

CRYSTAL STRUCTURE OF SILANE

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By

WILLIAM MAXWELL SEARS, B.Sc. (Hon.)

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AUTHOR: William Maxwell Sears, B.Sc. (Hon.) (Acadia University)

SUPERVISOR: Professor J. A. Morrison

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SCOPE AND CONTENTS:

The lattice parameters and crystal symmetry of silane (SiH_4) are examined by X-ray powder diffraction. Comparisons are made with vibrational spectrum and birefringence measurements and with respect to an order-disorder transition between the two solid phases of silane.

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CHAPTER I

INTRODUCTION

The purpose of this experimental investigation was to obtain, by X-ray diffraction, information concerning the crystal symmetry of silane (SiH_4). The structures of the solid phases of CH_4 and CD_4 are known in reasonable detail and, from this, much can be deduced about the structures of solid CHD_3 , CH_2D_2 and CH_3D . No reports of the structure of solid silane appear in the literature, however, as is also the case for some other methane analogues (GeH_4 , SnH_4 , SiD_4 and other deuterated forms). Knowledge of the structure of silane would be expected to add to our understanding of the properties of these molecular solids.

The simplest model substances for molecular solids are the rare gas crystals. The rare gases, which interact through Van der Waals forces, tend to adopt close-packed crystal structures (fcc or, under some circumstances, hcp (He excluded)). Methane, which is the lightest of the molecules with tetrahedral symmetry, has macroscopic properties not unlike those of solid argon. Also the tetrahedral molecules solidify by the action of Van der Waals forces and can often be considered spherical. The exceptions are when the atoms occupying the tetrahedral positions are not small compared to the central atom or when the central atom is massive

enough or the temperature low enough to cause the molecules to adopt a crystal structure of low symmetry in which the molecules do not rotate easily.

Thus one might expect methane to form a close-packed structure in the solid phases at least in its high temperature phase. Actually, CH_4 seems to form fcc solids in all phases that differ in the degree of orientational ordering of the hydrogen atoms (Clusius, 1934,1940; James and Keenan, 1959; Yamamoto, 1968,1973; and Bloom and Morrison, 1973). Refer to Table 1.1 for more detail on these structures.

Deuterated methane (CD_4) starts to show deviations from the fcc packing as it undergoes phase transitions at lower temperatures. There is a doubling of the unit cell (to 32 molecules) in phase II and a further tetragonal distortion (of about 2%) in phase III (Press, 1972). As the molecules become ordered at lower temperatures they have less tendency to pack as spheres.

From birefringence measurements (Ballik, et al, 1973) there is evidence that the partially deuterated methanes undergo similar distortions.

Replacing the hydrogen by heavier atoms, as in CCl_4 , CBr_4 or CF_4 , results in even more distortion from cubic symmetry (Greer and Meyer, 1969). In the case of CF_4 , there results a C-centered monoclinic cell not far distorted from a face-centered tetragonal one (but which is a large distor-

tion from fcc).

From this, one might expect a structure for silane (which has at least two solid phases (lambda point at 63.45 °K and melting point at 88.5°K)) to be distorted from fcc, somewhere in between those of CD_4 and CF_4 because of the heavier silicon atom. There should also be ordering effects from phase I to II.

A method for depositing a powder rather than single crystals of silane was sought as being the simplest way to obtain basic information. However, all that could reasonably be expected from the results would be the determination of the Bravais lattice for the silicon positions. Nevertheless, even this limited information could be of value for making general deductions about molecular ordering in the silane lattice as well as for comparison with indirect structural information obtained from Raman and infrared data (Fournier, et al, 1972).

TABLE 1.1

CRYSTAL STRUCTURES OF SOME METHANE ANALOGUES

Solid	Temperature Range	Technique	Structure	Reference
CH ₄ I	20.4 to 90.7°K	X-rays (powder)	fcc (4 mol., a=6.00Å at 70°K)	Greer and Meyer (1969)
CH ₄ *	<20.4°K	X-rays (powder)	fcc (4 mol., a=5.90Å at 20°K, a=5.87Å at 4.2°K)	Greer and Meyer (1969)
CD ₄ I	27.0 to 89.7°K	Neutrons (crystal)	Fm3m (4 mol., a=5.85Å at 34.5°K)	Press (1970,72)
CD ₄ II	22.1 to 27.0°K	Neutrons (crystal)	Fm3c (32 mol., a=11.64Å at 24.5°K)	Press (1972)
CD ₄ III	0 to 22.1°K	X-rays (powder)	tetragonal (32 mol., a=11.48Å, c=11.66Å at 6°K)	Bol'shutkin, et al (1971)
CF ₄ I	76.2 to 89.5°K	X-rays (powder)	monoclinic?	Greer and Meyer (1969)
CF ₄ II	0 to 76.2°K	X-rays (powder)	Cc? (4 mol., a=8.71Å, b=4.16Å, c=15.27Å, β=150.7° at 40°K)	Greer and Meyer (1969)

* The achievement of structures analogous to II and III of CD₄ appears to be complicated by nuclear spin conversion (Colwell, et al, 1962,63; Piott, thesis,1971; and Ballik, et al, 1972).

CHAPTER II

APPARATUS AND TECHNIQUE

The basic idea was to have a simple apparatus by means of which silane, in the form of a powder, could be deposited onto a copper substrate located in the X-ray beam. The copper would be thermally attached to a reservoir containing liquid nitrogen.

X-RAY WINDOWS:

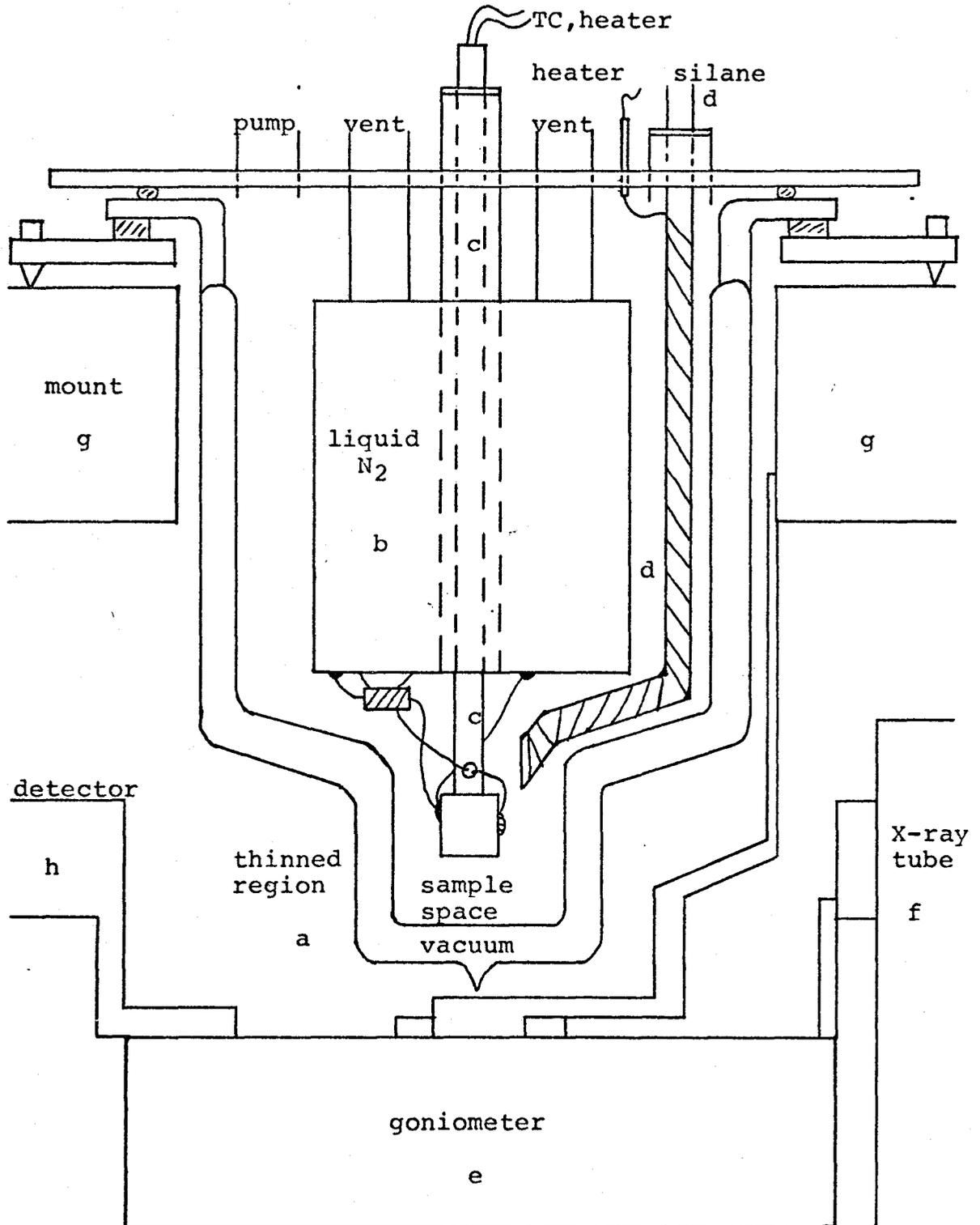
To simplify construction, the tail section of the Pyrex glass vacuum jacket which surrounds the sample space (shown as (a) in figure 2.1) served as an X-ray window. The glass was thinned in this region to about 2mm total path. This eliminated the possibility of using copper X-rays which would be all but completely absorbed by 2mm of Pyrex. Copper X-rays would have had the advantage of an expanded diffraction spectrum which, in retrospect, would have brought in lower angle peaks and improved resolution. With the molybdenum radiation, some peaks may have been lost in low angle background scatter, occurring at a Bragg angle of 5° and less. The glass absorbed all but about 8% of the Mo radiation so that noise was somewhat of a problem.

CRYOSTAT:

The liquid nitrogen container ((b) in figure 2.1) held about 1.5 litres which was sufficient to last for 12 to

FIGURE 2.1

CRYOSTAT AS MOUNTED FOR X-RAY DIFFRACTION MEASUREMENTS



16 hours. It was usually connected to a rotary oil pump for reducing the pressure and hence the temperature of the nitrogen. Thus the temperature of the copper substrate, and of the silane, could be lowered to about 60°K.

The substrate consisted of a block of copper (1/2"x 1/2"x3/8") with one surface serrated by machined grooves about 1/32" in depth. It was suspended by means of a thin-walled German silver tube that passed through the central tube of the nitrogen container ((c) figure 2.1) and was held by a Cajon fitting at the top of the cryostat. The copper substrate was thus positioned in the tail of the Dewar where the glass was thinned and it could be raised and turned for alignment and deposition purposes. The copper substrate was thermally connected by 12-30 gage and 10-22 gage copper wires to the nitrogen container. Some of these wires (12-30 gage) ran through a brass block suspended below the container by nylon threads. The block was wound with a heater for temperature control. A thermocouple (copper-constantan) was soldered to the side of the copper substrate. The heater and thermocouple wires were led up the center of the German silver tube that held the substrate and to the outside through an Apiezon wax seal. The temperature was controlled by manual variation of a Hewlett-Packard d.c. power supply and the thermocouple voltage was measured to one microvolt with a Hewlett-Packard digital voltmeter.

The fixed junction of the thermocouple was kept in

an ice bath at 0°C. The thermocouple was calibrated in situ by immersing the copper substrate to which it was attached in pure liquid N₂ and then in pure liquid O₂. Barometric pressure and room temperature were recorded and corrections made for the variation of the boiling temperatures of N₂ and O₂ with pressure (Stimson (1961) (O₂), Giauque and Clayton (1933) (N₂)). The calibration was expressed in terms of a linear deviation from a standard table for copper-constantan thermocouples. The accuracy of this method in the temperature range of interest (50 to 90°K) was better than 0.1°K which was deemed to be sufficient.

A stainless steel tube ((d) figure 2.1) was bent to provide a direct path for the silane to strike the copper substrate. It was hoped thus to deposit silane without appreciable grain growth. This was not realized as will be mentioned later. To prevent condensation of silane in it, the tube was wound with a heater. The lead wires were led through the top plate (brass) via an Apiezon wax seal and connected to a Variac.

In the first experiments, the tail section of the glass Dewar was left unsilvered so that alignment and deposition could be observed directly. However, the influx of radiant energy to the substrate proved to be too great and silvering of the entire Dewar became necessary. This made alignment a little more difficult.

MOUNTING AND ALIGNMENT:

The cryostat was mounted above an X-ray generator and

horizontal goniometer (Philips) and was connected to vacuum systems by flexible bellows and copper connections. The mount, which was built by Mr. Fred Long for some other low temperature experiments, had translational adjustments to help align the stage and was physically coupled to the theta drive of the goniometer. The goniometer (e), the X-ray tube (f) and the mount (g) are depicted in figure 2.1.

On the 2-theta drive, the detection system consisted of a monochromating carbon crystal and a scintillation-photomultiplier tube ((h) figure 2.1). These and the accompanying single channel analyser and chart recorder were also supplied by the Philips company.

The copper substrate was used to line up the cryostat and served as a reference for the silane peaks. The copper Bragg angles were recorded at both room and low temperatures to determine the effect of thermal expansion on the cell parameters. The main Bragg angles used in this regard, at both room and liquid nitrogen temperatures, are shown in table 2.1. The effect of temperature between 50 and 90°K was so small that it could be neglected.

The presence of Mo K-Beta radiation Bragg peaks, despite the monochromator, seems to have indicated faulty alignment. This did not, however, seem to cause any problems in the interpretation of diffraction patterns. The copper Mo K-Beta angles are listed in table 2.1.

TABLE 2.1

COPPER (FCC) DIFFRACTION ANGLES FOR MOLYBDENUM RADIATION

HKL	$K\alpha_1$	$K\alpha_2$	$K\tilde{\alpha}$	$K\beta$
111	9.78°	9.84°	9.80°	8.71°
200	11.31°	11.38°	11.33°	10.07°
220	16.11°	16.21°	16.14°	14.32°
311	18.99°	19.11°	19.03°	16.86°
222	19.87°	19.99°	19.91°	17.63°
400	23.10°	23.25°	23.15°	20.47°
331	25.32°	25.48°	25.37°	22.41°
420	26.02°	26.19°	26.08°	23.02°

The Bragg angles of copper at low temperatures were occasionally recorded during (but sometimes had to be recorded after) the deposition of the silane and measurement of its Bragg peaks. This was because the substrate had often to be shifted to get the maximum intensity of the silane spectrum (deposition and measurement were performed with the substrate in different positions). Because of this limitation, the results of some experiments had to be rejected for lack of good copper peaks as reference.

INTRODUCTION AND DISPOSITION OF SILANE:

The silane was introduced (figure 2.2) at a pressure of about 150 lb/sq. in. through a needle valve.

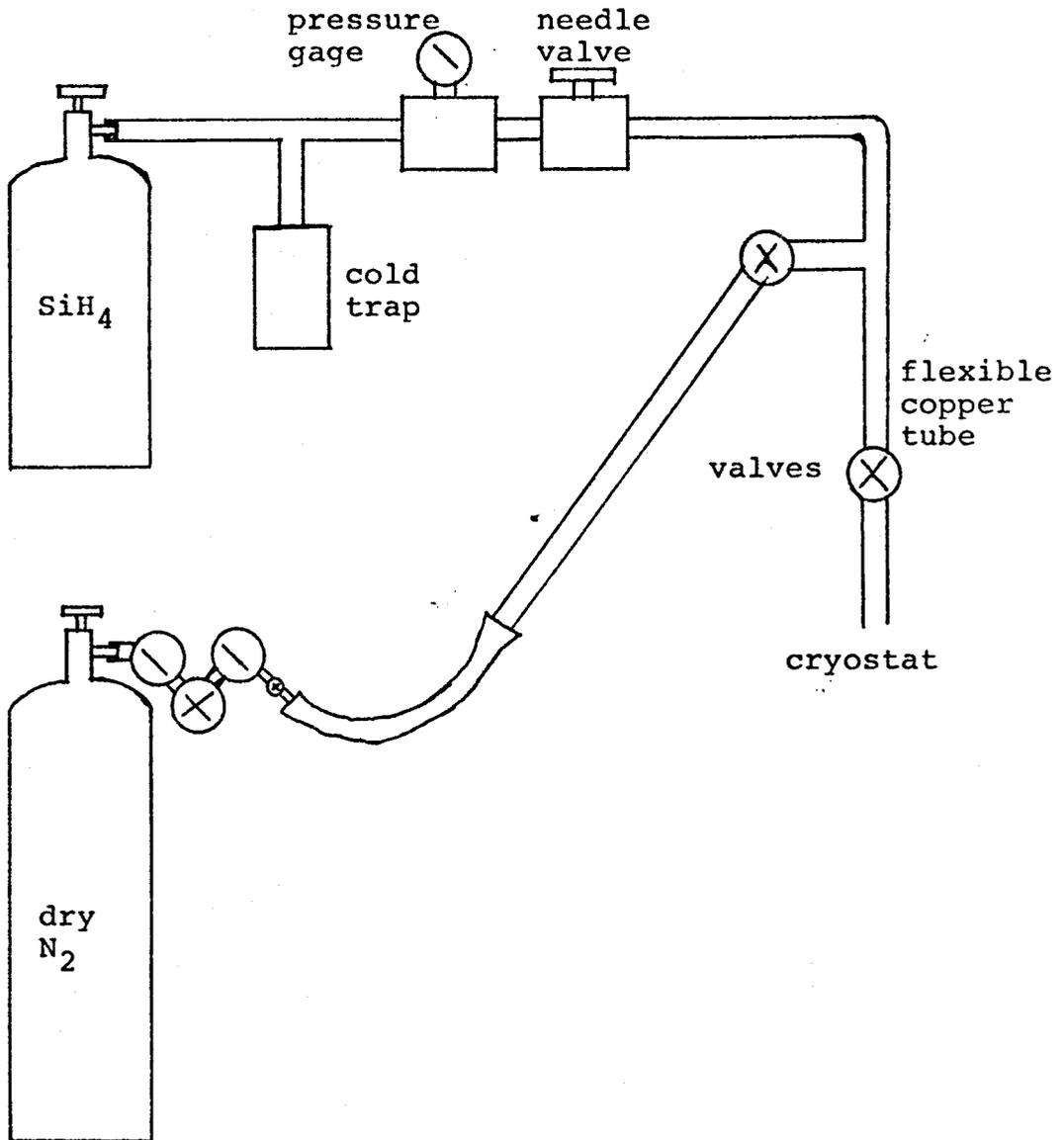
Because it reacts violently with O_2 , silane has to be disposed of carefully. The disposal scheme used in the present experiments was a simple cold trap connected to the pumping line. All of the silane was caught in a demountable trap immersed in liquid nitrogen. After an experiment, the silane caught in the trap was vented to a fume hood in a stream of helium or nitrogen.

PROBLEMS OF DEPOSITION:

Deposition of the silane on the copper substrate had to be carried out slowly as otherwise the energy released in sublimation raised the temperature of the substrate too much.

As mentioned before, the influx of radiant energy through the unsilvered tail caused temperature instabilities.

FIGURE 2.2
SILANE INPUT SYSTEM



This radiant energy combined with the heat of sublimation of silane and with the thermal conduction caused by gases in the sample space (silane and hydrogen from oxydized silane) quickly heated the substrate to the melting point of silane.

The sample space could not be pumped on during deposition and measurement as silane's relatively high vapour pressure (about 1mm) would cause it to pump away without any staying deposited.

Some useful measurements (experiment 5 table 2.2) were obtained, before the Dewar was completely silvered, by placing liquid nitrogen around the outside of the tail while silane was being deposited and then removing it during an X-ray measurement. By this means, measurements could be made for 5 to 10 minutes before the silane melted. The silane had the appearance of a frozen semitransparent drop with obvious grain growth. It appeared that a few millilitres had been condensed.

The rest of the measurements in table 2.2 were made after the tail of the glass Dewar was silvered. This improved temperature stability immensely and made the process of taking data much less hectic. The silane still had to be deposited fairly slowly so that the temperature of the substrate did not increase too much.

COOLING THE CRYOSTAT:

The substrate cooled more rapidly and to a lower temperature with about 100mm Hg pressure of nitrogen exchange gas in the sample space. This obviously cooled the inside

TABLE 2.2

SILANE PEAKS FROM USEFUL EXPERIMENTS

Experiment	Bragg Angle (deg.)	Relative Weight (deg.)	Temperature (°K)	Angle Corrected to 77.35°K (deg.)
5..1	5.45	0.10	≈73	5.42
	6.65	0.07	≈77	6.65
	9.63	0.10	≈83.38	9.70
	10.71	0.07	≈85.45	10.82
5..3	5.15	0.07	≈74	5.13
	9.38	0.07	≈83.38	9.45
8.A.1	5.23	0.10	68.07	5.17
	5.38	0.10	68.07	5.32
	5.50	0.07	68.07	5.44
	6.77	0.10	68.07	6.69
	7.36	0.10	68.07	7.28
8.A.2	5.31	0.10	66.26	5.24
	5.54	0.10	66.26	5.47
	5.81	0.10	66.26	5.73
	6.52	0.10	66.26	6.43
	6.69	0.10	66.26	6.60
8.A.3	5.54	0.07	65.84	5.46
	5.81	0.07	65.84	5.73
	7.01	0.07	65.84	6.91
	14.83	0.07	65.62	14.62
8.B	5.33	0.10	66.61	5.26
	5.53	0.10	66.61	5.46
	5.80	0.05	66.61	5.72
	6.20	0.07	66.61	6.12
	6.60	0.07	66.68	6.52
	7.00	0.10	66.68	6.91
	9.00	0.10	≈65.62	8.87
	9.50	0.10	≈65.62	9.37
	10.98	0.07	≈65.62	10.82
	21.93	0.07	≈68.07	21.67
9.A	5.42	0.10	63.11	5.33
	5.76	0.05	63.11	5.66
	6.03	0.10	63.11	5.93
	6.08	0.10	63.11	5.98
	6.29	0.07	63.25	6.18
	7.04	0.07	63.25	6.92

TABLE 2.2 (CON'T)

Experiment	Bragg Angle (deg.)	Relative Weight (deg.)	Temperature (°K)	Angle Corrected to 77.35°K (deg.)
9.A	8.67	0.07	63.69	8.53
	9.40	0.10	63.76	9.25
9.B	5.53	0.07	64.41	5.44
	5.79	0.07	64.41	5.70
	6.15	0.10	64.41	6.05
	6.37	0.10	64.41	6.27
	6.72	0.07	64.55	6.62
	7.02	0.07	64.55	6.91
	8.63	0.07	64.48	8.50
	9.38	0.10	64.48	9.23
	9.58	0.10	64.48	9.43
	13.88	0.07	65.13	13.67
	14.58	0.07	65.13	14.36
11.B	5.48	0.10	77.14	5.48
	9.24	0.10	77.46	9.24
	19.26	0.07	77.77	19.27
12.C	5.27	0.07	84.98	5.32
	5.57	0.07	84.98	5.62
	5.95	0.07	85.10	6.01
	6.22	0.10	85.10	6.28
	6.46	0.05	85.10	6.52
	9.79	0.05	85.10	9.88
	13.85	0.07	85.10	13.98
12.D	5.42	0.05	77.27	5.42
	5.64	0.05	77.39	5.64
	5.87	0.05	77.39	5.87
	5.93	0.05	77.39	5.93
	6.18	0.05	77.33	6.18
	6.52	0.05	77.27	6.52
	7.34	0.05	77.27	7.34
	8.22	0.05	77.46	8.22
	9.28	0.07	77.46	9.28
	9.48	0.10	77.39	9.48
	9.68	0.10	77.39	9.68
	10.05	0.05	77.27	10.05

of the glass Dewar (completely silvered) and thus it could no longer supply radiant energy to the substrate. It required about an hour for the substrate to cool to liquid nitrogen temperatures (about 80°K), then another hour to solid nitrogen temperatures (the lowest temperature reached was about 59°K) and, in the next hour, the temperature would rise to about 63°K (caused by the freezing out of the exchange gas).

CHAPTER III

DATA REDUCTION

Very few measurements were obtained below 63.45°K, the lambda point of silane, (only 9A in table 2.2) and so it is the structure of the higher temperature phase about which most of the information has been collected.

It was obvious during the experiments that the intensities of the peaks varied with time. This was probably caused by continuous grain growth. A similar effect was observed in measurements on CF₄ by Greer and Meyer (1969). Thus, it is not possible to make deductions from the relative intensities of the diffraction peaks.

The resolution of the peaks varied considerably, with base widths usually of the order of 0.25° or less. The accuracy of the positions of the peaks is estimated to be about 0.1° and is limited by the certainty of the copper spectrum. The precision was usually better than 0.05° but was sometimes worse. Relative weights are assigned to the peaks listed in table 2.2.

PRELIMINARY ANALYSIS OF THE DIFFRACTION DATA:

A schematic diagram of all distinct silane reflections obtained, corrected to about 77°K, is shown as figure 3.1. As can be seen in table 3.1a, there is a dispersion of peak positions around various angles within about 0.1°. In select-

FIGURE 3.1

SCHEMATIC OF MEASURED SILANE REFLECTIONS
(See table on next page)

Vertical Scale: *'s represent number of observations
Horizontal Scale: Bragg angle in degrees

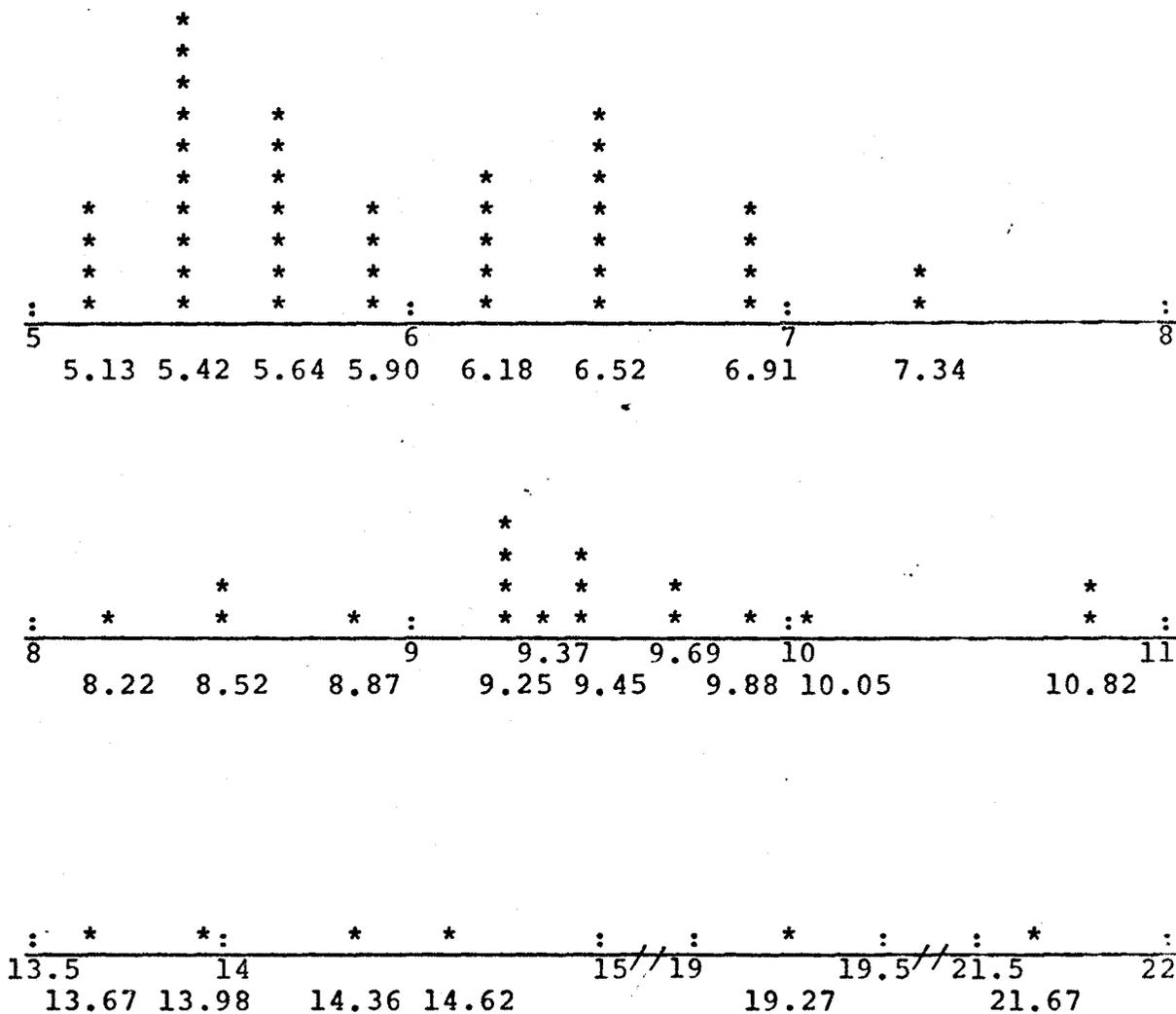


TABLE 3.1a

DISTINCT SILANE BRAGG ANGLES CHOSEN FOR OBSERVED GROUPS
(Supplement to Figure 3.1)

Experiment	Angle (77°K) (deg.)	Angle Chosen (deg.)
5..3	5.13	5.13
8.A.1	5.17	
8.A.2	5.24	
8.B	5.26	
5..1	5.42	5.42
8.A.1	5.44	
8.A.2	5.47	
8.A.3	5.46	
8.B	5.46	
9.A	5.33	
9.B	5.44	
11.B	5.48	
12.C	5.32	
12.D	5.42	
8.A.2	5.73	5.64
8.A.3	5.73	
8.B	5.72	
9.A	5.66	
9.B	5.70	
12.C	5.62	
12.D	5.64	
9.A	5.93	5.90
9.B	6.05	
12.C	6.01	
12.D	5.87	
8.B	6.12	6.18
9.A	6.18	
9.B	6.27	
12.C	6.28	
12.D	6.18	
5..1	6.65	6.52
8.A.1	6.69	
8.A.2	6.60	
8.B	6.52	
9.B	6.62	
12.C	6.52	
12.D	6.52	

TABLE 3.1a (CON'T)

Experiment	Angle (77°K) (deg.)	Angle Chosen (deg.)
8.A.3	6.91	6.91
8.B	6.91	
9.A	6.92	
9.B	6.91	
8.A.1	7.28	7.34
12.D	7.34	
12.D	8.22	8.22
9.A	8.53	8.52
9.B	8.50	
8.B	8.87	8.87
9.A	9.25	9.25
9.B	9.23	
11.B	9.24	
12.D	9.28	
8.B	9.37	9.37
5..3	9.45	9.45
9.B	9.43	
12.D	9.48	
5..1	9.70	9.69
12.D	9.68	
12.C	9.88	9.88
12.D	10.05	10.05
5..1	10.82	10.82
8.B	10.82	
9.B	13.67	13.67
12.C	13.98	13.98
9.B	14.36	14.36
8.A.3	14.62	14.62
11.B	19.27	19.27
8.B	21.67	21.67

ing the best angle for the data reduction that follows, a simple average was usually not taken. Instead, the measurements which were felt to be the most reliable were used. Often, these were the ones that occurred most frequently. The most reliable measurements came from experiment 12.D and, in general, from the measurements at lower angles (5 to 7°).

The results were corrected to the condition of $T = 77.35^\circ\text{K}$ using a coefficient of expansion of $1.2 \times 10^{-3}/^\circ\text{K}$, determined from two successive experiments (12.C and 12.D) carried out at about 85 and 77°K respectively. The accuracy is difficult to judge but the result is probably precise to the order of 10%. The expansivity of methane as measured by Greer and Meyer (1969) is about $0.62 \times 10^{-3}/^\circ\text{K}$ in this temperature range which is of the order of that of silane.

Only the eight lowest angle diffraction peaks were used in the attempt to index the structure. They were the most definitive and least subject to ambiguity from superlattice reflections. The peaks at higher angles were, however, used later as an added confirmation to the final structure.

A standard least squares technique was used along with much trial and error in performing the indexing. A least squares residue was defined as chi squared divided by the number of data points.

As mentioned in chapter I the published determinations of the structure of the three solid phases of CD_4 (Press (19

72), Bol'shutkin et al (1971)) show phase I to be fcc (4 molecules), phase II to be fcc (32 molecules) and phase III to be distorted to a face-centered tetragonal (also 32 molecules). This trend was taken as a guide in the attempt to resolve the structure of solid SiH_4 .

Two attempts were made to index the silane lines to a cubic structure (Table 3.1). The better fit (#1), as shown by the least squares residue (0.72), has a calculated density ($0.88 \pm 0.03 \text{ gm/cm}^3$) which is larger than the measured one of $0.73 \pm 0.02 \text{ gm/cm}^3$ (Klein et al (1969)) by much more than the combined estimated uncertainties. The alternate fit (#2) produced a reasonable calculated density ($0.76 \pm 0.03 \text{ gm/cm}^3$) but the least squares residue (2.41) was unacceptably large.

Next, hcp structures based on transformations of the fcc structures were tried. These could not be indexed with the observed reflections, however, and a least squares refinement was therefore not attempted.

Finally a successful indexing was obtained by a large distortion of the doubled cubic cell to tetragonal somewhat similar to the lowering of symmetry (presumably caused by tetrahedral rather than spherical molecules being packed into the structure) in the case of CF_4 (Greer and Meyer (1969)). This indexing was close enough that a further lowering of the symmetry could not be justified with the available data.

FINAL INDEXING OF THE DIFFRACTION DATA:

Various likely tetragonally distorted unit cells were

TABLE 3.1

TRIAL CUBIC CELLS FOR SILANE
(32 molecules per unit cell)

Bragg Angle (observed)	Cubic Cell #1		Cubic Cell #2	
	HKL	Bragg Angle (calculated)	HKL	Bragg Angle (calculated)
5.13°	130	5.16°	113	5.14°
5.42°	113	5.41°	222	5.37°
5.64°	222	5.66°	230	5.59°
5.90°	230	5.89°	123	5.80°
6.18°	123	6.11°	400	6.21°
6.52°	400	6.53°	330	6.58°
6.91°	330	6.93°	240	6.94°
7.34°	240	7.31°	233	7.28°

#1 $a = 12.46 \pm 0.1 \text{ \AA}$

Density = $0.88 \pm 0.03 \text{ gm/cm}^3$

Residue = 0.72

#2 $a = 13.12 \pm 0.1 \text{ \AA}$

Density = $0.76 \pm 0.03 \text{ gm/cm}^3$

Residue = 2.41

tried. Some could be rejected on density grounds and others because one of the unit cell lengths was too short to accommodate any arrangement of the silane molecules (given bond lengths and Van der Waals radii). The one tetragonal fit which survived and which also had the lowest least squares residue, is shown as table 3.2. This seems to be an ideal fit with the correct density ($0.77 \pm 0.03 \text{ gm/cm}^3$) reasonable lattice parameters ($a = 12.5 \pm 0.1 \text{ \AA}$ and $c = 14.2 \pm 0.1 \text{ \AA}$) and a very low least squares residue of 0.072. This is a distortion of 13.6% from the cubic and the extinction shown by the indexing shows that the 32 molecules are arranged in body-centered symmetry.

The higher angle reflections could easily be indexed to body-centered tetragonal as can be seen in table 3.2. There are many more possible Bragg reflections as the angle increases, however, and it was not thought worthwhile to include them in a least squares fit (it is enough to notice they can be made to fit closely with reflections implied by the lower eight peaks).

The reflections which were observed of the low temperature phase fit in with those of the higher phase and suggest a similar structure. However, more work, especially at lower temperatures, obviously needs to be done to determine this.

TABLE 3.2

TETRAGONAL I CELL FOR SILANE
(32 molecules per unit cell)

Bragg Angle (observed)	HKL	Bragg Angle (calculated)
5.13°	130	5.15°
5.42°	222	5.42°
5.64°	123	5.63°
5.90°	132	5.89°
6.18°	114	6.18°
6.52°	040	6.52°
6.91°	330	6.91°
7.34°	224	7.36°
8.22°	341	8.28°
8.52°	006	8.62°
8.87°	116	8.92°
9.25°	440	9.24°
9.37°	244	9.29°
9.45°	350	9.52°
9.69°	442	9.68°
9.88°	145	9.85°
10.05°	161	10.04°
10.82°	046	10.83°
13.67°	248	13.69°
13.98°	275	13.97°
14.36°	084	14.36°
14.62°	457	14.60°
19.27°	3710	19.28°
21.67°	3712	21.68°

$$a = 12.5 \pm 0.1 \text{ \AA}$$

$$c = 14.2 \pm 0.1 \text{ \AA}$$

$$\text{Density} = 0.77 \pm 0.03 \text{ gm/cm}^3$$

$$\text{Residue} = 0.072^*$$

* This is based on a least squares reduction of the first eight angles only.

CHAPTER IV

CONCLUSIONS

As expected, the structure of silane was found to be distorted from fcc by an amount greater than that reported for CD_4 . Also, as expected, only the Bravais lattice (body-centered tetragonal) could be determined. The possible existence of a lower crystal symmetry (especially with respect to possible hydrogen positions) can not be eliminated.

If the orientations of the silane molecules were completely disordered in phase I, the structure would be highly symmetric (fcc). The observed distortion implies a certain amount of ordering. However, since a second phase exists at lower temperatures, it seems probable that phase I is only partially ordered.

A summary of information about silane, including that presented in this thesis, is given in table 4.1.

SPACE GROUP AND VIBRATIONAL SPECTRUM OF SILANE:

According to measurements of the infrared and Raman spectra of silane (Fournier, et al, 1972), the vibrational spectrum of solid silane in phase I is similar to that of the liquid. This implies that orientational disorder in the solid (phase I) is a dominant feature, as in phase I of the methanes. Also, according to Fournier, et al (1972), phase II shows more definite structure and is ordered. In partic-

TABLE 4.1

SUMMARY OF PHYSICAL PROPERTIES OF SILANE

Boiling point	161°K	
Triple point	88.48°K	Klein, et al, 1969; Clusius, 1933; Stock, 1925; Stock and Somieski, 1916.
Lambda point	63.45°K	
Vapour pressure at triple point is about 1mm.		
Density		
of liquid	0.68 gm/cm ³	(88.5°K) Stock and Somieski, 1916
of solid	0.73±0.02 gm/cm ³	(77°K) Klein, et al, 1969
of solid	0.77±0.03 gm/cm ³	(77°K) This Thesis
Lattice parameters of phase I (77°K)		
body-centered tetragonal (32 molecules per unit cell)		
	a = 12.5±0.1 Å	
	c = 14.2±0.1 Å	
Possible space groups (phase I or II)		
	I $\bar{4}$, I4, I4 ₁ , I4/m, I4 ₁ /a	
Expansivity	1.2 X 10 ⁻³ /°K	
Birefringence		
	phase I	>2 X 10 ⁻³
	phase II	>5 X 10 ⁻³

ular, it is suggested that possible factor groups are tetragonal (S_4 , C_4 , C_{4h}), trigonal (C_{3v} , D_3 , D_{3d}) and hexagonal (C_{3h} , C_6 , C_{6h}).

When we compare these deductions with the present work, somewhat different conclusions result. The direct X-ray measurements show that disorder observed in phase I can not be as extensive as in the methanes.

As mentioned before, the X-ray measurements obtained below the lambda point of silane suggest that phase II is also body-centered tetragonal. If this is the case then the factor groups suggested above can be further reduced to the tetragonal ones (S_4 , C_4 , C_{4h}) and to the space groups among them which are body-centered. These are S_4^2 or $I\bar{4}$, C_4^5 or $I4$, C_4^6 or $I4_1$, C_{4h}^5 or $I4/m$ and C_{4h}^6 or $I4_1/a$. This also suggests that the symmetry can not be lower than tetragonal (trigonal or hexagonal structures seem doubtful).

ESTIMATION OF BIREFRINGENCE:

As a test of the deductions made from the results of the X-ray diffraction measurements, an attempt was made to estimate the optical birefringence of the crystalline phases of silane. The structure, which has been proposed, would be expected to lead to fairly strong birefringence.

The method used was that developed by Ballik, et al (1973) for the measurement of weak birefringence in the three phases of the solid isotopic methanes. However, solid silane turned out to have a birefringence that was considerably

stronger than that of the methanes and consequently could not be measured with nearly the same accuracy.

The silane was condensed into the optical cell (see Ballik, et al (1973) for details) as a liquid and then slowly frozen. Crystallites several square millimetres in cross-section developed, some of which were oriented with axes in the plane of the optical plates that formed the thin cell (0.89mm thick). The birefringence at a temperature of about 77°K was estimated to be a minimum of 2×10^{-3} .

When the silane was cooled below the lambda point (63.45°K), the crystallites first showed considerable strain birefringence before shattering into tiny fragments. Even though the sample was maintained in the vicinity of 60°K for about 48 hours, no significant annealing was observed. Thus, it was not possible to estimate the birefringence of phase II in the normal way. With a quartz wedge of known retardation (i.e. thickness times birefringence) inserted in the light path and with a chart of the colours in various orders of retardation, the birefringence of the two solid phases was estimated and compared. The birefringence of phase II was found to be at least 5×10^{-3} .

Some recrystallization of the silane occurred after the specimen had been allowed to stand for several days in the temperature range 65 to 75°K. The birefringence was found to have dropped back down to the value observed before for phase I.

A model calculation was performed to check that the observed birefringence was consistent with the deduced structure of phase I. The model was that used by Ballik, et al (1973) based upon work done by Cowley (1970). The dielectric constant of solid silane appears not to be known and so it was assumed to be about 10% larger than that of solid methane. A computer calculation based on a structure corresponding to a distortion of 13.6% from face-centered cubic (4 molecules per unit cell) yielded a birefringence of 7×10^{-3} which is in reasonable agreement with that observed.

"THE END"

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