Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Electron diffraction study of the phase transition of hydrogen sulfide at −170 °C.

By N. KITAMURA, Y. KASHIWASE, J. HARADA and G. HONJO. *Physics Department, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo, Japan*

Solid hydrogen sulfide has been known to show two jumps of dielectric constant at −170 °C. and −147 °C. (Smyth & Hitchcock, 1934) with heat tonings of 361 and 180 cal./mol., respectively (Clusius, 1933). From early X-ray studies, a simple face-centred cubic structure of lattice constant $a = 5.77 \sim 5.79$ Å has been reported for this substance (Natta, 1931; Vegard, 1931; Vegard & Oserød, 1942).

Here, formation and change of solid hydrogen sulfide have been studied by electron diffraction in a range from the temperature of liquid nitrogen up to ca. −150 °C., where the crystal sublimed under the reduced pressure of electron diffraction camera. Well-dried hydrogen sulfide gas, purified by fractional distillations, was condensed on a collodion film kept at a low temperature in the electron diffraction camera (Honjo *et al.*, 1956). When the gas

Table 1. *The observed and calculated spacings of tetragonal and cubic structures of hydrogen sulfide*

	Tetragonal				Cubic	
hkl	d_c	d_o	I	hkl	d_o	I
201	3·534 Å	3·528 Å	m	—	—	—
400	3·386	3·386	vs	111	3·314 Å	vs
221	3·133	3·131	vs	—	—	—
420	3·029	3·024	m	200	2·870	vs
321	2·783	2·768	vvw	—	—	—
401	2·622	2·623	vvw	—	—	—
421	2·445	2·449	m	—	—	—
440	2·394	2·392	m	—	—	—
431, 501	2·267 ⎫	2·264	m	—	—	—
600	2·257 ⎭					
620	2·141	2·139	vw	—	—	—
002	2·070 ⎫	2·074	s	220	2·030	s
441	2·073 ⎭					
601	1·982 ⎫	1·986	m	—	—	—
202	1·980 ⎭					
621	1·902	1·905	s	—	—	—
631	1·815 ⎫	1·816	vvw	—	—	—
322	1·813 ⎭					
402	1·762	1·768	s	311	1·731	s
641	1·710 ⎫	1·715	w	—	—	—
422	1·709 ⎭					
800	1·693	1·698	w	222	1·675	m
820	1·642	1·647	w	—	—	—
651	1·599	1·602	vvw	—	—	—
442	1·566 ⎫	1·555	w	—	—	—
801	1·567 ⎭					
821	1·527 ⎫	1·524	vw	—	—	—
602	1·526 ⎭					
660	1·489	1·492	vw	400	1·435	w
10,00, 860	1·354	1·351	w	—	—	—
102	1·328	1·330	m	—	—	—
802	1·311	1·314	w	331	1·317	m
10,01, 861 ⎫	1·287	1·291	m	420	1·283	m
822 ⎭						
10,21, 661	1·264	1·271	w	—	—	—
842	1·222	1·225	vvw	—	—	—
10,41	1·203	1·205	vvw	—	—	—
880	1·197	1·179	vw	422	1·170	w
10,02, 862	1·133 ⎫	1·163	w	—	—	—
881	1·150 ⎭					
12,00	1·128	1·130	vvw	333, 511	1·104	w
10,22	1·118	1·117	vw	—	—	—

condensed slowly, small crystallites grew from many nuclei giving Debye–Scherrer patterns. When condensed rapidly, crystals from a small number of nuclei grew larger giving spotty patterns and, under favourable conditions, net patterns due to single orientation.

Cubic and tetragonal crystals were found to be formed and to exist stably above and below ca. $-170\,^{\circ}$C., respectively. They transformed reversibly to each other at $-170\,^{\circ}$C. The observed spacings and intensities of the Debye–Scherrer patterns of the cubic and the tetragonal forms are given in Table 1. The cubic pattern is due to a face-centred lattice of $a = 5.74$ Å, which coincides well with the previous X-ray data. The tetragonal pattern can be indexed with a lattice of $a = 13.51$ Å and $c = 4.14$ Å.
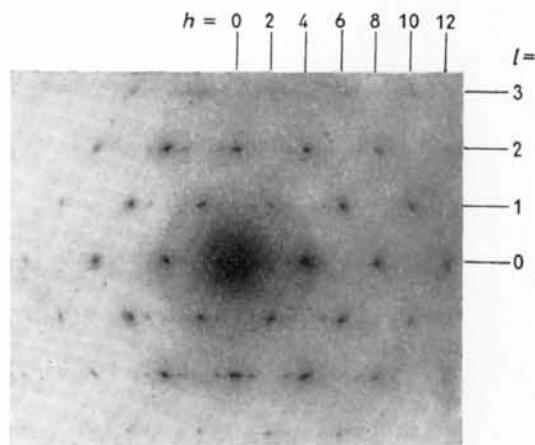

Fig. 1. A $(h0l)$-net pattern due to the tetragonal crystal of hydrogen sulfide.

Fig. 1 shows a $(h0l)$-net pattern due to the tetragonal crystal. The axial ratio $c/a = 0.306$ can be confirmed from this pattern. The reflexions other than those with $h = 4n$, $l = 2m$ and $h = 4n + 2$, $l = 2m + 1$ are generally weak, but there is no systematic absence.

When the tetragonal crystal was heated, the pattern shown in Fig. 1, transformed to a net pattern of the cubic crystal shown in Fig. 2. The transformation proceeded as follows. The tetragonal $(h00)$-spots with $h = 4h^*$ became to be the cubic $(h^*h^*h^*)$-spots without appreciable change of their positions and shapes. While the tetragonal $(h0l)$-spots with $l \neq 0$ were first elongated into streaks along the tetragonal [100]-axis, and then those with $l = 2n + 1$ vanished and those with $l = 2n$ changed to the cubic $(2l + h^*, 2l + h^*, h^*)$-spots. Thus, the tetragonal [100]- and [001]-axes transform to the cubic [111]- and [110]-axes, respectively. The (400)- and (002)-spacings of
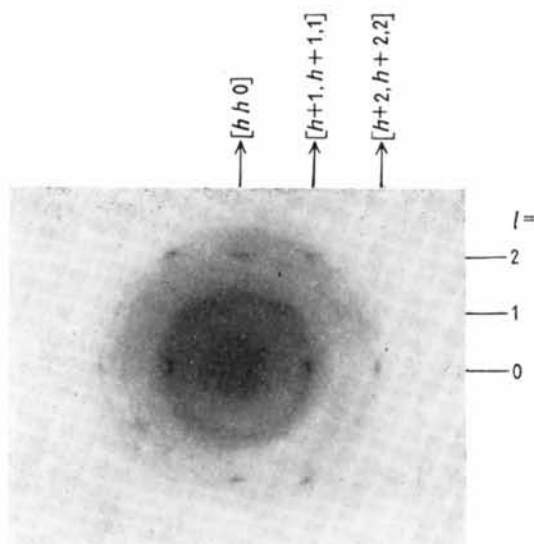

Fig. 2. The $(2l + h, 2\bar{l} + h, h)$-net pattern due to the cubic crystal, which has transformed from the pattern shown in Fig. 1. It is noted that the traces of transitional streaks are found on the layer lines with $l = 1$ or -1.

the tetragonal crystal are nearly equal to the (111)- and (220)-spacings of the cubic crystal and the volume of the tetragonal unit cell (755 Å³) is about four times as large as that of the cubic unit cell (186 Å³).

It is noteworthy that the polymorphism of hydrogen sulfide is quite different from that of ice. The hexagonal and cubic ices, which are isomorphous to cristobalite and tridymite, respectively, are both open structures with hydrogen bonds, and the transformation between them can hardly occur reversibly. While the thermal and dielectric data suggest that the molecules in solid hydrogen sulfide rotate almost freely above $-170\,^{\circ}$C. and the rotational motion is set frozen below this temperature. It is natural that the crystal structure transforms at this temperature from the cubic closest packed structure with high symmetry to the less symmetric tetragonal structure.

References

CLUSIUS, K. (1933). *Z. Elektrochem.* **39**, 598.

HONJO, G., KITAMURA, N., SHIMAOKA, K. & MIHAMA, K. (1956). *J. Phys. Soc. Japan*, **11**, 527.

NATTA, G. (1931). *Nature, Lond.* **127**, 129.

SMYTH, P. C. & HITCHCOCK, C. S. (1934). *J. Amer. Chem. Soc.* **56**, 1084.

VEGARD, L. (1931). *Z. Kristallogr.* **77**, 23.

VEGARD, L. & OSERØD, L. S. (1942). *Avh. Norske Vidensk. Akad. Oslo*, I, (Naturv. Kl.), No. 7.