase was measured in the temperature range 860 to 1093 K. Three different wavelengths (457.9, 488.0, and 514.5 nm) of an argon-ion laser were used. The absolute value of the refractive index was measured at two different temperatures (858 and 878 K) in order to establish the sign of the derivative $dn/\partial T$. During the thermooptical procedure the temperature changed continuously at a rate of 0.5 °C per minute. About 80 refractive-index values, each calculated for a complete change in the interference order, were obtained for every wavelength. The experimental values were fitted to a linear function by the least-squares method and the results are presented in Table I. The standard deviation is about 1×10^{-5} and the overall error was estimated to $\pm2\times10^{-5}$, which is far below the error of the light scattering data. It could therefore be neglected when estimating the accuracy of the Brillouin-scattering results.

B. Growth of single crystals and x-ray diffraction

Single crystals of fcc-Li_2SO_4 were grown from the melt in cylindrical sample cells; they were examined by transmission x-ray diffraction to check the single-crystal quality and to determine their orientation. During crystal growth, followed by x-ray analysis and the light scattering measurements, the samples have to be kept in high-temperature surroundings, since fcc-Li_2SO_4 exists in the temperature range 848–1133 K. The high-temperature thermostat used was especially designed for growing crystals, performing Brillouin-scattering studies, and at the same time, allowed x-ray analysis to be made[20] and the crystals could therefore be grown directly in position for the light scattering studies.

The sample cells were made of Vycor tubing of ≈ 3 mm diameter and ≈ 15 mm length, with an optical quartz window at the bottom for laser irradiation of the

TABLE I. Refractive index of fcc Li_2SO_4 expressed by the equation $n = a + bT$, where T is in K. σ is the standard deviation.

λ (nm)	a	$-10^5 b$	$10^5\sigma$	Temperature (K)
457.9	1.497 051	2.98	1.01	860–1104
488.0	1.495 144	3.00	0.98	861–1103
514.5	1.494 141	3.00	0.62	860–1088

sample.[20] The sample cell was fused to another Vycor tubing of 9 mm diameter and ≈200 mm length used for positioning the sample along the axis of the thermostat. Facilities were available for rotating the tubing about this axis to examine different crystal orientations. The sample cells were carefully cleaned to reduce parasitic scattering. Every cell was tested by taking the Brillouin spectrum of ethyl alcohol for which the intensity ratio of the Rayleigh and Brillouin peaks are known.

The starting materials were of quality Merck suprapure $Li_2SO_4 \cdot H_2O$. Anhydrous materials were obtained by drying the salt under vacuum at 600 K for 48 hours. By repeatedly filling and melting small amounts of the salt in the 3-mm-diameter cell a clear melt, free of air bubbles, of approximately 7–8 mm height was obtained, which was used for crystal growing. The crystal was grown by slowly lowering the melt along a temperature gradient in the thermostat, i.e., by a modified Bridgman technique.[20] The thermostat was constructed with a large opening in the central part, which allowed for x-ray analysis and at the same time introduced the necessary temperature gradient for crystal growth.[20] The crystals were clear, colorless, and cylindrical in shape, 3 mm in diameter and ≈7 mm long.

Transmission Laue x-ray diffraction was used to determine the orientation of each of the three studied crystals. Three photographs at three different orientations were taken for crystal 1 and 2, while four different photographs were used for crystal 3. The orientations of the crystal axis with respect to the laboratory reference frame were expressed in terms of the Euler angles (Ψ, Θ, Φ), as defined by Goldstein.[22] They were obtained from the Laue diffraction spots by the method of stereographic projection using a Wulff net.[23] In Fig. 1 a schematic drawing of one of the Laue photographs is presented in which the identified spots are marked with their Miller indices. The Euler angles, determined for the three crystals studied, are shown in Table II, where Φ_{rot} specifies the angular interval over which Brillouin spectra were recorded. The overall uncertainties in the determination of the Euler angles were estimated to be ±2°.

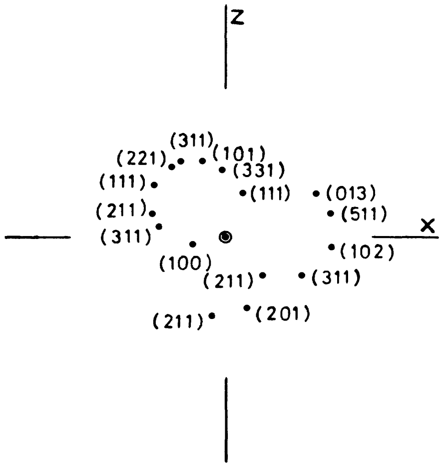

FIG. 1. Laue diffraction spots identified by their Miller indices of a fcc Li_2SO_4 single crystal. The Euler angles (Ψ, Θ, Φ) are $\Psi = 66.5°$, $\Theta = 39.0°$, and $\Phi = 107.0°$. The x axis represents the direction of the polarization of the incident beam, the y axis (into the paper) represents the direction of the scattered light, and the z axis represents the direction of the incident laser beam.

C. Brillouin-scattering spectrometer

The Brillouin-scattering apparatus, described in detail in Ref. 20, consisted of the following basic components: A Spectra Physics model No. 165-00 argon-ion laser operating in single mode at 488.0 nm and with an output power of about 200 mW; a triple-pass piezoelectrically scanned Fabry-Perot interferometer stabilized for both mirror parallelism and plate separation by a Burleigh DAS-10 system and scanned with a Burleigh RC-43 ramp generator; a cooled ITT FW-130 photomultiplier tube selected for a dark current of less than five counts per second. Photon counting was used, the signal was stored in a multichannel analyzer (Tracor Northern 1705), and the spectra were displayed on a recorder. All spectra were recorded in right-angle scattering geometry. The scattering angle was determined to an accuracy of ±0.1° and scattering angles of 91.0°, 89.9°, and 91.2° were employed for the three crystals, respectively. Each spectrum was recorded over 1.7 interferometric orders. The free spectral range of the interferometer was chosen to be 27.27±0.05 GHz and the total finesse of the whole spectrometer was above 40 during all measurements. Long accumulation times of several hours and stabilization of the interferometer were necessary to obtain the very weak transverse modes in the Brillouin spectra.

III. EXPERIMENTAL RESULTS

A. Brillouin spectra

Three single crystals have been examined by Brillouin scattering for different crystal orientations and for a range of temperatures (889–1106 K). Brillouin scatter-

TABLE II. Crystal orientation as specified by the Euler angles for three Li_2SO_4 single crystals. The Euler angles (Ψ, Θ, Φ) are given and Φ_{rot} specifies the angular interval over which Brillouin spectra were taken.

Crystal	Ψ (deg)	Θ (deg)	Φ (deg)	Φ_{rot} (deg)
1	66.5	39.0	107	88–190
	66.3	39.0	111	
	66.5	39.0	203	
2	314.5	36.0	154	95–255
	315.0	36.5	168	
	314.0	37.0	216	
3	17.0	298.5	322	292–32
	17.3	298.0	352	
	17.0	299.0	2	
	17.3	298.0	12	

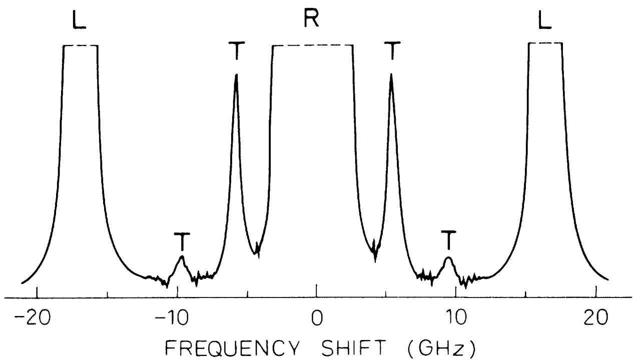

FIG. 2. Brillouin spectrum of fcc Li_2SO_4 at 938 K; R, L, and T are Rayleigh, longitudinal Brillouin, and transverse Brillouin components, respectively.

ing in a material is the inelastic scattering of incident light due to propagating thermal sound waves of which there are three in a cubic crystal; the longitudinal and the two transverse. The spectrum of a cubic crystal therefore consists of a longitudinal doublet (L), which is generally relatively strong, and two transverse doublets (T_1 and T_2), which often are considerably weaker in intensity. In the present study the longitudinal L and the transverse T_1 components were observed in all spectra, however, the transverse T_2 mode could only be seen in three of the spectra. In Fig. 2 a spectrum is shown in which even the weak-intensity T_2 doublet is present. The most intense feature of the spectrum was the central peak, the Rayleigh peak, due to elastic scattered light. The intensity of the Brillouin components depend on the magnitudes of the photoelastic constants, on the crystal orientation, and on the temperature. A typical value of the intensity ratio between the central component and the longitudinal Brillouin components was 100:1. The intensity ratio between the longitudinal and the transverse T_1 components was typically 4:1 and between the T_1 and T_2 components about 3:1. Because of the high contrast of the Fabry-Perot spectrometer when working in triple pass the intense central component did not seriously affect the Brillouin components, even though the intensity difference was three orders of magnitude between the central line and the weak transverse modes. The free spectral range (27.27 GHz) was chosen to get overlapping of the longitudinal (~ 17 GHz) modes in the Brillouin spectra. The use of overlapping orders made it easier to resolve the low-frequency and weak-intensity transverse mode.

A striking feature of the spectra was the variation of the frequency shift as the crystal was rotated, see Fig. 3, where the observed frequency shifts for different crystal orientations at a fixed temperature are given for each crystal. This indicates a large elastic anisotropy of fcc-Li_2SO_4, see Sec. III B below. In order to determine the temperature dependence of the elastic constants Brillouin spectra were recorded at the following temperatures; crystal 1 was analyzed at 976 K, crystal 2 at four different temperatures in the range 944–1045 K, and crystal 3 at 11 different temperatures in the range 889–1106 K. In Fig. 4 the temperature dependence of the longitudinal and the transverse frequency shift for crystal 3 is shown for a fixed crystal orientation.

The uncertainty of the Brillouin shift was estimated to be 1% for the longitudinal mode, 2% for the transverse mode T_1, and about 3% for the weak T_2 mode. The uncertainties are the estimated overall errors which include uncertainties in the shift position, the free spectral range as well as errors introduced due to misalignments of the optics.

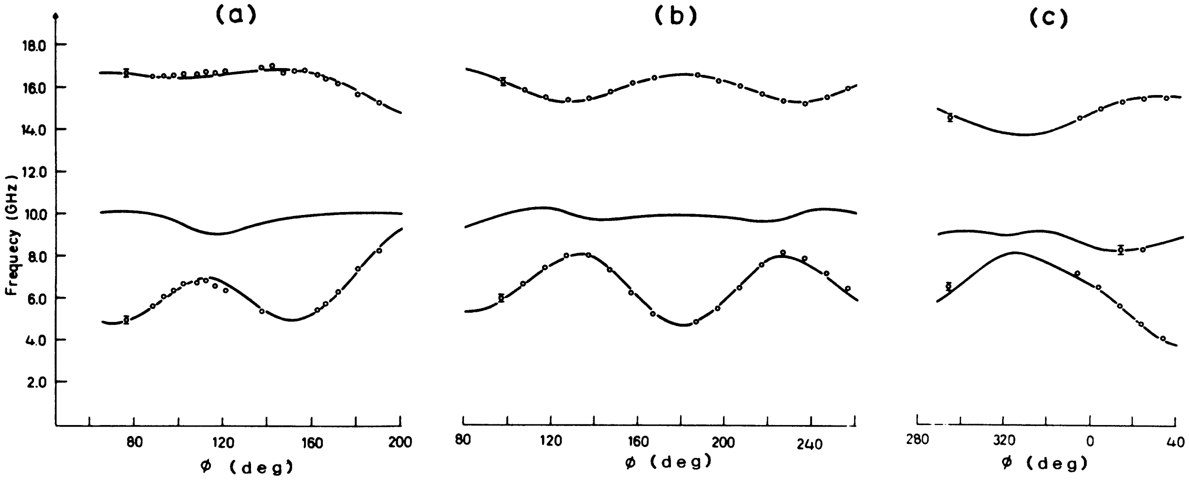

FIG. 3. Observed (circles) and calculated (solid lines) Brillouin shifts of fcc Li_2SO_4 vs rotation angle Φ for (a) crystal 1 at 976 K, (b) crystal 2 at 944 K, and (c) crystal 3 at 1085 K. The solid lines were calculated from the determined values of the elastic constants.

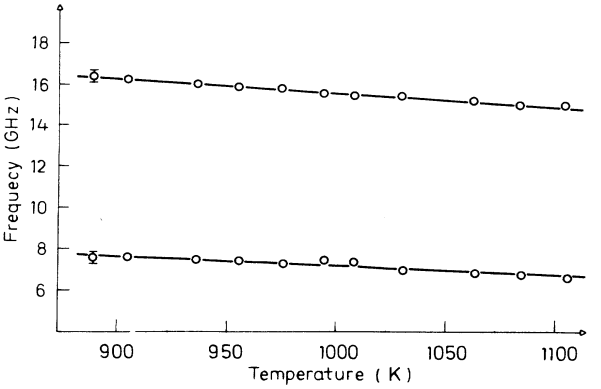

FIG. 4. Temperature dependence of the acoustic mode frequencies in fcc Li_2SO_4 at fixed Euler angles (Ψ, Θ, Φ); $\Psi=17.2°$, $\Theta=298°$, and $\Phi=292°$.

B. Elastic constants

The Brillouin data were used to calculate the elastic constants of which there are three (C_{11}, C_{12}, and C_{44}) for a cubic crystal. The method has been described in a separate paper[20] and is essentially the same as that used by Stoicheff and coworkers.[14] The analysis starts with the Brillouin equation

$$\Omega_\mu = \pm 2nk_0 V_\mu(\hat{\mathbf{q}})\sin(\alpha/2) \tag{1}$$

which relates the frequency shifts of the scattered light Ω_μ to the acoustic velocity $v_\mu(\hat{\mathbf{q}})=\omega_\mu(\mathbf{q})/|\mathbf{q}|$. In Eq. (1) n is the refractive index of the crystal, k_0 is the length of the wave vector of the incident light in vacuo, and α is the scattering angle. The experimentally measured Brillouin shift Ω_μ is equal to the frequency $\omega_\mu(\mathbf{q})$ of the acoustic mode which is responsible for the scattered light. The relationship between the adiabatic elastic constants of a crystal and the frequency $\omega_\mu(\mathbf{q})$ of the three acoustic modes propagating with wave vector $\mathbf{q}$ in the crystal is given by

$$|\Lambda_{ij}-\rho\omega^2\delta_{ij}|=0 , \tag{2}$$

where

$$\Lambda_{ij}=(C_{11}-C_{44})q_i^2+C_{44}q^2 \quad \text{for } i=j \tag{3}$$

and

$$\Lambda_{ij}=(C_{12}+C_{44})q_iq_j \quad \text{for } i\neq j , \tag{4}$$

where q_i are the components in the crystal reference frame of the acoustic wave vector $\mathbf{q}$ with $q^2=\sum_{i=1}^{3}q_i^2$. In the calculations $\mathbf{q}$ was specified by the Euler angles of Table II, refractive index data were taken from Table I, and a set of trial values of C_{11}, C_{12}, and C_{44} were fed as starting values into Eq. (2), i.e., a 3×3 eigenvalue problem; as a result the three mode frequencies $\omega_\mu(\mathbf{q})$ were generated. Calculated and experimentally measured mode frequencies were compared and a least-squares fit was computed for each crystal.[24] Excellent agreement was obtained between the fit and the observed frequencies as can be seen in Fig. 3. It is then to be noted that, despite low intensities of the transverse modes, close agreement is obtained even in the case of the two single observations of the T_2 mode [see Fig. 3(c)].

Figure 5 summarizes the results of the elastic constants versus temperature and values are given as linear functions of temperature in Table III. The absolute values of the elastic constants are estimated to be accurate to better than 1% considering the uncertainties in scattering angle, temperature, density, and refractive index. The errors in the determination of the Brillouin shifts and the orientation angle affect mainly the relative value of the elastic constants. It is difficult to describe this sort of uncertainty analytically since it depends on a number of factors, for instance, of the accuracy in the Euler angles Ψ, Θ, Φ themselves, i.e., on the crystal orientation. For this reason, the best estimate of the effect of such uncertainties was to introduce deliberate errors in the data and observe the change in the recalculated values of the elastic constants. The resulting inaccuracy was estimated to be less than 5%.

The values of the elastic constants have been used to determine the elastic wave velocities in principal symmetry directions of the fcc phase of Li_2SO_4. In the calculations density data were obtained from structure parameters[25] which resulted in the following relation (in $\mathrm{kg\,m^{-3}}$)

$$\rho=2313.07-0.2752T, \quad 853\leq T\leq 1123 \text{ K} . \tag{5}$$

Results for the velocities in $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions as a function of temperature is given in Table IV. The adiabatic bulk modulus B and the elastic anisotropy parameter A are readily derived from the elastic constants according to the following equations

$$B=\frac{C_{11}+2C_{12}}{3} , \tag{6}$$

$$A=\frac{2C_{44}}{C_{11}-C_{12}} . \tag{7}$$

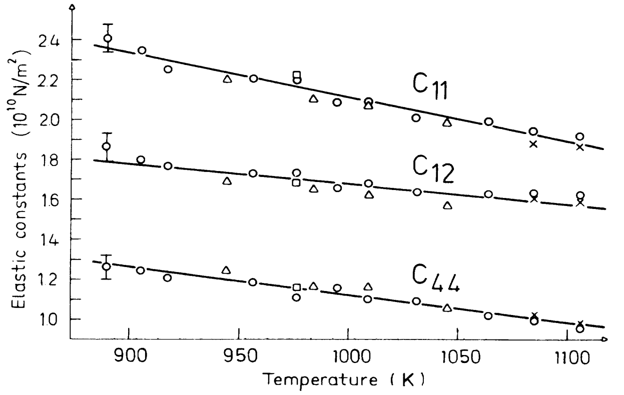

FIG. 5. Experimental values of the elastic constants vs temperature for fcc Li_2SO_4 from crystal 1 (squares), crystal 2 (triangles), and crystal 3 (circles), respectively.

TABLE III. Elastic constants (in 10^{10} N m^{-2}) of fcc Li_2SO_4 expressed by the equation $C_{nm} = a + bT$, where T is in K. The temperature range is 889–1106 K.

C_{nm}	a	$-10^3 b$
C_{11}	4.28 ± 0.17	2.2 ± 0.16
C_{12}	2.70 ± 0.13	1.0 ± 0.18
C_{44}	2.51 ± 0.10	1.4 ± 0.12

The temperature dependence of the corresponding parameters are shown in Figs. 6 and 7. The elastic anisotropy is a measure of the departure from perfect elastic isotropy for which $A = 1$. The large and similar values of Fig. 7 indicate that all the investigated crystals were high-quality single crystals.

IV. DISCUSSION

A comparison of the present results with those of other solid electrolytes is limited by the few cases for which absolute values of the elastic constants have been reported, see Table V. Dorner, Windscheit, and von der Osten have measured the elastic constants of AgBr in the high-conductivity temperature range by means of neutron scattering technique.[11] Although the accuracy of their results is not better than 20% it can be seen from Table V that the elastic constants are of the same order as the corresponding values of Li_2SO_4. It should be pointed out that neutron data may differ by about 10% from Brillouin results due to the distinction between first sound and zero sound.[26] This is, however, within the accuracy of the neutron scattering results. Brillouin-scattering techniques were used in the study of solid $SrCl_2$ over a wide temperature range, from room temperature over the diffuse transition range 900–1050 K to the superionic conducting range above 1050 K.[9] The elastic constants for $SrCl_2$ at a temperature just above the transition to the superionic phase are shown in Table V. Also presented in Table V are recent results of the elastic constants of AgI, obtained in the solid-electrolyte α phase from Brillouin scattering measurements in this laboratory.[20] The results of Table V all show similar values of the elastic constants for solid electrolytes.

TABLE IV. Velocities of sound (in m s^{-1}) in high symmetry directions of fcc Li_2SO_4 expressed by the equation $v = a + bT$, where T is in K.

v	Direction	a	$-b$
v_L	⟨100⟩	4 588.4	1.369
	⟨110⟩	5 483.9	1.638
	⟨111⟩	5 729.4	1.694
$v_{T_1} = v_{T_2}$	⟨100⟩	3 632.5	1.290
	⟨111⟩	2 786.0	1.192
v_{T_1}	⟨110⟩	3 681.6	1.337
v_{T_2}	⟨110⟩	2 351.8	1.325

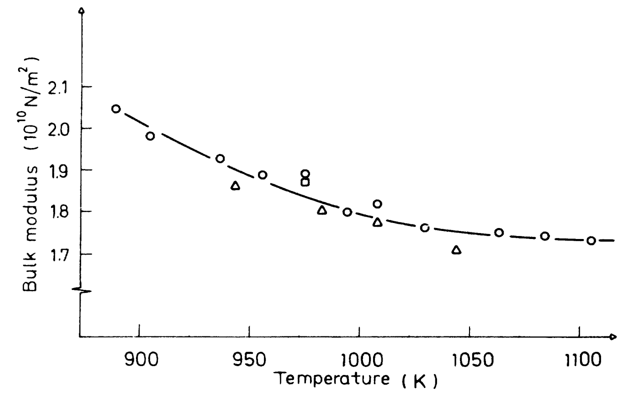

FIG. 6. Experimental values of the bulk modulus vs temperature for fcc Li_2SO_4 from crystal 1 (squares), crystal 2 (triangles), and crystal 3 (circles), respectively. Dashed line represents a guide line.

Harley *et al.*[3] have studied the Brillouin spectra of several fluorite crystals which behave like solid electrolytes at elevated temperatures. The data presented in their work are, however, the Brillouin frequency shifts rather than the elastic constants, since a determination of the elastic constants requires data for the refractive index and density which are not accurately known for these materials. The results, however, are interesting from the point of view of the temperature dependence of the elastic constants, see below.

In the present study a linear decrease in temperature of the elastic constants was observed in the high-conductivity high-temperature phase of Li_2SO_4. This is in agreement with theoretical predictions for the behavior of cubic crystals at high temperatures on the basis of a quasiharmonic-anisotropic continuum model.[27] In the special case of a solid electrolyte the transition into the high-conductivity phase is often characterized by a dras-

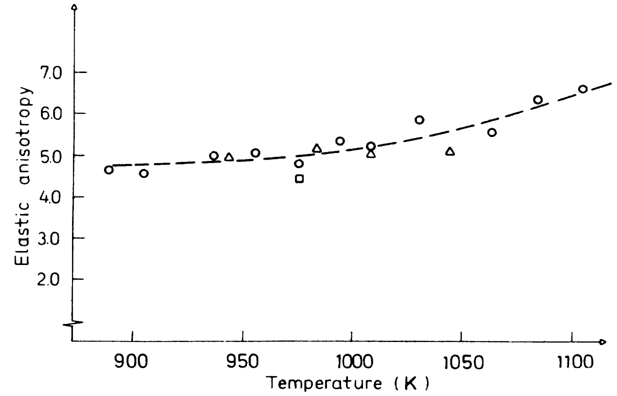

FIG. 7. Experimental values of the elastic anisotropy vs temperature for fcc Li_2SO_4 from crystal (squares), crystal 2 (triangles), and crystal 3 (circles), respectively. Dashed line represents a guide line.

TABLE V. Elastic constants of some solid electrolytes.

Material	Elastic constants (10^{10} N m^{-2}) C_{11}	C_{12}	C_{44}
Li_2SO_4	2.3	1.8	1.2
AgBr[a]	3.0	2.2	0.8
AgI[b]	1.5	1.3	0.6
$SrCl_2$[c]	3.5	1.9	0.5

[a] Reference 11.
[b] Reference 20.
[c] Reference 9.

tic change especially in one of the elastic constants, namely C_{11}, while C_{12} and C_{44} are less affected. The effect is demonstrated in the work of Catlow, Harley, and Hayes on the fluorites.[28] Here the transition to the high-conductivity state is a smooth transition due to a gradual occupation of interstitial lattice positions, which are empty at low temperatures. For temperatures below the range where the gradual occupation of the interstitial position begins, the elastic constant C_{11} of, for example, BaF_2 and PbF_2, decreases linearly and then falls dramatically. In the high-conductivity state C_{11} again decreases linearly with the temperature. The same behavior is observed for $SrCl_2$.[9] The drastic change of C_{11} in the transition range may be due to the dynamic disorder in a solid electrolyte, represented by a molten sublattice of mobile ions. Subbaswamy[13] and Huberman and Martin[29] have predicted the existence of an interaction between the diffusing ions and an acoustic wave in solid electrolytes. This interaction is capable of altering the frequencies, width, and intensities of the Brillouin-scattering peaks in a manner which is well known from the similar problem of acoustic and molecular reorientation coupled modes in solids.[30,31] The change in the bulk modulus observed in the fluorites[28] is consistent with this type of coupled-mode behavior. For the fluorites the softening of the longitudinal mode is possible to observe due to the gradual transition to the conducting state. Gradual transitions also occur for $SrCl_2$ (Ref. 9) and AgBr.[11]

The situation is different for lithium sulphate, where there is a first-order phase transition between the monoclinic temperature phase and the highly conductive phase. To our knowledge, the elastic constants have neither been studied for the room-temperature phase of Li_2SO_4 nor for the room-temperature phases of similar systems, e.g., sodium sulphate. It is, however, possible to estimate the order of magnitude for the elastic constants of the room-temperature phase of Li_2SO_4 from the general systematics that can be found from numerous studies of other ionic compounds.[32,33] It is found that the elastic constants decrease with increasing mass of the cation or anion and with reduced cation charge. Also, polyatomic anions have larger elastic constants than monoatomic ones. From comparisons with data one might expect that the elastic constants of the room temperature phase of Li_2SO_4 are of the same order as those of, say, $SrSO_4$, for which the elastic constants are reported to be 10.4×10^{10}, 7.7×10^{10}, and 1.4×10^{10} N m^{-2} for C_{11}, C_{12}, and C_{44}, respectively. Extrapolating the values of the elastic constants found in the present study for Li_2SO_4 to room temperature gives 3.5×10^{10}, 2.4×10^{10}, and 2.1×10^{10} N m^{-2} for C_{11}, C_{12}, and C_{44}, respectively, i.e., C_{11} and C_{12} are considerably lower than those of $SrSO_4$. Thus it is suggested that the same behavior is present in Li_2SO_4 as in the fluorites discussed above, i.e., there is a correlation between low elastic constants and the dynamic disorder of a solid electrolyte.

In the case of fcc Li_2SO_4 it is of interest to compare with other cubic crystals which are also characterized by plastic behavior. A plastic phase is generally observed to have a low entropy of fusion and a high degree of translational and rotational disorder.[34,35] Also, it is found that optical spectra from plastic phases tend to closely resemble the equivalents of the liquid states.[36,37] The high-conductivity fcc phase of Li_2SO_4 is definitely characterized by each of these properties, as discussed in the following paragraph.

The heat of fusion is certainly small, whereas the phase transition to the high-conductivity phase involves an extremely high heat of transformation, roughly three times that of melting.[38] Both translational and rotational modes are definitely observed in Li_2SO_4, in this case due to diffusing Li[1,17] and rapidly reorienting sulphate ions.[1,15] The cations are very mobile and responsible for the high conductivity of the plastic phase. High-cation mobility has also been observed in other sulphate crystals for such large species as K^+ and Rb^+, which has lead to speculation that the cation diffusion is coupled to the anion rotation. Then the unusually large activation energy for cation diffusion found for the sulphate based solid electrolytes can be explained by the similar activation energy of SO_4^{2-} rotation as obtained from Raman measurements.[19] The optical spectra of the liquid and the plastic phase are certainly very similar in the case of Li_2SO_4, as already reported from previous Brillouin[39] and Raman[19] scattering studies from this laboratory. Moreover, the Brillouin spectra reveal a distinct jump in the longitudinal frequency shift at the phase transition to the molten phase, which has also been observed for many other plastic single crystals.[40-42]

In Table VI some values of the elastic constants and the anisotropy for other cubic plastic crystals[43-36] are given together with present results for Li_2SO_4. Although the elastic constants differ considerably, by more than an order of magnitude, the elastic wave velocities are, due to the different densities, comparable. What is more significant is then to compare the values for the elastic anisotropy since here the density effects are canceled. The present results show, in contradiction to other plastic crystals with the exception of solid methane, a large value of anisotropy. This reflects large differences of the acoustical wave velocities in different crystal directions, see Table IV and Fig. 3. The longitudinal velocity varies more than 20% from its highest value (⟨111⟩ direction) to its lowest value (⟨100⟩ direction). The corresponding difference between the highest and lowest velocity value for the T_1 mode is more than a factor of 2.5. The largest longitudinal value differs by a

TABLE VI. Elastic constants and anisotropy of some cubic plastic crystals.

Material	Temperature (K)	Elastic constants (10^9 N m^{-2}) C_{11}	C_{12}	C_{44}	Elastic anisotropy A
γ-oxygen[a]	54	2.60	2.06	0.28	1.02
Cyclohexane[a]	279	2.86	2.47	0.36	1.86
Pivalic acid[b]	298	3.30	1.46	0.64	0.69
Succinonitrile[c]	293	5.07	3.54	0.65	0.85
CH_4[d]	90	1.96	1.45	0.92	3.6
Li_2SO_4	920	23.0	18.0	12.0	4.8

[a] Reference 43.
[b] Reference 44.
[c] Reference 45.
[d] Reference 46.

factor of more than 4.5 from the lowest transverse value. The temperature dependence of the elastic anisotropy of Li_2SO_4 is shown in Fig. 7. The observed increase ($\sim 30\%$) as temperature is increased is in accordance with observations in other solid electrolytes, such as AgBr, $SrCl_2$, and the fluorides. The result shows that near the melting point the softening of the lattice is more pronounced for certain directions.

It is interesting to note large values for the elastic anisotropy in both solid methane[46] and fcc Li_2SO_4, see Table VI, since these materials in several respects show a similar behavior. Among the properties in common are the tetrahedral structure of the sulphate ion and the CH_4 molecule as well as the fcc structure of their lattice. Moreover, reorientation motions, as observed for the sulphate ion, have also been proposed for the methane molecule in solid methane.[46] Rand and Stoicheff[46] have calculated the ratios of the wave velocities in different high-symmetry directions for CH_4 in order to compare these ratios with the corresponding ratios of the rare-gas solids.[14] In Table VII those ratios of argon and methane are compared with the corresponding ratios of Li_2SO_4. It is apparent that the ratios v_L/v_T are in close agreement for these solids with the exception of v_L/v_{T_1} in the $\langle 110 \rangle$ direction. In this direction the difference between the ratios for argon and CH_4 and for argon and Li_2SO_4 is 20% and 30%, respectively. This anomaly is due to the low values of the T_1 $\langle 110 \rangle$ velocity mode in both CH_4 and Li_2SO_4. For CH_4, molecular-dynamics simulation studies, based on potentials which ignore angle-dependent interactions between the molecules, show that the observed values of the velocities cannot be reproduced in these calculations.[46] The same inadequacy has been encountered in the treatments of another molecular solid, namely β-nitrogen.[47] For both materials it was concluded that the effect is due to a rotation-translational coupling which, according to theories,[48] lowers the value of the sound velocity. Considering the similarities between Li_2SO_4 and CH_4, it is apparent that the same coupling may occur in Li_2SO_4. The extremely low value of the T_1 $\langle 110 \rangle$ transverse velocity mode may therefore be explained by an interaction between transverse mode oscillations and reorientations of the sulphate ion.

TABLE VII. Ratios of sound velocities in high-symmetry directions of some fcc crystals.

Material	$\langle 100 \rangle$ V_L/V_T	$\langle 111 \rangle$ V_L/V_T	$\langle 110 \rangle$ V_L/V_{T2}	$\langle 110 \rangle$ V_L/V_{T1}
Argon[a]	1.46	2.27	1.66	2.75
CH_4[b]	1.46	2.44	1.69	3.2
Li_2SO_4	1.42	2.60	1.69	3.6

[a] Reference 14.
[b] Reference 46.

V. CONCLUSIONS

The elastic constants and their temperature dependence in single crystals of solid electrolyte Li_2SO_4 have been accurately determined in the fcc high-temperature high-conductivity range. Comparisons with low-conductivity sulphate crystals reveal low values of the elastic constants which reflects the extreme disorder of the superionic conducting phase of Li_2SO_4. Compared to other plastic crystals, an unusually large elastic anisotropy was observed. The effect is interpreted as being due to a rotation-translational coupling between different modes of motions in the solid, in accordance with similar observations of anomalously slow propagation of transverse acoustic modes in other solid-rotor phases.

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[1]A. Lundén, A. Bengtzelius, R. Kaber, L. Nilsson, K. Schroeder, and R. Tärneberg, Solid State Ionics **9/10**, 89 (1983).

[2]K. Funke, in *Microscopic Structure and Dynamics of Liquids*, edited by J. Duprey and A. J. Dianoux (Plenum, New York, 1978); in *Solid Electrolytes*, edited by P. Hagenmuller and W. Van Grool (Plenum, New York, 1978); in *Topics of Current Physics 15, Superionic Conductors*, edited by M. B. Salamon (Springer, Berlin, 1979).

[3]R. T. Harley, W. Hayes, A. J. Rushworth, and J. F. Ryan, J. Phys. C **8**, L530 (1975).

[4]D. Gallagher, Ph.D dissertation, University of Illinois, Urbana-Champaign, 1978.

[5]G. Winterling, W. Senn, M. Grimsditch, and R. Kaliyar, in *Proceedings of the International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1977).

[6]M. V. Klein, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1973).

[7]R. W. Impey, M. L. Klein, and I. R. McDonald, J. Phys. C **17**, 3941 (1984); J. Chem. Phys. **82**, 4690 (1985).

[8]T. Hattori, J. Phys. Colloq. **C6**, 920 (1981).

[9]Cao-Xuan An, Phys. Stat. Sol. **43**, K69 (1977).

[10]C. R. A. Catlow, I. P. Comins, F. A. Germano, R. T. Harley, and W. Hayes, J. Phys. C **11**, 3197 (1978).

[11]B. Dorner, J. Windscheit, and W. von der Osten, in *Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1977).

[12]R. Aronsson, H. E. G. Knape, and L. M. Torell, J. Chem. Phys. **77**, 677 (1982).

[13]K. R. Subbaswamy, Solid State Commun. **19**, 1157 (1976); **21**, 371 (1977).

[14]W. S. Gornall and B. P. Stoicheff, Phys. Rev. B **4**, 4518 (1971); S. Gewurtz and B. P. Stoicheff, *ibid.* **10**, 3487 (1974); *ibid.* **11**, 1705 (1975).

[15]L. Nilsson, J. O. Thomas, and B. C. Tofield, J. Phys. C **13**, 6441 (1980).

[16]A. Kvist and A. Lundén, Z. Naturforsch. Teil A **20**, 235 (1965).

[17]R. Aronsson, L. Börjesson, and L. M. Torell, Phys. Lett. **98A**, 205 (1983).

[18]R. Aronsson, H. Knape, A. Lundén, L. Nilsson, L. M. Torell, N. Andersen, and J. Kjems, Radiat. Eff. **75**, 79 (1983).

[19]L. Börjesson and L. M. Torell, Phys. Rev. B **32**, 2471 (1985); Solid State Ionics **18/19**, 582 (1986).

[20]L Börjesson and L. M. Torell, preceding paper, Phys. Rev. B **36**, 4915 (1987).

[21]S. E. Gustafsson and E. Karawacki, Appl. Optics **14**, 1105 (1975); Optica Acta **22**, 569 (1975); Z. Naturforsch. **31A**, 956 (1976).

[22]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Cambridge, 1950), p. 107.

[23]B. D. Cullity, *Elements of x-ray Diffraction* (Addison-Wesley, Reading, MA, 1956).

[24]J. Kowalik and M. R. Osborne, *Methods for Unconstrained Optimization Problems* (Elsevier, New York, 1968).

[25]L. Nilsson, Ph.D. dissertation, Chalmers University of Technology, Göteborg, Sweden, 1981.

[26]H. E. Jackson, D. Landheer, and B. P. Stoicheff, Phys. Rev. Lett. **31**, 296 (1973).

[27]J. A. Graber and A. V. Granato, Phys. Rev. B **11**, 3990 (1975).

[28]C. R. A. Catlow, R. T. Harley, and W. Hayes, in *Proceedings of the International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1977); J. Phys. C **10**, L559 (1977).

[29]B. A. Huberman and R. M. Martin, Phys. Rev. B **13**, 1498 (1976).

[30]L. L. Chase, in *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976).

[31]T. Bischofeiger and E. Courtens, Phys. Rev. Lett. **35**, 1451 (1975).

[32]H. B. Huntington, in *Solid State Physics*, edited by Seitz and Turnbull (Academic, New York, 1958), Vol. 7.

[33]M. T. Sprackling, in *Plastic Deformation of Simple Ionic Crystals* (Academic, London, 1976).

[34]L. A. K. Staveley, Annu. Rev. Phys. Chem. **13**, 351 (1962).

[35]J. Timmermans, J. Phys. Chem. Solids **18**, 1 (1961).

[36]J. E. Bertie and S. Sunder, J. Chem. Phys. **59**, 3853 (1973).

[37]G. Ewing, J. Chem. Phys. **40**, 179 (1964).

[38]K. Schroeder and C. A. Sjöblom, High Temp. High Pressures **12**, 327 (1980).

[39]R. Aronsson, H. E. G. Knape, and L. M. Torell, Phys. Lett. **73A**, 210 (1979).

[40]L. Boyer, R. Vacher, M. Adams, and L. Cecchi, in *Proceedings II of the International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971).

[41]M. Djabourov, C. Levy-Mannheim, J. Leblond, and P. Papon, J. Chem. Phys. **66**, 5748 (1977).

[42]V. J. Tchippe and L. L. Abels, Phys. Lett. **60**, 129 (1977).

[43]H. Kiefte and M. J. Clouter, J. Chem. Phys. **62**, 4780 (1975); S. F. Ahmed, H. Kiefte, and M. J. Clouter, *ibid.* **69**, 5468 (1978).

[44]M. J. Bird, D. A. Jackson, and J. G. Powles, Mol. Phys. **25**, 1051 (1973).

[45]H. Fontaine and C. Moriamez, J. Chim. Phys. **65**, 969 (1968).

[46]S. C. Rand and B. P. Stoicheff, Can. J. Phys. **60**, 287 (1982).

[47]M. L. Klein and J. J. Weis, J. Chem. Phys. **67**, 217 (1977).

[48]O. Schnepp and A. Ron, Disc. Faraday Soc. **48**, 26 (1969).