# LATTICE VIBRATION SPECTRA Part LXIV. Raman spectroscopic study of lithium hydrogensulfide LiSH: dynamic disorder and order-disorder phase transition

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#### ABSTRACT

Raman spectra (4000-50 cm<sup>-1</sup>) of lithium hydrogensulfide are recorded in the range from 70 to 300 K. The temperature dependence of frequencies and halfwidths of the SH<sup>-</sup> stretching and librational modes yields clear evidence for a disorder-order phase transition at 222 K and thermally activated dynamic disorder of the SH<sup>-</sup> ions in the room temperature polymorph. Down to 70 K the increasing splitting of the in-plane libration can be interpreted by a Landau-type order parameter. This splitting reflects increasing dynamic interactions (factor group splitting) of adjacent (in [100]) SH<sup>-</sup> ions due to the ordering process. The halfwidths of the stretching and out-of-plane librational modes exhibit an Arrhenius-type behaviour. The activation energies derived are 1.9 kJ mol<sup>-1</sup> for both vibrations. The activation temperature (230 K) is in good agreement with that of the change of the specific heat at 228 K. The order mechanism and a plausible structure of the ordered phase below 222 K are discussed.

#### INTRODUCTION

The alkali metal hydrogensulfides exist in several crystalline polymorphs involving different degrees of order of the  $SH^-$  ions. X-Ray and neutron diffraction studies of the heavier alkali metal hydrogensulfides, e.g. NaSH [1-3] or CsSH [4], established that in the cubic high-temperature modifications (HTM) the  $SH^-$  ions are reorienting between three-dimensional quasi-equilibrium positions whereas in the room-temperature modifications (RTM)

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(trigonal, NaSH, KSH, RbSH; tetragonal, CsSH) reorientational 180° jumps between two split positions occur [5]. New neutron powder diffraction studies of all of these alkali metal hydrogensulfides confirm a fully ordered polymorph at temperatures lower than about 100 K [6,7].

The occurrence of very rapid reorientational motions with residence times of  $\approx 10^{-12}$  s [3,4] and relatively large jump distances of the SH<sup>-</sup> ions down to 100 K are in contrast to the much less dynamic behaviour of the hydroxide ions in the respective alkali metal hydroxides (e.g. RbOH and CsOH [8]). In LiOH, the high ionic strength of lithium ions together with the higher charge asymmetry of OH<sup>-</sup> in comparison to SH<sup>-</sup> ions prevents any dynamic disorder of the hydroxide ions and structure transformations and, hence, forces a layer structure [9].

Comparison of LiOH with LiSH has so far been impossible because of the limited stability of lithium hydrogensulfide and various preparative problems, which are the primary reasons for the rare studies in the past [10]. We have therefore developed a new preparative technique for hydrogensulfides and have established the crystal structure of LiSH by single-crystal X-ray methods [11]. At room temperature a 180° splitting of the H-positions exists. The question arises as to whether dynamic or static disorder of the SH<sup>-</sup> ions causes this splitting and if ordering of the protons occurs at low temperatures.

In this paper we analyse the Raman spectra of LiSH in terms of phase transition, disorder and hydrogen bonding. For this purpose the temperature dependence of band frequencies and halfwidths (full width at half maximum, FWHM) of the stretching and librational modes of the SH<sup>-</sup> ions ( $\nu$ (SH), R(SH)) have been recorded in the range 70-300 K.

## EXPERIMENTAL

LiSH was prepared by the reaction of lithium amide  $\text{LiNH}_2$  with liquid hydrogen sulfide at 423 K and  $25 \times 10^6$  Pa in an autoclave [11]. Polycrystalline samples were enclosed in glass capillary tubes under a dry argon atmosphere to prevent decomposition reactions with moisture.

The Raman spectra were recorded on a Dilor OMARS 89 multichannel Raman spectrograph (resolution  $<4 \text{ cm}^{-1}$ ) in the usual right angle geometry. For excitation the 514.5 nm line of an Ar<sup>+</sup> ion laser was employed. The laser power at the sample must be reduced to about 50 mW to avoid light-induced decomposition of LiSH to Li<sub>2</sub>S and H<sub>2</sub>S. The low-temperature spectra were recorded using a VC30 cryostat (Oxford Instruments) with a CF104 cell system and a DTC-2 temperature controller. The accuracy of the temperatures given is about  $\pm 2$  K. Due to the instability and high reactivity (e.g. with water) of LiSH no IR or high-temperature Raman spectra could be recorded. The halfwidths (FWHM) of the Raman bands obtained were fitted to a simple Arrhenius' law:

$$\ln(1/\Delta \nu_{1/2}) = V/k T^{-1} + C$$

where  $\Delta v_{1/2}$  values are the halfwidths of the respective bands, V is the potential barrier, T the temperature, and k the Boltzmann constant. The correlation times  $\tau$  are connected with the halfwidths by  $\Delta v_{1/2} = 1/c\pi\tau$  (where c is the velocity of light). In order to eliminate temperature independent parts of the halfwidths, experimental halfwidths were corrected by the halfwidths obtained by extrapolation to T=0 K. For further details see ref. 12.

#### STRUCTURE AND GROUP THEORETICAL TREATMENT

LiSH tP6 crystallizes at 295 K in the tetragonal space group  $P4_2/mmc-D_{4h}^9$ with two formula units in the unit cell [11]. Lithium occupies tetrahedral sites  $(D_{2d})$  in a distorted cubic close-packed arrangement of sulfur  $(D_{2h})$  (see Fig. 1). The H atoms are disordered at two residence maxima  $(C'_{2v})$  linearly connected via sulfur. They are oriented to adjacent SH<sup>-</sup> ions forming linear chains parallel to [100] and [010]. The very short distance of neighbouring residence maxima of the H atoms of 144 pm prevents occupation of both maxima at the same time. Therefore we assumed a dynamic disorder of the protons with cooperative reorientation motions leading to an equal arrangement of all SH<sup>-</sup>



Fig. 1. Crystal structure of LiSH [11] (tetrahedral arrangement of  $SH^-$  ions around  $Li^+$  with split positions of the protons forming linear chains parallel to [100] and [010]; distances are given in pm).

dipoles in one chain [11]. This assumption is also supported by the small enthalpy effect of  $\Delta H = 0.05 \text{ kJ mol}^{-1}$  at 228 K obtained by differential scanning calorimetry (DSC) [11].

The disorder of the protons leads to loss of exact translation symmetry and, hence, there is no possibility for a group theoretical treatment of all zonecentre normal modes. For the translatory modes of the Li<sup>+</sup> ions and the SH<sup>-</sup> ions as a whole a group theoretical prediction can be done assuming that the disorder of the protons does not affect the crystallographic site symmetries of these ions. This gives the following expressions for the translations (T) and lattice vibrations (T') of LiSH with the factor group  $D_{4h}$ 

$$\Gamma_{\rm T'}({\rm Li^+}) = A_{\rm 2u}({\rm IR}) + B_{\rm 1g}({\rm Ra}) + E_{\rm g}({\rm Ra}) + E_{\rm u}({\rm IR})$$

$$\Gamma_{T'}(SH^-) = A_{2u} + B_{2u}(silent) + 2 E_u$$

and

 $\Gamma_{\rm T} = A_{\rm 2u} + E_{\rm u}$ 

This treatment predicts six optical phonon modes  $(A_{2u}, B_{1g}, B_{2u}, E_g, 2E_u)$ . Two modes (species  $B_{1g}$  and  $E_g$ ) with only lithium ion motions are allowed with the Raman experiments.

## RESULTS

Raman spectra of LiSH in the SH<sup>-</sup> stretching ( $\nu$ (SH)), SH<sup>-</sup> librational (R(SH)), and translatory mode (T') region at various temperatures are shown in Fig. 2. The spectra obtained exhibit the following main features.

(i) There is only one SH<sup>-</sup> stretching mode in the whole temperature range studied. The band energies are larger than that of free (gaseous) SH<sup>-</sup> ions at 2541 cm<sup>-1</sup> [13]. The temperature dependence of  $\nu$ (SH) (see Fig. 3) is negative (d $\nu$ (SH)/dT<0). Therefore we assume that linear hydrogen bonds are not present [14] (by analogy to the temperature behaviour of  $\nu$ (OH) in solid hydroxides [15]).

(ii) The librational modes of the SH<sup>-</sup> ions can be attributed to the bands in the range 340-440 cm<sup>-1</sup>. At T > 220 K only two very weak and broad scattering peaks are found at 423 and 351 cm<sup>-1</sup> (300 K). Whereas the low-energy libration is not essentially affected by change in temperature, an increasing splitting of the high-energy libration takes place below 220 K (see Fig. 3).

(iii) In the translatory mode region below  $340 \text{ cm}^{-1}$ , six well resolved bands are observed at 300 K (and nine at 90 K). This is in contrast to the prediction of only two Raman allowed translatory modes by simple group theory treatment (see above).

(iv) The halfwidths of both the  $SH^-$  stretching mode and the low-energy libration at  $351 \text{ cm}^{-1}$  decrease continuously from 300 to 90 K as shown in Fig.



Fig. 2. Raman spectra of LiSH at various temperatures (×relative intensity).

3. The results of the fittings  $(\ln 1/\Delta \nu_{1/2} \text{ vs. } 1/T)$  are summarized in Table 1. In the case of both the stretching and the librational modes, Arrhenius' law is fulfilled as shown by the regression coefficients r. For both bands the same activation energy (V) of  $1.9 \pm 0.2$  kJ mol<sup>-1</sup> is obtained. The respective activation temperature (V/k) is in good agreement with the temperature of the small thermal effect at 228 K in the DSC experiments [11].



Fig. 3. Temperature shifts of both energies and halfwidths (FWHMs) of the SH<sup>-</sup> stretching mode  $\nu$ (SH) and the low-energy libration  $R_{oop}$  of LiSH.

## TABLE 1

Potential barriers (V), activation temperatures (V/k) and correlation times  $(\tau)$  at 300 K of the reorientational motions of SH<sup>-</sup> ions in LiSH derived from the temperature dependence of the halfwidths of the SH<sup>-</sup> stretching and librational modes  $\nu$ (SH) and R(SH) ( $R_{oop}$  at 351 cm<sup>-1</sup>, see Fig. 3) (r, straight line correlation coefficient; k, Boltzmann constant)

range (K)	v (kJ mol <sup>-1</sup> )	V/R (K)	r	t <sub>300</sub> (ps)
180-240 120-220	$1.85 \pm 0.1$ $1.90 \pm 0.2$	$221 \pm 10$ $230 \pm 20$	0.993 0.995	$2.30 \pm 0.2$ $0.46 \pm 0.5$
	range (K) 180-240 120-220	range (K) $(kJ mol^{-1})$ 180-240 $1.85 \pm 0.1$ 120-220 $1.90 \pm 0.2$	range (K)(kJ mol <sup>-1</sup> )(K) $180-240$ $1.85 \pm 0.1$ $221 \pm 10$ $120-220$ $1.90 \pm 0.2$ $230 \pm 20$	range (K)(kJ mol <sup>-1</sup> )(K) $180-240$ $1.85 \pm 0.1$ $221 \pm 10$ $0.993$ $120-220$ $1.90 \pm 0.2$ $230 \pm 20$ $0.995$

## DISCUSSION

In order to interpret the dynamic disorder of the SH<sup>-</sup> ions and the orderdisorder phase transition of LiSH, several aspects of the results obtained must be discussed in more detail.

(i) The discrepancy between the observed and calculated number of

translatory modes in the disordered RTM of LiSH is due to the incorrect assumption that the potential symmetry of the disordered  $\rm SH^-$  ions is equal to the crystallographic site symmetry of the S atoms  $(D_{2h})$ . This discrepancy is removed if the real potential symmetry of the center of gravity of the  $\rm SH^-$  ions in the structure, i.e.  $C'_{2v}$ , is used. There are two crystallographically equivalent quasi-equilibrium sites for this center of gravity. Due to the disorder both orientations of the  $\rm SH^-$  ions are equally occupied.

This type of disorder does not neglect the selection rule  $\vec{q} \approx 0$  because distortion of the rigid heavy-atom lattice due to proton jumps is unlikely. The Raman spectra obtained can be interpreted as composed of modes owing to the two energetically equivalent orientations of one SH<sup>-</sup> ion. A factor-group treatment of the disordered phase of LiSH using  $C'_{2\nu}$  potential symmetry for the center of gravity of the SH<sup>-</sup> ions (instead of  $D_{2h}$ , see above) leads to the following expressions for the translatory modes

$$\Gamma_{\rm T'}({\rm Li}^+) = A_{\rm 2u}({\rm IR}) + B_{\rm 1g}({\rm Ra}) + E_{\rm u}({\rm IR}) + E_{\rm g}({\rm Ra})$$

and

$$\Gamma_{T'}(SH^-) = A_{1g}(Ra) + A_{2g}(silent) + A_{2u} + B_{1g} + B_{2g}(Ra) + B_{1u}(IR)$$
  
+  $E_g + 2 E_u$ 

This calculation predicts six Raman allowed translatory modes as observed in the Raman spectra above 220 K (see Fig. 2).

The observation of two librational modes in the temperature range 300–220 K agrees with the site symmetry  $C'_{2v}$  of the two split positions. The vibrational modes of the librations are in-plane  $(R_{ip})$  and out-of-plane  $(R_{oop})$ . Factor group splittings cannot be observed because of the great disturbance of the phase coherence of the  $R_{ip}$  and  $R_{oop}$  owing to the disorder of the SH<sup>-</sup> ions.

(ii) The Raman spectra give clear evidence for an increasing order of the  $SH^-$  ions with decrease in temperature. This is inferred from the increasing splitting of the high-energy libration connected with further reduced half-widths of the bands (see Fig. 3) and the appearance of additional scattering peaks in the region below 340 cm<sup>-1</sup> below 220 K. This behaviour represents an order-disorder phase transition as is also shown by the thermal effect at 228 K in the DSC experiments. This phase transition of a dynamically disordered state into an ordered one is of higher order as shown by the monotonous slopes of the FWHMs versus temperature curves (see Fig. 3).

The change of the halfwidths of the Raman bands (stretching modes and librations) is obviously caused by coupling of these vibrations to thermally activated jumps of the SH<sup>-</sup> ions (jump barrier height 1.9 kJ mol<sup>-1</sup>). The correlation times  $\tau$  derived from the FWHMs at 300 K indicate that the time of coherence of the stretching modes being in phase is one order of magnitude

higher than that of the libration. This means that the libration is much more strongly coupled to the reorientational motion than the stretching vibration.

The magnitude of the splitting of the high-energy libration is a function of temperature as shown in Fig. 3. The increasing splitting  $\delta$  of this libration below 220 K is due to an increase of order of the SH<sup>-</sup> ions and can be taken as an order parameter  $\eta$  according to Landau's theory. Thus, a linear dependence of the square of this splitting ( $\delta^2$ ) as a function of temperature is obtained in the range 70–222 K as shown in Fig. 4.

(iii) A model for the hitherto unknown structure of a fully ordered lowtemperature polymorph (LTM) of LiSH can be derived on the basis of the following conclusions. Reduced dynamics of the SH<sup>-</sup> dipoles in the SH-SH chains result in a dipole moment vector in one direction of the chain. Dipoledipole interactions of parallel chains favor an antiferroelectric order in the (110) planes (see Fig. 1). Minimum proton-proton repulsive interactions arise if both the chains are directed in [110] and [110] and the protons are fixed around a  $4_2$ -screw axis. (However, lithium proton repulsive interaction is larger than that in the RTM.)

This structure model proposed for the low-temperature polymorph of LiSH is consistent with the space group  $P4_2/m$ - $C_{4h}^2$ , 4 formula units in the unit cell,



Fig. 4. Order-disorder phase transition of LiSH shown by the increasing splitting  $\delta$  of the highenergy libration  $R_{ip}$  in the light of Landau's theory  $(\delta^2 \propto T)$ .

cell dimensions  $a_{\rm LTM} \approx (2)^{1/2} a_{\rm RTM}$ ,  $c_{\rm LTM} \approx c_{\rm RTM}$ , and site symmetries  $S_4$  (Li),  $C_{\rm s}$  (S) and  $C_{\rm s}$  (H). In Table 2 the result of a group theoretical treatment is given. The prediction of nine translational modes, two in-plane and one out-of-plane librations, and two stretching bands in the Raman spectra agrees with the spectra observed at T < 220 K with the exception of the factor group splitting of the stretching mode (see below).

An alternative structure model in space group  $P4_2/mbc$ , which avoids the enlarged proton lithium repulsion mentioned above, requires a larger unit cell with eight formula units [14]. However, there are no further reasons for this larger cell nor spectroscopic evidence. Thus, for example, the number of Raman allowed translational modes is larger than that observed in the spectra, namely thirteen instead of nine [14]. Furthermore this structure model does not fulfil Landau's condition of order-disorder phase transition (group-supergroup relation).

(iv) The allowance of two in-plane librations  $R_{ip}$  (species  $A_g$  and  $B_g$ ) in the case of the LTM (instead of one  $R_{oop}$ , see Table 2) indicates that the higherenergy libration, which splits into two components below 220 K (see Fig. 2), must be assigned to the in-plane libration. The splitting  $\delta$  of  $R_{ip}$  (see Fig. 3), taken as an order parameter in Fig. 4 (see above) is due to an increased factorgroup interaction. The large amplitudes of librational motions reduce the dipole moment of the SH–SH chains and, hence, the dipole–dipole interaction forces. In contrast to that, no factor-group splitting of the SH<sup>-</sup> stretching mode is observed because with this vibration dipole–dipole interaction forces between the antiferroelectric ordered chains are not affected. The low-frequency libration at  $350 \pm 1$  cm<sup>-1</sup>, which reveals only small temperature dependence in frequency (similar to that found for the mean value of the two highenergy librations), must be attributed to the degenerate  $R_{oop}$  mode ( $E_g$ ).

The different temperature dependence of the halfwidth of  $R_{oop}$  compared to

TABLE 2

 $C_{4\mathbf{h}}$ n  $n_{T'}$ Mode  $n_{\mathrm{T}}$ Activity  $n_{\rm R}$  $n_1$  $A_{\rm g}$ 4 2 1 1  $\nu(\mathrm{SH}), R_{\mathrm{in}}$ Ra 2  $R_{\text{oop}}$  $\nu(\text{SH}), R_{\text{ip}}$  $A_{\mathrm{u}}$ 4 1 1 IR  $B_{g}$ 6 4 1 1 Ra  $B_{u}$ 2 1 1  $R_{oop}$ Silent  $E_{g}$ 4  $R_{oop}$ 3 1 Ra  $E_{\rm u}$ 6 1 3 1 1  $\nu(SH), R_{ip}$ IR Σ 36 3 21 8 4

Factor group treatment of the phonon modes of the ordered low-temperature polymorph of LiSH  $(n_i, SH^- \text{ stretching modes}; n_R, \text{ librations (in-plane, out-of-plane)}; n_{T'}, \text{ translatory modes}; n_T, \text{ translations)}$ 

that of  $R_{ip}$  (see Fig. 3) allows the conclusion that reorientational motions of the SH<sup>-</sup> ions are in the same direction as the normal coordinate of  $R_{oop}$ . This conclusion was also reached in former work [11] considering the respective bond distances.

(v) As concluded from the negative temperature shift of v(SH) no hydrogen bonds should be present in the linear S-H $\cdots$ S-H chains. The S $\cdots$ S distance of 392 pm (see Fig. 1) along [100] and [010] in the RTM is 26 pm shorter than those in the low-temperature and room-temperature modifications of CsSH [7] where unambigious H-bonds are present [14]. The low cation potential of Cs<sup>+</sup> compared to that of Li<sup>+</sup> enables a nearly undisturbed arrangement of SH····SH hydrogen bonds. The angles of such hydrogen bonds are always close to 90° [7] as are those of the hydrogen bonds in solid  $H_2S$ [16] and the intramolecular bond angle of hydrogen sulfide. This behaviour is obviously caused by the very small acceptor strength of SH<sup>-</sup> ions compared to that of OH<sup>-</sup> ions (which relates to the small sp-hybridization tendency of the valence orbitals of sulfur). In LiSH, the Li<sup>+</sup> ions enforce a linear arrangement of the SH<sup>-</sup> ions with relatively short S $\cdots$ S distances. Although the H $\cdots$ S distances are much shorter in LiSH as compared to CsSH and H<sub>2</sub>S, no Hbonds are formed because the protons (due to the 180° arrangement) are directed to a region of minimum electron density of adjacent SH<sup>-</sup> ions. Additionally the acceptor strength of the SH<sup>-</sup> ions is weakened owing to very strong cation interaction forces. However, this first interpretation of SH<sup>-</sup>···SH<sup>-</sup> hydrogen bonds must be improved in future work.

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