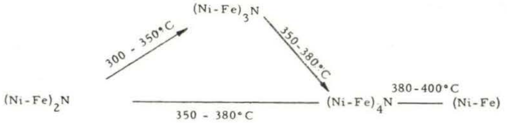
préciser notre observation.

L'expérience du chauffage sous vide des nitrures, effectuée dans le microscope électronique, montre que le processus inverse (dénitruration) se produit comme suit :



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Structure and Phase Transition of Solid Hydrogen Sulphide

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The structures and phase transitions of solid hydrogen sulphide were studied by electron diffraction and X-ray diffraction.

New two tetragonal phases were found to exist at low temperature besides the known cubic phase. The structures of the two tetragonal phases are related closely to each other and to that of the cubic phase. In the process of phase transition, streaks along the tetragonal [100]-axis or the cubic [111]-axis were observed on net patterns of electron diffraction. These streaks suggest the process of rearrangement of molecules. The locations of hydrogen sulphide molecules of the tetragonal phases were determined from Patterson maps.

One of the tetragonal structures belongs to space group $P4_2$ or $P\bar{4}$ having lattice constants of $a=6.75$Å and $c/a=0.612$. Four molecules in the unit cell are at a general position with parameters $x=0.190$, $y=0.280$ and $z=0.250$.

The molecules in the other tetragonal structure deviate slightly from the position to make up less symmetric structure having a-period twice as large as that of the high symmetric one.

Clusius[1] has reported that solid hydrogen sulphide have two transition points at −170 °C and −147°C with heat tonings of 361 and 108 cal/mol, respectively. The measurement of dielectric constant by Smyth and Hitchcock[2] indicated also phase transitions to occur at these temperatures. Alpert[3] studied these transitions by N.M.R. and concluded that the transition at −170°C is an order-disorder transition. Previous X-ray studies[4] of this substance found only a face centred cubic structure throughout the whole range of low temperature from 20°K to 150°K.

Recently, the present authors[5] reported that a first order phase transition from the cubic structure ($a=5.74$Å) to a tetragonal structure ($a=13.51$Å, $c/a=0.306$) is observed by electron diffraction for the substance.

The low temperature phase was re-examined by X-rays and it was proved that the tetragonal phase do exist in lower temperature range besides the cubic phase in higher temperature range. Our experiment was performed in a way similar to those of the previous observers[4], but with a precaution to prevent the temperature rise of specimen due to heat radiation. Fig. 1 (a) and (b) reproduce X-ray Debye-Scherrer patterns of the tetragonal and cubic structures. Thus, the first order transition of hydrogen sulphide was established.

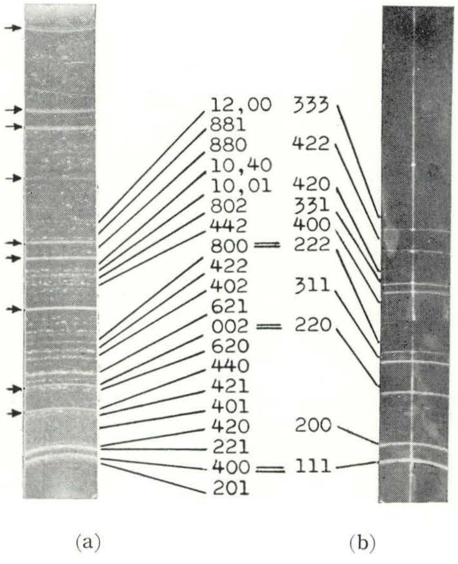
The crystals, condensed from vapour phase under favourable conditions, grow sufficiently large to give single crystal patterns of electron diffraction. Their orientation was at random. By a great number of repetitions of trial condensation, a number of single crystal patterns of distinct orientations were observed. Fig. 2 *(a)*, *(b)* and *(c)* show the *(h0l)*-, *(hk0)*- and *(hhl)*-net patterns.

The intensities of reflections in these patterns were measured by photometry and visual method. Referring also to the intensity distributions in Debye-Scherrer patterns of X-ray and electron diffractions, relative intensities of about four hundred distinct reciprocal lattice points were determined. From these intensity data, Patterson maps of (00*l*), (100)- and (110)-projections of the tetragonal structure were constructed as shown in Fig. 3. These maps implie that the sixteen molecules in the unit cell reported previously[5] ($a=13.51$Å, $c/a=0.306$) are in the neighbourhoods of the follwing positions:

$$(000),\ (1/2\ 00),\ (0\ 1/2\ 0),\ (1/2\ 1/2\ 0) \\ +(000),\ (1/4\ 1/4\ 0),\ (1/4\ 0\ 1/2),\ (0\ 1/4\ 1/2)\,. \quad (1)$$

As reported before, there is a close relation between the cubic and the tetragonal lattices as follows. The tetragonal [100]- and [110]-axes transform into the cubic [111]- and [110]-axes, respectivly. The (400)- and (002)-spacings of tetragonal structure are nearly equal to the (111)- and (220)-spacings of cubic structure. Moreover, in the process of transition, characteristic streaks appear along the tetragonal [100]-axis or the cubic [111]-axis, as showe in Fig. 4, while the tetragonal (4*h*,00)-reflections transform into the cubic (*hhh*)-reflections without appreciable change of their positions and shapes.

This relation suggests a scheme of lattice transformation as depicted in Fig. 5. Rigid and open circles in this figure represent



(a) (b)

Fig. 1. X-ray Debye-Scherer patterns of a) the tetragonal and b) the cubic structures of H_2S crystal. The diffraction rings from alumium rod are shown by arrows.

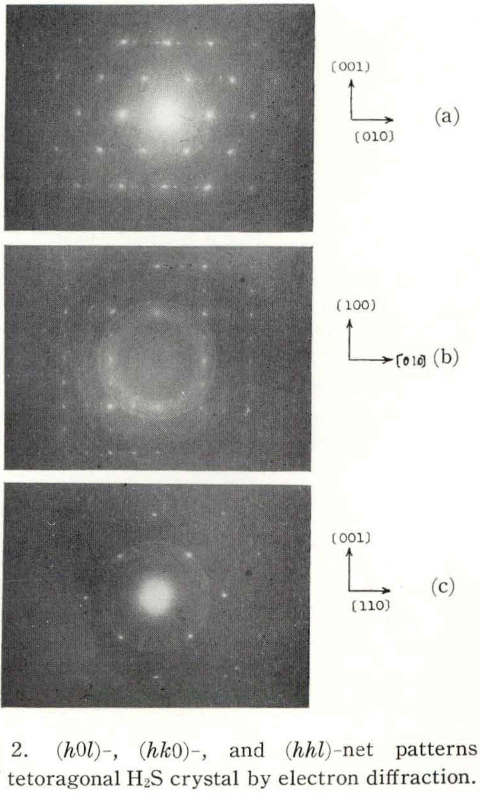


Fig. 2. *(h0l)*-, *(hk0)*-, and *(hhl)*-net patterns of tetoragonal H_2S crystal by electron diffraction.

sulphur atoms on two successive cubic (110)-planes. When the transformation starts from the cubic structure, the cubic (111)-atomic planes perpendicular to the (110)-planes of Fig. 5 a) displace along [112]-direction until a parallelogram indicated by the dotted line turns into a tetragonal base indicated by the full line. The positions of sulpher atoms at this stage, shown in Fig. 5 a), are nothing but the positions (1). Then, the slight deviations of sulphr atoms (about 1Å) from the positions given by (1) occur to make up the final tetragonal structure.

Detailed inspection of the net patterns in Fig. 2 shows a discrepancy between (*hk*0)- or (*hhl*)-net patterns and (*h*0*l*)-net pattern. While the main spots in these net patterns are consistent with each other, the reflections with indices of odd *h* or *k*, which is found in the (*h*0*l*)-net pattern, can not observed in the (*hk*0)- and (*hhl*)-net patterns even on the (*h*00)- and (00*l*)-reciprocal row which are held common with the (*h*0*l*)-net pattern. The appearance of the odd order reflections on the

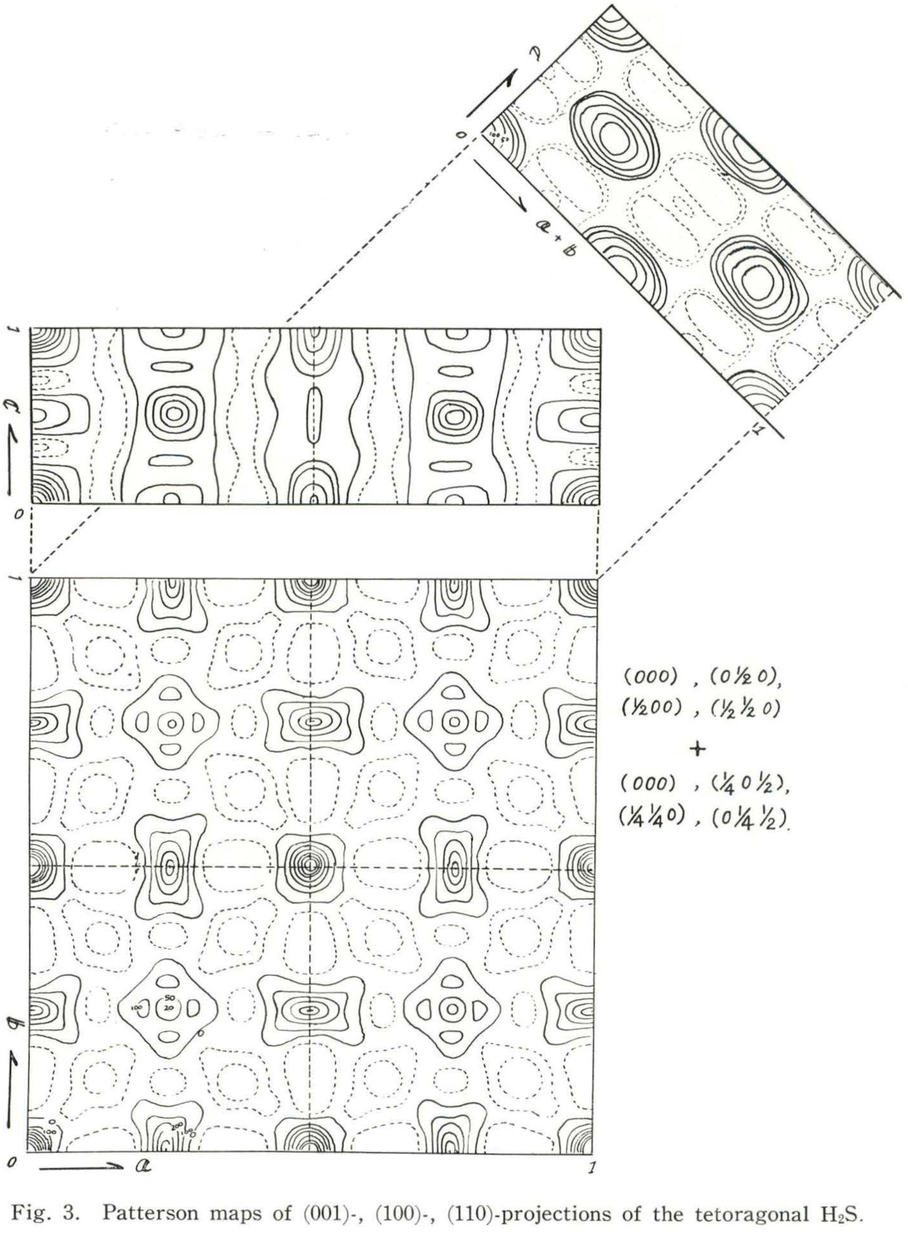
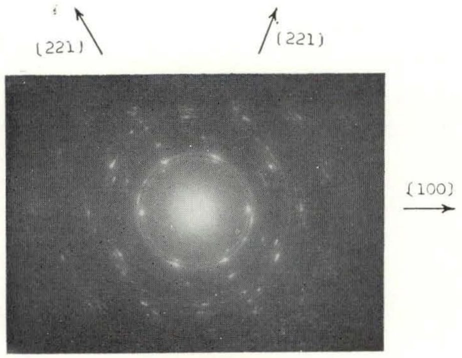
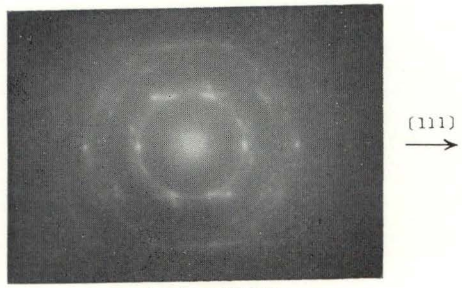


Fig. 3. Patterson maps of (001)-, (100)-, (110)-projections of the tetoragonal H_2S.



tetragonal



in the transition process (cubic)

Fig. 4. Electron diffraction patterns taken in the process of lattice transformation from cubic to tetragonal structure of H_2S crystal.

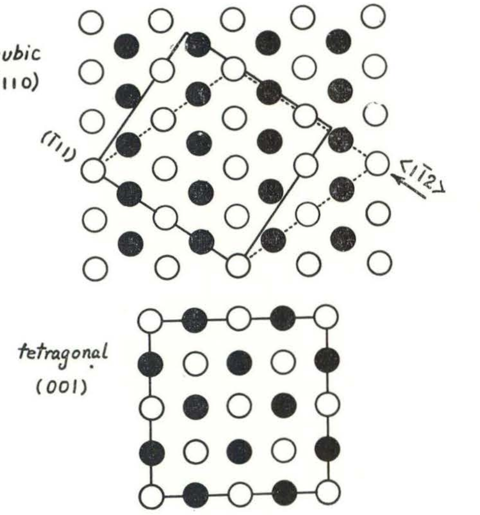


Fig. 5. A scheme of lattice transformation from cubic to tetragonal structure of H_2S.

$(h00)$- and $(00l)$-reciprocal rows in the $(h0l)$-net pattern can not be explained by multiple scattering, since the odd order reflections in the $(h0l)$-net pattern appear up to high scattering angle. Therefore, it should be concluded that there exist two tetragonal phases besides the cubic phase. The two tetragonal phases are closely related with each other, and the lattice constant a of one of them is equal to 13.51Å reported previously[5] and that of another is one half of the value. Let us call the former and the latter structures Phase I and Phase II, and the cubic structure Phase III.

The structure of Phase II belongs to space group $P4_2$ or $P\bar{4}$. The unit cell contains four hydrogen sulphide molecules which are at general positions. The positions of molecules were determined from comparison between the observed intensities and the calculated intensities with varying parameters x and y. The best fit was obtained for $x=0.190$ and $y=0.280$ and $z=0.25$.

The intensities of reflections with even h calculated from the above structure also coincide well with the observed intensities of them in the $(h0l)$-net pattern of Phase I. From the (010)-Patterson map of Phase I, it is supposed that the reflections with odd h or k appear by further shifts of molecules along the c-axis. However, detail of the structure has not yet been established.

The above mentioned three phases, Phase I, II and III, might correspond to the three phases predicted by other physical data[1),2),3)]. The correpondence, however, have not been certain because of the difficulty of precise determination of temperature of specimen under electron irradiation.

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