The Crystal Structures of Some Alkali Hydrosulfides and Monosulfides.

By

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(With 3 Figures.)

In this report are described the crystal structures of K_2S, $CsSH$, NH_4SH, and of the dimorphous substances $NaSH$, KSH and $RbSH$. (For some further substances conf. the Note at the end of the paper.)

Experimental Methods.

As these compounds are hygroscopic, exposure to air or water was avoided at all stages of preparation and manipulation.

Densities were determined by pycnometric or suspension methods.

X-ray photographs were taken with $MoK\alpha$ exclusively. Specimens were sealed into glass or silica tubes. Powder specimens were ordinarily rotated during exposure. For high temperature a coil of nichrome wire was passed about the horizontal tube and a measured current passed, a rough control being effected by the melting points of known substances. The possibility of irreversible reaction at high temperature was in most cases excluded by taking a later photograph at room temperature; under these conditions the powder lines were identical with those of the original preparation. In general spacings and intensities are averaged from photographs of at least two preparations; the former are corrected by the usual methods, the latter are visual readings. Intensities are calculated from the formula

$$I \alpha \frac{1 + \cos 2\theta}{\sin^2\theta \cos\theta} H F^2$$

in which are used the F curves of James and Brindley[1]) except in the case of NH_4[2]).

Powder photographs were indexed with the Hull Davey charts, oscillating crystal photographs by the Bernal method.

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1) R. W. James, G. W. Brindley, Z. Krist. 78, 470. 1931.

2) R. W. G. Wyckoff, Z. Krist. 75, 529. 1931.

Lattice constants are in general believed to be accurate to .02 Å. Powder cameras of radius 20 or 13 cm. were used.

Experimental Results.

CsSH.

CsSH has been described as crystallising from water in a white mass[1]). It was more conveniently prepared by passing H_2S over the metal which is protected from the air by an inert liquid such as toluene. Gas is evolved and the white precipitate is collected in a capillary for examination by the powder method.

Symmetry cubic: constants $a = 4.29$, $r_x = 3.41$, $Z = 1$.

Since there is no reason to doubt that this symmetry and unit are correct, the positions are necessarily *Cs* 000, *SH* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the two ions necessarily have spherical symmetry. This structure accurately reproduces the observed intensities. The powder lines, and hence the structure, remain unchanged on heating to at least 200°.

The lattice constants of the following compounds having this *CsCl* structure will give an idea of the relative crystal sizes of the spherical anions: *CsCl* 4.11, *CsCN* 4.25[2]), *CsBr* 4.29, *CsSH* 4.29, $CsNO_3$ 4.51 at 200°[3]), *CsI* 4.56.

Table I. *CsSH* Powder Data $a = 4.291$.

h k l	*a*	Intensity calc.	Intensity obs.
100	4.31	28	4
110	4.31	70	10
111	4.31	10.5	3
200	4.30	14	4.3
210	4.30	16	4.3
211	4.29	30	7
220	4.29	10	3.3
300. 221	4.29	7.7	2.3
310	4.29	14	4.3
311	4.29	4.5	1.3
222	4.29	3.5	1.0
320	4.28	3.4	1.3
321	4.29	16	3.7
400		1.6	abs.
410. 322	4.29	4.4	0.7
411. 330	4.29	7.8	0.9

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1) W. Biltz, E. Wilke-Dörfurt, Z. anorg. Ch. **48**, 300. 1906.

2) G. Natta, L. Passerini, Gazz. **61**, 191. 1931.

3) Unpublished data of the writer.

NH_4SH.

Although this compound has long been known it has never been described satisfactorily for our purposes. It is obtained by chilling a mixture of NH_3 and H_2S gases and is the only solid phase in this system stable above $-18°$[1]. The product sublimes slowly in a closed vessel at room temperature to give large irregular colorless transparent crystals. The crystals show the uniaxial negative cross, and by immersion in CH_2I_2 it was found that $\omega > 1.74$, $\varepsilon < 1.74$, with a moderate birefringence. For purposes of photographing, single crystals may be preserved for several weeks in glass tubes filled with mineral oil and sealed with paraffin. The primary beam leaves a turbid trace in such crystals without, however, affecting the quality of the photographs. The structure determination is based on Laue, oscillation and powder photographs. The density $r_{\text{pyc}} = 1.17$, $r_{\text{susp}} = 1.19$.

Tetragonal, D_{4h}, $c = 4.009$, $a = 6.011$, $c/a = .667$, $r_x = 1.16$, $Z = 2$.

Characteristic absences: $hk0$ with the index sum odd.

The only arrangement which provides for the observed characteristic absences, for the absence of 002, and for the spatial requirements of NH_4 and SH groups is given by D_{4h}^7 with N in 000, $\frac{1}{2}\frac{1}{2}0$, and with S in $0\frac{1}{2}u$, $\frac{1}{2}0\bar{u}$.

In estimating the only variable u it is noted that the reflections $hk3$ with the index sum even are absent on powder and oscillation photographs; this indicates that $u = \frac{1}{3}$, a value that gives satisfactory agreement with all powder and oscillation intensity data and which is therefore used in all subsequent calculations. On a Laue photograph, however, several reflections $hk5$ with the index sum odd are absent, whereas several such are observed present when the index sum is even; this indicates that $u = .350 = \frac{7}{20}$. The final value may be safely written $u = .34 \pm .01$.

Previously known crystals with this structure include PH_4I and the tetramethyl ammonium halides; for these the range of c/a is .71—.73 and of u is .35—.40. It is of interest that PH_4I has a moderate positive birefringence, while $N(CH_3)_4I$ is negative with $\omega = 1.66$, $\varepsilon = 1.65$ according to my data; the corresponding bromide and chloride have also been described as weakly negative. A similar reversal of optical character is found in the isomorphous crystals $Mg(OH)_2$ and $Ca(OH)_2$, which are respectively positive and negative.

The following distances are calculated for this structure: S—S 4.01 along the principal axis, 4.47 oblique to it; N—$4S$ 3.30, 4.02, the sulfur thus forming two successive tetrahedrons around each nitrogen.

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[1] L. Scheflan, C. Mc Crosky, J. Amer. chem. Soc. 54, 193. 1932.

NH_4SH does not have a triple point like an ordinary undissociating substance but rather a three phase line with the limits 88° (maximum sublimation point) and about 120° (minimum melting point) according to Scheffer1). One would expect solid NH_4SH, since it contains two different kinds of hydride ions, to exist in other modifications; a search for these and an investigation of the temperature variation of c/a of the tetragonal phase would be of interest. The dissociation pressure data for NH_4SH in the range 0—44°2) fall on a straight $\log K$-$1/T$ line which moreover passes through Scheffer's points at 81—88°; this possibly excludes a transition in this region.

Table II.

Powder and Oscillation Photographic Data for NH_4SH.

$a = 6.011,\ c = 4.009,\ u = .33.$

$h\,k\,l$	$1/d^2$		Intensity		
	calc.	powder	powder	osc.	calc.
100	0.0277		0		0
110	0.0553	.0538	5	st.	30
001	.0622		0	0	2.4
101	.0899	.0890	7	st.	210
200	.1107	.1098	10		266
111	.1176	.1167	8	st.	225
210	.1384		0	0	0
201	.1729		0	w.	0
211	.2006	.2000	7	st.	117
220	.2214	.2206	7		72
300	.2490		0	0	0
002	.2490		0	0	0
310	.2767	.2770	5	st.	18
102	.2766			m. st.	36
221	.2836		0	w.	0
112	.3041	.3093	5	m.	31
301	.3113			st.	30
311	.3389	.3388	6	st.	53
320	.3598		0		0
202	.3598		0	w., o.	0
212	.3872	.3892	5	st.	48
321	.4219	.4217	4	st.	39
400	.4427	.4427	4	st.	20
410	.4709		0	0	0
222	.4703		0	0	0
401	.5054			0	1

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1) F. E. Scheffer, Z. physikal. Ch. **76**, 161. 1911.

2) Landolt Börnstein, Tabellen.

Table II (continued).

$h\,k\,l$	$1/d^2$		Intensity		
	calc.	powder	powder	osc.	calc.
330	.4981	.5016	4	m.	5
302	.4979			m.	15
312	.5256	.5305	4	m.	21
411	.5326			mst.	27
420	.5534	.5544	5	st.	27
003	.5600			w.	7
331	.5603			st.	11
103	.5875		0	0	0
113	.6153	.6132	4	m.	9
322	.6096			mst.	22
421	.6158			w.	0
203	.6707	.6730	2	m.	19
402	.6921		0	0	0
213	.6946		0	0, w.	0
430, 500	.6919		0	0	0
510	.7194	7206.	4	m.	7
412	.7193			mst.	17
332	.7469	.7522	3	m.	5
341, 501	.7540			st., m.	16
511	.7816	.7818	3	m.	9
223	.7813			m.	14
520	.8026		0	0	0
303	.8086		0	0	0
422	.8025		0	0	0
313	.8367		0	mw.	12
521	.8647	.8621	band	m.	12
440	.8856	.8800		m.	7
323	.9198		0	0	0
530	.9408	.9390	3	w.	5
432, 502	.9406			m., m.	10

KSH.

Gay-Lussac and Thenard[1]) showed that when K is warmed in a current of H_2S an exothermal reaction takes place leaving a residue of solid KSH. I verified this convenient method of preparation by taking powder photographs of the product.

I was able to show in the same way that on leaving K in contact with liquid H_2S at room temperature for a day or so there is a complete conversion to KSH.

According to Rule's method[2]) an alcoholic solution of the metal

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1) See Gmelin-Kraut's Handbuch d. Anorganischen Chemie. 1906.

2) A. Rule, J. chem. Soc. London **99**, 558. 1911.

alcoholate, on saturation with H_2S, yields with evolution of heat an alcoholic solution of KSH from which the product may be precipitated as a white crystal powder by the addition of ether or benzene. The reaction runs as well with methyl as with ethyl alcohol; owing to the greater solubility of KSH in CH_3OH than in C_2H_5OH the addition of benzene may not precipitate the product but merely form a second liquid phase. If on the other hand the ethyl alcohol solution is slowly evaporated at room temperature colorless transparent crystals with well-developed faces are obtained; this phase was likewise identified as KSH by its diffraction pattern. Microscopic examination shows that these crystals consist for the greater part of twins, according to a law to be described presently. However, one crystal was found which gave a typical uniaxial negative interference figure. This crystal originally was so oriented as to give an uncentered figure with the axis emerging outside the field; on accidentally subjecting the crystal to pressure a well-defined oriented zone was developed which gave a nearly centered figure. This was doubtless a case of artificial twinning made possible through the presence of a glide plane. Cleavage fissures were noted parallel to the growth faces of some crystals.

For the density I found $r_{\text{susp}} = 1.68$, $r_{\text{pyc}} = 1.74$.

From powder photographs the following structure was deduced.

Symmetry trigonal, rhombohedral translation group.

$\alpha = 68°51'$, $a = 4.374$, $r_x = 1.70$, $Z = 1$. The lattice may also be defined by two other sets of axes: a hexagonal prism with $a' = 4.95$, $c' = 9.94$, $c/a = 2.005$; a face centered rhombohedron with $\alpha'' = 97°$ —, $a'' = 6.60$, $Z = 4$.

K and S are necessarily in 000, uuu. The observation that all reflections with the index sum odd are absent shows that $u = \frac{1}{2}$ very nearly, and calculation shows that a departure of u from this value by .03 brings calculated and observed intensities into conflict, whereas the agreement with $u = \frac{1}{2}$ is satisfactory throughout. The adoption of this special value increases the symmetry from C_{3v}^5 to D_{3d}^5.

Oscillation photographs of twinned crystals afford a confirmation of this structure as well as a deduction of the twinning law. The twinning plane (and probably the glide plane) is found to be (110)″, the growth and cleavage face is (100)″.

It may be fairly stated that this structure has not heretofore been found either in AB or in ABX crystals, although its similarity to known structures is striking. Thus on the one hand the KSH structure may be derived from the $NaCl$ structure by simply compressing the latter along a trigonal axis; there is no change in coordination, but there is a consider-

Table III. Powder Photograph of *KSH*, Trigonal Phase.

Quadratic form $\frac{1}{d^2} = \frac{4\sin^2\theta}{\lambda^2} = \frac{1}{d_0^2}\left[(h^2+k^2+l^2)+c(hk+kl+hl)\right].$

$c = 0.5303,\ d_0 = -3.933.$

$(h\,k\,l)''$	$(h\,k\,l)'$	$(h\,k\,l)$	$1/d^2$ calc.	$1/d^2$ obs.	Intensity calc.	Intensity obs.
$11\bar{1}$	10.1	100	0.0647		< 0.1	0
111	00.3	111	.0911		< .1	0
200	10.2	110	.0950	0.0953	18	10
$2\bar{2}0$	11.0	$1\bar{1}0$	.1636	.1640	8	7
220	10.4	211	.2188	.2171	5	5
$3\bar{1}\bar{1}$	20.1	$11\bar{1}$	.2282		< .1	0
$31\bar{1}$	11.3	210	.2547		< .1	0
$22\bar{2}$	20.2	200	.2586	.2590	4.2	4.8
311	10.5	221	.3075		< .1	0
222	00.6	222	.3643	.3647	0.8	1.8
400	20.4	220	.3800	.3820	2.4	3.3
$3\bar{3}1$	21.1	$2\bar{1}0$	.4009		< .1	0
$4\bar{2}0$	21.2	$21\bar{1}$	.4222	.4233	3.8	4.3
$4\bar{2}\bar{2}$	30.0	$2\bar{1}\bar{1}$	.4907	.4897	1.7	2.3
420	11.6	321	.5279	.5259	2.6	3
$42\bar{2}$	21.4	310	.5436	.5439	2.4	3
$4\bar{4}0$	22.0	$2\bar{2}0$	.6543	.6535	0.9	1
422	10.8	332	.7023	.7050	0.8	1
$4\bar{4}2$	31.2	$3\bar{1}0$	.7493	.7483	1.4	1.5
600, $44\bar{2}$	30.6	330, 411	.8551	.8574	0.6	1
440	20.8	422	.8658	.8702	0.5	1
$6\bar{2}0$	31.4	$32\bar{1}$	.8708		1.1	
$6\bar{2}\bar{2}$	40.2	$22\bar{2}$	.9129	.9122	0.5	0.5
$62\bar{2}$	22.6	420	1.019	1.027	0.8	0.5
620	21.8	431	1.027		0.8	
$44\bar{4}$	40.4	400	1.034		0.4	
442	10.10	433	1.067	1.072	0.7	0.8
$6\bar{4}0$	32.2	$3\bar{2}1$	1.077			
$6\bar{4}\bar{2}$	41.0	$3\bar{2}\bar{1}$	1.145	1.146	0.7	0.6
$6\bar{4}2$	32.4	$41\bar{1}$	1.198	1.197	0.6	0.6
622	20.10	442	1.230		0.3	0
$64\bar{2}$	31.8	521	1.357	1.352	0.5	0.5
640	21.10	532	1.394	1.394	0.5	0.5
$6\bar{4}\bar{4}$	50.2	$4\bar{1}\bar{1}$	1.404			

able departure from the axial ratio $c/a = 2.45$, or the angle $\alpha'' = 90°$, characteristic of the cubic close packing of spheres. On the other hand, *KSH* is crystallographically strongly reminiscent of calcite.

The sketch shows a twin of *KSH* as observed; it appears as a nearly square orthorhombic prism terminated at one end by a flat dome. The observed spacing of the prism face is 3.25 Å., and from layer line separations the observed translations are 3.30 Å. along the prism axis, 4.95 Å. and 17.17 Å. along the horizontal axes. The translations calculated from the foregoing structure of *KSH* are $[100]''$ 6.61 Å., $[1\bar{1}0]''$ 4.95 Å. and $[441]''$ 34.35 Å.; the latter is calculated to depart from the normal to the two former by less than 2′ of arc. The calculated spacing of (200) is 3.25 Å. The agreement serves to orient the twin unambiguously. The positions and intensities of all reflections are moreover accounted for by the foregoing structure which is thereby given a desired confirmation. Thus the apparent halving of $[100]''$ and $[441]''$ is merely an expression of the previous observation that all reflections with the index sum odd are absent due to the pseudo

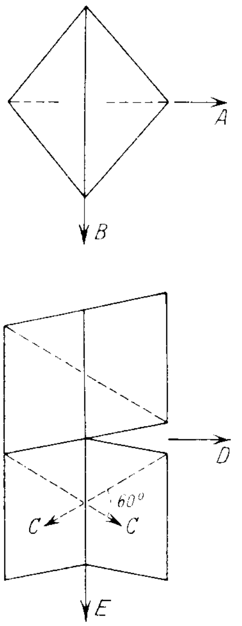


Fig. 1.

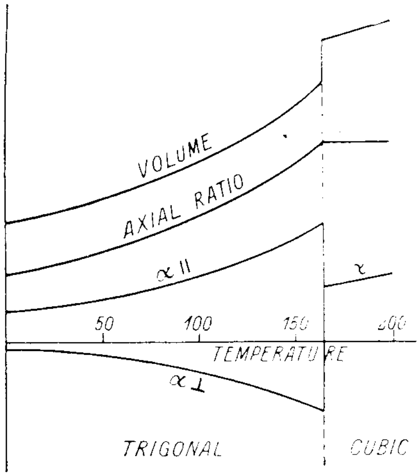


Fig. 2.

Figure 1. *KSH* rhombohedron $(100)''$ twinned according to $(110)''$ law, showing planes and axes.

Top View

$A = [441]''$, trace of $(1\bar{1}0)''$.

$B = [1\bar{1}0]''$, trace of $(110)''$ twin plane.

Side View

C = trigonal axes $[111]''$ intersecting at 60°

$D = [441]''$ trace of $(11\bar{8})''$

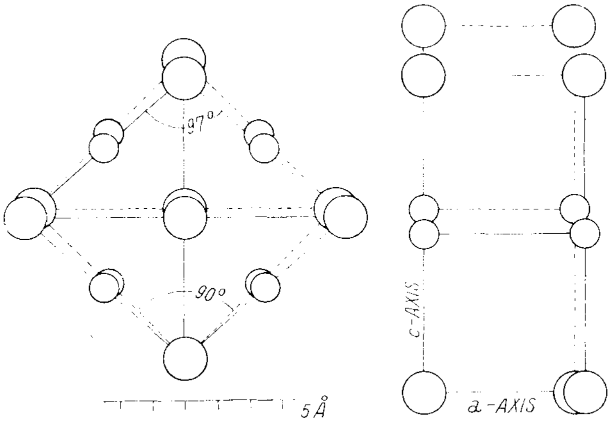
$E = [001]''$ trace of $(110)''$ twin pane

Figure 2. Predicted thermal expansion of *KSH* type (schematic). $\alpha_{\parallel}$, $\alpha_{\perp}$ = expansion coefficients parallel and ⊥ the 3-fold axis.

body centering of a K by an S atom. The pseudo cubic nature of the lattice is easily discernible in oscillation photographs of a single crystal about the pseudo cube edge $[100]''$. The axes of the orthorhombic prism with $Z = 8$ used in indexing the oscillation photographs of a twin are

Axis	Length	Normal Plane	Spacing	
$[001]''$	6.61	$(11\bar{8})''$	.414	
$[1\bar{1}0]''$	4.95	$(1\bar{1}0)''$	2.47	
$[441]''$	34.35	$(110)''$	2.17	= twinning plane

On heating a powder specimen of KSH to about 150° the spacings of $1\bar{1}0$ and of $2\bar{1}\bar{1}$ become slightly smaller, the spacings of 211, 220 and 321 increase considerably, the spacings of 200 and $21\bar{1}$ do not change appreciably. The axial ratio approaches 2.10 and α is about 67°. This shows that the lattice has contracted slightly normal to the principal axis and expanded considerably parallel to the axis, that is, that it exhibits the same type of anisotropy of expansion as does calcite. At 200° the powder lines show the presence of a $NaCl$ cubic phase with $a = 6.63$, with the axial ratio 2.45 and $\alpha = 60°$. By taking photographs at intermediate temperatures it was estimated that the transition occurs in the range 160—170°. The coordination remains unchanged through the transition, that is, each Me is surrounded by six equidistant S atoms at the points of an octahedron. While this octahedron is regular in the cubic phase, it is flattened between parallel faces in the trigonal phase



a) Figure 3. *b*)

a) Centered rhombohedron net $(100)''$ of KSH showing positions of atoms relative to (000) at 25° (full lines) and at 200° (broken lines). *b*) Prism face $(2\bar{1}\bar{1})''$ of the same.

Table IV.

Powder Photographs of Alkali Hydrosulfides, Cubic Forms.

NaSH

at 200°, $a = 6.05$

$h\,k\,l$	a	Intensity	
		calc.	obs.
111	6.11	2.8	3
200	6.05	45	10
220	6.06	33	6
311	6.05	0.7	2
222	6.05	11	4
400	6.02	5	2
331	6.04	.5	1
420	6.05	14	2
422	6.05	10	2

KSH

at 200°, $a = 6.63$

$h\,k\,l$	a	Intensity	
		calc.	obs.
111		0	0
200	6.71	20	10
220	6.65	14	8
311		0	0
222	6.65	5	4
400	6.63	2.5	2
331		0	0
420	6.62	6.5	2
422	6.61	5	1

RbSH

at 200°, $a = 6.93$

$h\,k\,l$	a	Intensity	
		calc.	obs.
111	6.92	11	w.
200	6.95	27	s.
220	6.93	21	m.
311	6.92	6	w.
222		8	0

so that six of its edges (100 translation) are shorter than the remaining six edges (1$\bar{1}$0 translation).

The discontinuous nature of the transition is represented schematically by the variation of the linear expansion coefficients ($\alpha_{\parallel}$ and $\alpha_{\perp}$) with temperature (Figure 2). Of chief interest is the fact that $\alpha_{\perp}$ changes its sign discontinuously at the transition point; while doubtless there are other substances which exhibit this phenomenon I am not aware of any measurements which show it. It is evident that a twinned crystal, on heating above the transition point, becomes a single crystal, and the two trigonal axes, previously inclined at 60°, come into coincidence. In other words (110)″ is a symmetry plane in the cubic system, but not in the trigonal system; and it is impossible for a crystal to twin on a plane of symmetry.

From the foregoing it is apparent that low *KSH* crystals bear a resemblance to calcite, while the high temperature form is isostructural with *NaCl*. The points of similarity are summarised as follows:

	Low *KSH*	Calcite	High *KSH*	Rock Salt
Growth Face	(100)″	100		100
Cleavage	(100)″	100		100
Twin Plane	(110)″	110		
Glide Plane	present	110		110
Birefringence	negative	negative	isotropic	isotropic
Major expansion	parallel *c*	parallel *c*	isotropic	isotropic
Rhomb Angle	97°	101° 50′	90	90

NaSH and *RbSH* proved to be isomorphous with *KSH* and therefore require only a brief description.

NaSH.

Gay-Lussac and Thenard stated that when *Na* is warmed in a current of H_2S the product of the exothermal reaction consists of Na_3S_2H, that is, a mixture of Na_2S and *NaSH* in equal amounts. I verified this fact by showing that the product gives the powder lines of these two solid phases with about the same intensity.

NaSH was also obtained by the reaction of the metal with liquid H_2S at room temperature.

By Rule's reaction it is precipitated as a white powder which shows no tendency to crystallise from the ethyl alcohol solution. On standing in the presence of toluene plus a small quantity of methyl alcohol the powder becomes crystalline, but the X-ray diffraction effects remain unchanged — that is, the composition of the solid phase is in both cases *NaSH*.

The colorless crystals are optically uniaxial negative with moderate birefringence. They appear as small well formed rhombohedrons (100)″ with a slightly greater than 90°. The pseudo octahedrons (111)″ and $(11\bar{1})''$ truncate the corners of the pseudo cube on some crystals.

For the density of *NaSH* I found $r_{\text{pyc}} = 1.79$ or somewhat greater than the density of *KSH*. This is generally true when *Na* replaces *K* isomorphously in *MeX*, provided that *X* is not an excessively light atom.

As with *KSH* the structure of *NaSH* was first deduced from powder photographs and later confirmed by single crystal photographs. For the latter purpose a small rhombohedron was oscillated about the pseudo cube edge [100]″. The diffraction effects of *NaSH* closely parallel those of *KSH*. On powder photographs only one plane with the index sum odd, namely 100, reflects with appreciable intensity, the others are absent. The transition to the *NaCl* cubic phase was estimated to occur at 90°.

The lattice constants are

Trigonal phase: $\alpha = 68°5'$, $a = 3.986$; $c' = 9.12$, $a' = 4.46$, $c'/a' = 2.046$; $\alpha'' = 96°30'$, $a'' = 5.98$; $r_x = 1.76$.

Cubic phase: $a = 6.05$ at 200°.

RbSH.

RbSH has been crystallised from water solution in hygroscopic colorless needles[1]). The present material was prepared by the method used for *CsSH* as a white precipitate.

Table V. Powder Photograph of *NaSH*, Trigonal Phase

$c = -0.5436$, $d_0 = 3.559$.

$h\,k\,l$	$1/d^2$ calc.	$1/d^2$ obs.	Intensity calc.	Intensity obs.
100	0.0790	0.0799	2	1.5
111	.1056		0.3	0
110	.1150	.1156	11	10
$1\bar{1}0$	.2008	.2016	19	7
211	.2591	.2603	12	6.3
$11\bar{1}$	.2798		0.2	0
210	.3089		0.4	0
200	.3158	.3160	9	5.3
221	.3672		0.2	0
222	.4324	.4311	1.8	1.7
220	.4600	.4603	5	3
$2\bar{1}0$	.4806		.3	0
$21\bar{1}$	.5166	.5168	8.1	4.3
$2\bar{1}\bar{1}$	.6025	.6037	3.1	1.7
321	.6332	.6329	5.5	3
310	.6608	.6599	5.2	3
$2\bar{2}0$	.8033	.8044	1.8	0.8
332	.8356	.8340	1.7	0.8
$3\bar{1}0$	.9183	.9193	2.8	0.8
330, 411	1.035	1.035	1.1	0.8
422	1.037			
$32\bar{1}$	1.062	1.063	2.1	0.5
$22\bar{2}$	1.119		0.6	0
420	1.236	1.237	1.5	0.8
431	1.237			
400	1.263		0.5	0
433	1.268			
$3\bar{2}1$	1.320	1.319	1.3	0.5
$3\bar{2}\bar{1}$	1.406		1.2	0
$41\bar{1}$	1.464	1.462	1.0	0.5
442	1.469			

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[1]) W. Biltz, E. Wilke-Dörfurt, Z. anorg. Ch. 48, 300. 1906.

Table VI. Powder Photograph of $RbSH$, Trigonal Phase

$c = -0.5218,\ d_0 = 4.087.$

$h\,k\,l$	$1/d^2$ calc.	$1/d^2$ obs.	Intensity calc.	Intensity obs.
100	0.0599	0.0599	7.3	3.2
111	.0859		1.7	0
110	.0883	0.0881	25	10
$1\bar{1}0$	.1510	.1500	12	6.8
211	.2030	.2018	8	8
$11\bar{1}$	.2109		1.6	0
210	.2369		2.8	0
200	.2395	.2382	6.3	8.0
221	.2890		1.1	0
222	.3436		1.3	0
220	.3540	.3552	3.6	1.6
$2\bar{1}0$	.3618		1.6	0
$21\bar{1}$	.3905	.3897	6.7	2.6
311	.4399		0.6	0
$2\bar{1}\bar{1}$	.4529	.4553	2.4	0.6
321	.4945	.5001	4.1	1.1
310	.5050			
$2\bar{2}0$	.6038		1.6	0
332	.6611	.6664	1.3	0.4
$3\bar{1}0$	.6924	.6956	2.4	0.4

Comparison of Structures of Alkali Hydrosulfides and Halides.

The similarity in the structural functions of the SH group and the halogens is brought out by the following table.

Wurtzite Type CN 4	$NaCl$ Type CN 6	$CsCl$ Type CN 8
	$LiF \ldots LiI$	
	$NaF \ldots NaI$	
	$KF \ldots KI$	
	$RbF \ldots RbI$	$RbCl \ldots RbI$ at high press.
	CsF; $CsCl$ at high temp.	$CsCl \ldots CsI$
NH_4F	$NH_4Cl \ldots NH_4I$ at high temp.	$NH_4Cl \ldots NH_4I$
	$NaSH \ldots RbSH$ at high temp.	$CsSH$
	KSH Type (deformed $NaCl$) CN 6	PH_4I Type (deformed $CsCl$)
	$NaSH \ldots RbSH$	NH_4SH

The powder lines of this material are relatively weak owing probably to the fluorescence of the specimen in *MoK* radiation. In spite of this the 100 plane gives a reflection of appreciable intensity, other planes with the index sum odd are absent. The transition temperature was not determined.

The lattice constants are

Trigonal phase: $\alpha = 69°20'$, $a = 4.525$; $c' = 10.26$, $a' = 5.15$, $c'/a' = 1.990$; $\alpha'' = 97°20'$, $a'' = 6.85$; $r_x = 2.50$.

Cubic phase: $a = 6.93$ at 200°.

From this it would seem profitable to search for further high temperature phases of *CsSH* and NH_4SH, for a high pressure phase of *RbSH* having the *CsCl* structure and to follow the deformation (variation of axial ratio with temperature) of all the hydrosulfides into the low temperature region with a possibility of finding new modifications there. Investigation of the p—v—t relations and of the specific heat curves of all the alkali hydrosulfides would not only confirm the X-ray evidence but add much new thermodynamic information as well. Since there is doubtless a volume increase on heating *KSH* through the transition, it may be predicted that the transition temperature will increase with increasing pressure; this is the case with the transitions of the NH_4 and *Rb* halides to the *NaCl* structure.

Alkali Sulfides Me_2S.

Li_2S and Na_2S are known to possess the CaF_2 structure; from the radius ratio this structure would be predicted to be a stable one for the *K*, *Rb*, and *Cs* monosulfides as well. The latter have been decribed by Rengade and Costeanu as follows: K_2S and Rb_2S form regular isotropic octahedrons with the respective densities 1.805 and 2.912; Cs_2S forms anisotropic needles[1]).

K_2S was prepared in two ways, first by synthesis from the elements in an evacuated glass vessel, second by the reaction $KSH + K \rightarrow K_2S + H$, also in a glass vessel; in both cases the glass was attacked and the product was a light gray pulverulent mass. Both products give the powder lines characteristic of the CaF_2 structure, and the lines remain unchanged when the specimen is heated to 200° during the exposure. Thus there is no indication of the inversion reported to occur at 146° and one atmosphere[2]); it seems not improbable that Bridgman observed the transition point of a hydrated form.

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1) E. Rengade, N. Costeanu, C. r. **158**, 946. 1914.

2) P. W. Bridgman, Pr. Nat. Acad. Washington **51**, 76. 1915.

Symmetry cubic; $a = 7.35$, $r_x = 1.84$, $Z = 4$.

The distance K—S observed is 3.18, calculated from Zachariasen's radii 3.10.

It is certain that Rb_2S has the same structure with the cube edge $a = 7.71$ calculated from the above density and the Rb—S distance 3.34, in agreement with the distance 3.26 predicted from the known radii.

Table VII. Powder Photograph of K_2S

$a = 7.345$.

$h\,k\,l$	a	Intensity	
		calc.	obs.
111	7.34	5.3	5
200	7.34	5.3	5
220	7.32	22	10
311	7.35	2.0	4
222	7.34	1.5	3.8
400	7.34	3.9	5.5
331	7.32	1.1	3.5
420	7.35	2.0	3.8
422	7.34	8.0	7.5
333, 511	7.34	.8	3
440	7.35	2.5	4.5
531	7.35	0.8	2.5
442, 600	7.35	.7	1
620	7.35	3.4	5.5
444	7.35	.8	2
642	7.35	3.8	5.5
800	7.35	.4	.7
660, 822	7.35	1.9	3.5
840	7.35	1.0	1
664	7.35	.8	1
844		.7	0
862, 10.2.0	7.35	1.8	2

Discussion.

Radius of SH^-: The SH^- group has the same number of electrons as the argon atom and as the ions with the argon configuration, such as $S^=$, Cl^-, K^+, Ca^{2+}, etc., which differ in nuclear charge only. The method used by Zachariasen[1] for calculating crystal radii is therefore applicable to it and gives for the radius of the six-coordinated spherical group 1.99 Å, a value slightly larger than the radius of Br^- (1.96) and considerably larger than the isoelectronic Cl^- (1.81). The following shows

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[1] W. H. Zachariasen, Z. Krist. **80**, 137. 1931.

that this value of the radius correctly predicts the anion-cation distances found in the hydrosulfides, as the coordination number (*CN*) and the radius of the cation is varied.

	CN	anion-cation distance observed		calc.	anion-anion distance observed	
		low	high		low	high
$NaSH$	6	2.99 —	3.03	2.97	3.99, 4.46	4.28
KSH	6	3.31 —	3.32	3.32	4.37, 4.95	4.69
$RbSH$	6	3.34 —	3.47	3.47	4.53, 5.15	4.90
$CsSH$	8	3.71		3.76	4.29	
NH_4SH	4	3.30		3.30	4.01, 4.47	

It is also in agreement with the shortest S—S distances observed in $NaSH$ (3.99) and in NH_4SH (4.01); these should not be much less than twice the radius. For comparison the distance between S centers in cubic H_2S is 4.09.

Symmetry of SH^-: The foregoing analyses indicate that in $CsSH$ and in the high temperature phases of $NaSH$, KSH, and $RbSH$ the anions have spherical symmetry; this would necessitate the free rotation of the SH group in these crystals. Such rotation is not improbable in view of the recent finding that in the crystal lattice of H_2S the molecules are freely rotating[1]). This deduction followed from the observation that on heating solid H_2S through its transition at — 170° the dielectric constant rises to a relatively high value which differs little from that of liquid H_2S. It is of course in harmony with the independent observation that H_2S crystals above the transition diffract X-rays precisely like a cubic close packed assembly of spherical molecules. Since the moments of inertia of HS^- and H_2S cannot be very different, one would as readily expect to find free rotation in the ionic $MeSH$ lattice as in the molecular H_2S lattice.

While there is no reason to doubt that SH^- has spherical symmetry in $CsSH$ and in the cubic modifications of $NaSH$, KSH and $RbSH$, the question of its symmetry in the trigonal modifications of these crystals and in NH_4SH cannot be so readily answered. This problem can only be attacked by indirection since the scattering power of hydrogen for X-rays is negligible compared with that of sulfur.

Only two possible non-spherical configurations of SH^- need be considered, a linear group, and what may be called a planar group obtained

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[1]) J. D. Kemp, G. H. Dennison, J. Am. chem. Soc. **55**, 251. 1933; C. S. Hitchcock, C. P. Smyth, J. Am. chem. Soc. **55**, 1296. 1933.

by conceiving the hydrogen as being in continuous rotation, in the basal plane about the central sulfur atom, the rotation axis in both cases to coincide with the vertical crystal axis. The planar group has a center of symmetry which the linear group lacks. The fact that S apparently occupies a symmetry center of the space group D_{3d}^5 favors the choice of the planar group over the linear one, so far as the KSH type is concerned.

We may also find a suggestion in the anisotropic properties of crystals known to be constructed of non-spherical groups. It is known that crystals with planar groups, such as NO_3, all lying in parallel planes have negative birefringence and have the maximum thermal expansion normal to these planes; whereas crystals with linear groups, such as $N—N—N$, all lying on parallel axes, have positive birefringence and have the maximum thermal expansion normal to this axis[1]). The KSH type has negative birefringence and a maximum expansion normal to the basal plane; from this it would be concluded that SH^- is a planar group with its plane parallel to the basal plane, and not a linear group with its axis normal to the basal plane.

Physically we may picture the extreme thermal expansion parallel to the 3-fold axis when heat energy is imparted to the KSH crystal, as resulting from the ever wider excursions of the proton from the basal plane in its rotation about the central sulfur atom. At the transition temperature this process becomes discontinuous as the SH group makes a last sudden approach to sphericity and the crystal undergoes a volume increase.

In spite of the marked similarity between the trigonal KSH type and the calcite-$NaNO_3$ type, there is to be observed one difference: the effect at a given temperature of increasing the radius of the cation. In KSH this process is accompanied by increasing deformation of the lattice as measured by the departure of the rhombohedral angle from 90; while in the carbonates and nitrates the opposite is true. In the accompanying table the cation radius increases from top to bottom.

	α''		α''		α''
$LiNO_3$	103° 14′	$MgCO_3$	102° 58′	$NaSH$	96° 30′
$NaNO_3$	102° 40′	$CaCO_3$	101° 55′	KSH	97°
				$RbSH$	97° 20′

It is of interest that when a single $NaCl$ or KCl crystal is subjected to a deformation such as has been pictured above, that is, a compression normal to an octahedron face, the previously isotropic crystal assumes

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1) Unpublished data of the writer.

the optical character (uniaxial negative with the optic axis parallel to the direction of the pressure)1) actually observed in the *KSH* and calcite-$NaNO_3$ types.

In tetragonal NH_4SH it is not impossible that the *SH* ion has the configuration proposed for it in the *KSH* type. In both of these crystals, by analogy to solid H_2S, the *SH* group might be expected to "freeze" into the structure at a low temperature transition point; there are no experimental data on this point.

The foregoing picture of the symmetry of the *SH* ion is in general agreement with the theory of molecular rotation in the solid state as developed by Pauling2).

Thermochemistry of the H_2S molecule: The lattice energies of the cubic hydrosulfides as calculated from the simple Born theory, yield a new value for the heat of the ionic gas reaction:

$$H^+ + SH^- \rightarrow H_2S : \triangle H = 338 \text{ kilo calories.}$$

The thermochemistry of the compounds *MeSH*, Me_2S and H_2S will be made the subject of a further communication.

In conclusion I wish to thank Professor Albert Sauveur for placing at my disposal the X-ray apparatus used in the greater part of this work, and Professor B. E. Warren for discussion and criticism at various times during the course of the work.

Summary.

1. *CsSH* has the cubic *CsCl* structure, $a = 4.29$.
2. NH_4SH at room temperature is tetragonal with $c = 4.01$, $a = 6.01$; N at 000, $\frac{1}{2}\frac{1}{2}0$ and S at $\frac{1}{2}0u$, $0\frac{1}{2}\bar{u}$, $u = 0.34$.
3. The *KSH* structure type has one formula of *KSH* in D_{3d}^5; lattice constants are *NaSH* $\alpha = 68°5'$, $a = 3.99$; *KSH* 68°51', 4.37; *RbSH* 69°20', 4.53.
4. The following have high temperature cubic *NaCl* structures: *NaSH* $a = 6.05$; *KSH* 6.60; *RbSH* 6.93. The approximate transition temperatures are *NaSH*, 90°; *KSH*, 170°.
5. K_2S has the cubic CaF_2 structure $a = 7.35$ and is not dimorphous in the range 25—200°.

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2) F. Pockels, Lehrbuch d. Kristall Optik.

1) L. Pauling, Physic. Rev. **36**, 430. 1930. Pauling first suggested to me that the *SH* group is probably rotating in the *KSH* structure type.

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1. Attempts to isolate *LiSH* by the methods used for the other alkali hydrosulfides were inconclusive. From evidence to be presented elsewhere it may be doubted that this substance is thermodynamically stable under ordinary conditions.

2. From powder photographs, Li_2Se and Li_2Te have the CaF_2 structure with the cube edge (a), anion-cation distance (d) observed and calculated from Zachariasen's ionic radii, as follows:

	a	d(obs)	d(calc)
Li_2Se	5.94	2.57	2.54
Li_2Te	6.47	2.80	2.75

3. Powder photographs show clearly the marked anisotropy of thermal expansion of the isomorphous compounds NaN_3 and $NaNCO$ referred to above. The axes of the hexagonal unit containing three formulas are as follows:

	Temp.	c/a	c	a
$NaNNN$	25°	4.18	15.13	3.62
	200°	4.12	15.10	3.67
$NaNCO$	25°	4.24	15.15	3.58
	200°	4.16		