Compression and Phase Transitions of Solid NH_3, SiF_4, H_2S, and CF_4*

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Isothermal PV curves of solid NH_3, SiF_4, H_2S, and CF_4 have been observed by the direct piston displacement method up to pressures of 20 000 kg/cm² at various temperatures between 100° and 200°K. Relative volume changes and compressibilities are given for each substance except CF_4. Phase transitions have been observed as discontinuities in the piston motion. NH_3 exhibits no phase transitions. Phase diagrams are given for the other three substances. Comparison with previous work in the case of H_2S shows only partial agreement. In some instances the approximate volume changes accompanying the phase transitions have been determined.

I. INTRODUCTION

PV isotherms and phase transition parameters to 20 000 kg/cm² pressure have been observed for solid NH_3, SiF_4, and H_2S at various low temperatures. Some additional data have been obtained for CF_4. The piston displacement technique previously described[1,2] has been employed. The gases are condensed into the high-pressure cylinder and pressure applied directly to the samples after solidification. Plasticity of the samples is relied upon to transmit the uniaxial compressive applied stress throughout the sample as hydrostatic pressure. This method is valid only for nonbrittle substances with low shear strength. Past experience has shown that brittle behavior of a solidified gas sample is accompanied by crunching sounds and irregular piston motion as the pressure is varied. Except at the lowest temperatures, such behavior was not observed for the substances considered here.

The NH_3, SiF_4, and H_2S were obtained from Matheson lecture bottles. The CF_4 was from a sample supplied earlier through the kindness of Dr. R. M. Joyce of the DuPont Experimental Station, Wilmington, Delaware. The SiF_4 and H_2S were dried by passing through silica gel; purification was not found necessary for the NH_3 and CF_4. The purities were of the order of 99.5% or higher.

II. EXPERIMENTAL DETAILS

Unexpected difficulty was encountered in condensing the H_2S into the sample holders. Even when a constant temperature slightly above the triple point was maintained by a dry ice-acetone bath, the filling capillary invariably blocked after a small quantity of H_2S had condensed. This blocking was believed to have been caused by formation of a hydrate ($H_2S \cdot 6H_2O$) of much higher melting point. Successful condensation was achieved only after especially dried H_2S had been supplied by the Matheson Company. The gas was passed through a silica gel drying tube which was reactivated before each run. A larger diameter capillary was used

for the filling tube than had been necessary previously. This capillary was heated electrically to prevent blocking at the entrance to the sample chamber.

SiF_4 was also difficult to condense, because of its high triple point pressure (1320 mm Hg). The range of temperature for which condensation can occur without capillary blocking is very small. Even with the larger capillary first used for H_2S, a full cylinder of solid SiF_4 was never obtained.

As in the previous work,[1,2] the position of the piston was observed both for monotonically increasing and decreasing pressure. The hysteresis caused by friction in the sample holder varied considerably from run to run. It was generally less near the melting points of the substances than at lower temperature. The ammonia samples tended to have the largest friction, up to 20% of the maximum pressure. The magnitude of the friction was, as before, reduced by lining the cylinder with two layers of 0.005-in. indium foil.[3] To prevent extrusion of the solid, a brass ring of triangular cross section was placed ahead of the piston. Correction for friction was made by averaging the pressure on the two sides of the hysteresis curve at constant piston displacement. Account was also taken of the stretch of the press (by a blank run with no sample in the sample holder), and of the dilation of the pressure cylinder.

Sample holders of several diameters were used, ranging from $\frac{5}{8}$ in. (maximum pressure 3000 kg/cm²) to $\frac{1}{4}$ in. (maximum pressure 19 000–20 000 kg/cm²). The larger diameter holders gave more accurate PV data at the lowest pressures than could be obtained by extrapolation of the $\frac{1}{4}$ in. holder data below the equivalent frictional pressure. At least one run in a large holder was made near each temperature for which a PV curve was determined. The curves from the large and small cylinders agreed satisfactorily in the region of overlap.

Temperature control was obtained in a variable temperature cryostat of the Swenson type,[4] using liquid nitrogen as the coolant. Regulation to ±0.5 to 1.0°K was readily achieved. Temperature measure-
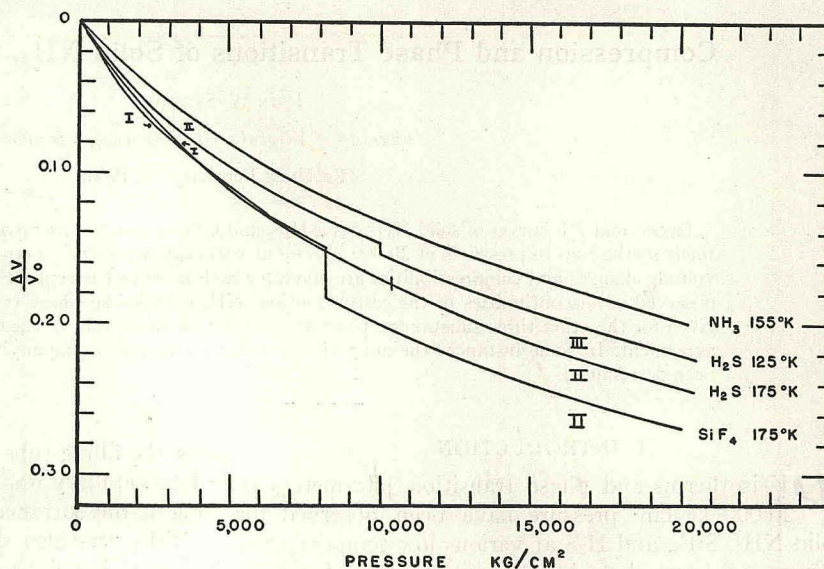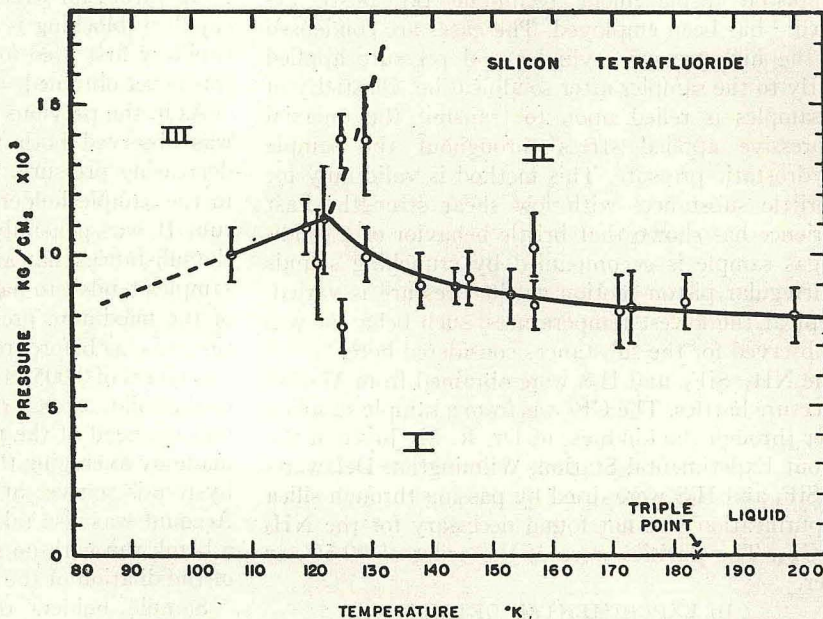
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* Supported by the Office of Ordnance Research, U. S. Army.
[1] J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).
[2] J. W. Stewart and R. I. LaRock, J. Chem. Phys. **28**, 425 (1958).

[3] R. Stevenson, J. Chem. Phys. **27**, 656 (1957).
[4] C. A. Swenson and R. Stahl, Rev. Sci. Instr. **25**, 608 (1954).

FIG. 1. Typical isotherms for solid NH_3, SiF_4, and H_2S.

FIG. 2. Phase diagram of solid SiF_4.

ment was by means of an indium resistance thermometer described elsewhere.[5,6]

Phase transitions in the solids were observed as discontinuities in the volume versus pressure curves. First-order transitions with large volume changes are readily identifiable in this apparatus, but the friction prevents distinguishing between a small first-order transition and a second-order transition with merely a break in the slope of the V vs P curve. Transitions of either type could normally be detected while a run was in progress by means of the drifting of the piston after the pressure was changed. Except at the lowest pres-

sures, the piston normally reached equilibrium within a few seconds after the application of each increment of weight on the dead weight gauge pan. The actual transition pressure was always taken as the mean of the apparent transition pressures with increasing and with decreasing pressure.

In order to locate the transitions as accurately as possible, the difference between the actual volume vs pressure curve and a straight line joining the points of lowest and highest pressure was plotted against pressure. This effectively magnified the scale of departures from a smooth curve. In most cases the transition points were easily identifiable. A few irregularities were observed with no apparent temperature correlation.

[5] J. W. Stewart, Rev. Sci. Instr. **30**, 949 (1959).
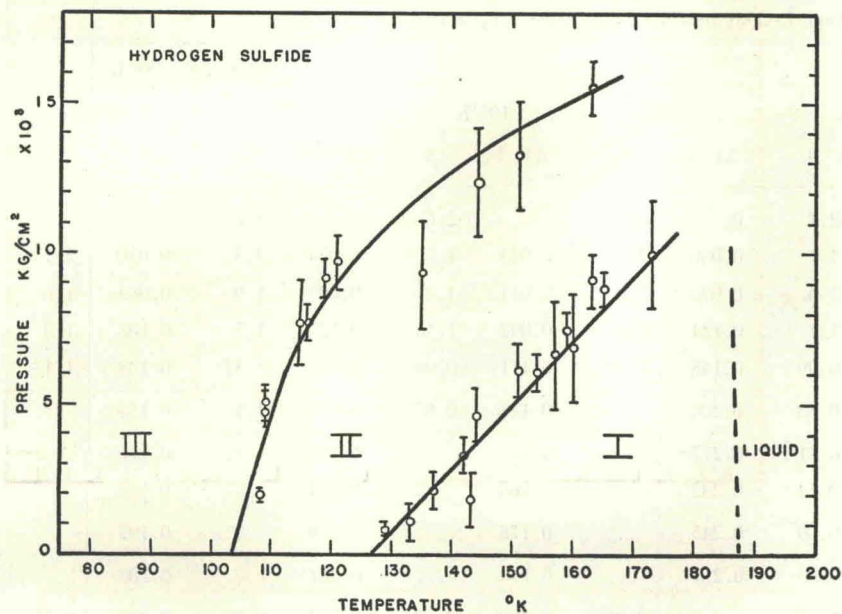[6] G. K. White and S. B. Woods, Rev. Sci. Instr. **28**, 638 (1957).

FIG. 3. Phase diagram of solid H_2S.

These were not transitions, but were caused by the piston temporarily "hanging up" due to friction. Such points were ignored in the determination of the location of the transition curves.

Several observations of phase transitions in SiF_4 and CF_4 were made at temperatures above their melting points at atmospheric pressure. This was done by applying pressure at a lower temperature and then by allowing the sample to warm up under pressure. Since it was impossible to reduce the pressure to zero without losing the sample by melting, no $\Delta V/V_0$ data were obtained at these temperatures.

III. RESULTS AND DISCUSSION

Figure 1 shows typical isotherms for solid NH_3, SiF_4, and H_2S. The phase diagrams of solid SiF_4, H_2S,
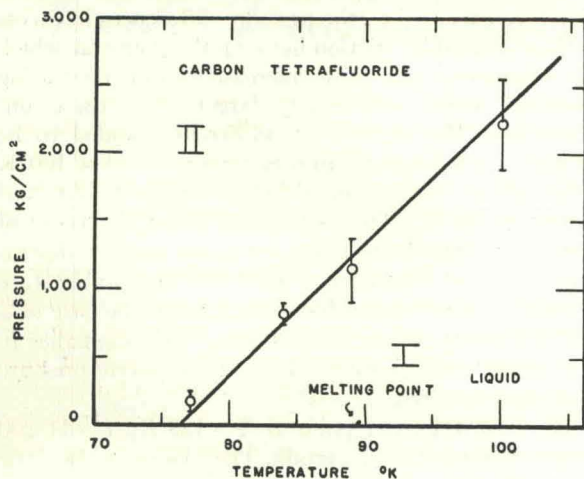
and CF_4 are shown below in Figs. 2–4. Table I lists the observed relative volume decreases as functions of pressure for NH_3, SiF_4, and H_2S. The results shown for each temperature were computed by averaging all the runs which were within $10°K$ of the temperature in question.

As before,[1,2] it was found convenient to represent the observed compressibility data in terms of Murnaghan's theory of finite strain.[1,7] This gives

$$P = (3/2\beta_0[y^7 - y^5][1 - \xi(y^2 - 1)],$$

where β_0 is the compressibility at zero pressure, y^3 the ratio of the volume V_0 at $P=0$ to the volume V at pressure P, and ξ is an adjustable constant. This relation is meaningful only for pressure below that of a transition. At a transition both β_0 and ξ change in a manner which is difficult to interpret. Differentiation of this equation allows the compressibilities to be determined more accurately than is possible by graphical means. The values of β in Table I were obtained in this manner for pressures below the transition, and estimated from the slopes of the curves for $P=20\,000$ kg/cm^2. The indicated values of ξ are those which give the best fit to the data.

The PV data are presented as relative volume decreases rather than as molar volumes because the available values of the densities of these substances do not appear to be sufficiently reliable, especially as to their temperature variation. The method previously used in this laboratory[2] for measurement of densities of solid CF_4, argon, and low melting hydrocarbons at $77°K$ is not applicable at the higher temperatures of present interest.

FIG. 4. Phase diagram of solid CF_4.

[7] F. Birch, J. Geophys. Research **56**, 227 (1952).

TABLE I. Compression of solid NH_3, SiF_4, and H_2S.

| Pressure Kg/cm² | NH₃ $MP=195°K$ | | | | SiF₄ $MP=183°K$ | | | | H₂S $MP=188°K$ | | | |
| | 155°K | | 110°K | | 175°K | | 105°K | | 175°K | | 125°K | |
	$-\Delta V/V_0$	β^a	$-\Delta V/V_0$	β	$-\Delta V/V_0$	β	$-\Delta V/V_0$	β	$-\Delta V/V_0$	β	$-\Delta V/V_0$	β
0	0	2.1	0	2.1	0	3.9	0	2.6	0	3.6	0	3.1
2000	0.037	1.7	0.034	1.7	0.060	2.3	0.043	1.7	0.054	2.5	0.050	2.1
4000	0.068	1.4	0.062	1.4	0.096	1.8	0.071	1.4	0.095	1.9	0.083	1.6
6000	0.093	1.2	0.087	1.1	0.124	1.4	0.092	1.16	0.127	1.5	0.108	1.3
8000	0.114	1.1	0.108	0.99	0.148	1.21	0.111	0.98	0.151	1.32	0.128	1.13
10000	0.132	1.0	0.124	0.88	0.200	...	0.128	0.87	0.170	1.17	0.154	...
12000	0.148	0.92	0.137	0.81	0.217	...	0.152	...	0.188	...	0.170	...
14000	0.162	0.85	0.148	0.74	0.232	...	0.166	...	0.204	...	0.184	...
16000	0.174	0.79	0.158	0.69	0.245	...	0.178	...	0.219	...	0.197	...
18000	0.186	0.73	0.167	0.66	0.257	...	0.190	...	0.231	...	0.208	...
20000	0.198	0.69	0.175	0.63	0.269	0.81	0.200	0.69	0.242	0.77	0.220	0.75
	No transition		No transition		I–II transition at 8200 kg/cm²		I–III transition at 10 200 kg/cm²		I–II transition at 10 400 kg/cm²		II–III transition at 10 000 kg/cm	
	$\xi=-1.2\pm0.2$		$\xi=-3.0\pm1.0$		$\xi=-3.7\pm0.3$		$\xi=-4.5\pm0.5$		$\xi=-2.3\pm0.2$		$\xi=-3.5\pm0.5$	
	$\rho=0.824^8$ gm/cm³		$\rho=0.832^8$ gm/cm³		$\rho=2.17^9$ gm/cm³				$\rho=1.17^{10}$ gm/cm³			

ᵃ β is the "instantaneous" compressibility, $-(1/V)(\partial V/\partial p)_T$, given in units of (kg/cm²)⁻¹ (×10⁻⁶).

NH₃

Solid ammonia shows no phase transitions below 19 000 kg/cm² in the range of temperature studied (100°–160°K). Its crystal structure is stated to be approximately face-centered cubic. No specific heat anomalies have been reported at atmospheric pressure between 20°K and the melting point. Furthermore, Smyth and Hitchcock[12] find that the dielectric constant of solid ammonia increases monotonically with temperature.

Ammonia evidently becomes brittle at the lower temperatures at which its compression was determined. The observed $\Delta V/V_0$'s at 110°K are too small compared with the values at 155°K, and the much larger value of ξ at the lower temperature also suggests that hydrostatic pressure was not being transmitted. Friction was considerably greater at 110° than at 155°K. It was therefore not feasible to go to lower temperatures.

SiF₄

This has been investigated over the temperature range 97°–200°K. There are no transitions at atmospheric pressure, but an unmistakable first order transition appears at high pressure (Fig. 2). The uncertainties of the individual points in the figure indicate the spread of pressures over which the observed transition could have occurred, and are based upon the sizes of the steps in which the pressure was varied. The "regions of indifference," (i.e., the pressure differences in excess of those caused by friction between the points at which the transition ran with increasing and decreasing pressure) were considerably larger than these uncertainties. The regions of indifference tended to be greater at low temperatures. Several runs below 100°K indicated no transition, although one was observed clearly at 108°K. This is believed to be the result of increasing sluggishness of the transition as the temperature is lowered. Phase I may exist as a metastable state at high pressure, somewhat analogous to the case of α and β mercury at low temperature.[13] No anomalies in the specific heat of solid SiF₄ at atmospheric pressure have been reported.

The I–II–III triple point at $T=123°K$, $P=11\ 200$ kg/cm² is somewhat uncertain. There seems to be little

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doubt that the principal first order transition curve slopes down on either side of this point, but the two observations of the hypothetical II–III transition shown in Fig. 2 are based on extremely small discontinuities in the V vs P data. The ΔV data are not accurate enough to check for thermodynamic consistency at the triple point. Owing to the difficulty of condensing SiF_4 without blocking the filling capillary, it was not possible to obtain a large sample which would have increased the sensitivity of the ΔV measurements. It is not feasible in this apparatus to vary the temperature at constant pressure in order to confirm the existence of this transition.

Above 140°K, the observed values of the relative volume change for the I–II transition were fairly consistent. They tended to increase slowly with rising temperature. Between 140° and 200°K, the average of nine separate I–II $\Delta V/V_0$'s was 0.031±0.010, corresponding to a change in molar volume of 1.5±0.5 cm^3/mole. The I–II transition curve may intersect the melting curve at a somewhat higher temperature than was reached in the present investigation. There appear to have been no experimental observations of the melting curve of SiF_4 above the triple point (1320 mm Hg, 182.9°K). The observed II–III ΔV was less than 0.2 cm^3/mole, and this transition could conceivably be second order.

X-ray diffraction studies at atmospheric pressure show that the silicon atoms in phase I of SiF_4 form a body-centered cubic structure. The over-all lattice is molecular rather than ionic. The higher pressure phases would presumably be close packed.

H_2S

There has been more previous work on solid H_2S than is the case for the other substances under consideration. The two phase transitions at atmospheric pressure were first observed by Giauque and Blue.[14] Their specific heat measurements indicated a first-order transition at 103.6°K, and an anomaly such as is characteristic of second order transitions at 126.2°K. Kruis and Clusius[15] determined the latent heat of the lower transition to be 568.3 cal/mole, and the excess heat at the upper transition (over a range of several degrees) to be 108.7 cal/mole. Dielectric constant,[12] visual,[16] and nuclear magnetic resonance[17] observations of solid H_2S indicate no change in the face-centered cubic structure at 126.2°K, but do suggest a change to a slightly anisotropic state at 103.6°K. The dielectric constant jumps[12] from 3.5 to 21 as the temperature is raised through 103.6°K.

Previous pressure studies have been made to 250

kg/cm² by Clusius[18] for the lower transition, and by Stevenson[19] to 10 000 kg/cm² for the whole phase diagram. Figure 3 shows the result of the present investigation. The agreement for the slopes of the I-II and II–III transitions is fairly good. However, Stevenson's phases δ and κ have not been observed in the present study. For these he reports volume changes of the order of one-quarter to one-half his values for the I–II and II–III transitions. The present measurements seem to preclude the existence of any discontinuities as large as these. The difficulty of distinguishing transitions with small volume changes from frictional irregularities of piston motion in this apparatus has been discussed previously.[20]

The observed $\Delta V/V_0$ for the lower transition near atmospheric pressure (0.006±0.001) corresponds to a molar ΔV of 0.16±0.03 cm^3/mole. With the latent heat of Clusius,[15] the Clausius-Clapeyron equation gives $dP/dT = 900$ kg/cm²°K at $P=0$, agreeing satisfactorily with the initial slope of the observed transition curve (Fig. 3). This result compares reasonably well with the measured values of 680 kg/cm²°K reported by Clusius and Weigand,[18] and 660 kg/cm²°K obtained from the phase diagram of Stevenson.[19] The latter reports a single value of $\Delta V/V_0$ for this transition to be 0.0021 (at 4000 atm pressure). This corresponds to a change of molar volume of 0.06 cm^3/mole, which appears to be too small.

Possibly both the transition curves intersect the melting curve. Stevenson[19] has evidence from one experimental point near 10 000 atm that the melting line is nearly vertical. No other observations of the melting curve seem to exist, nor have there been any direct measurements of the very small volume change upon melting at atmospheric pressure, from which the zero pressure slope of the melting curve might be calculated.

The x-ray diffraction studies of Justi and Nitka[9] indicate that the sulfur atoms in all three phases occupy a face-centered cubic lattice, with a change of less than 1% in the lattice constant (5.77 A) between 20° and 150°K. More recently, Reding and Hornig[21] have examined the infrared absorption spectra of thin films of solid H_2S at 66°, 112° and 140°K. They also conclude that the sulfur atoms occupy fcc sites in all three phases. The transitions apparently arise from variation of the positions of the hydrogen atoms. Phase III is shown to be ordered, while I and II are disordered. The basic cubic structure is quite open so that rearrangements of the hydrogens are possible without appreciable changes in the lattice constant. The nuclear magnetic resonance measurements of Alpert[17] show that neither

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transition arises from a change of rotational states of the molecules (as is the case with CH_4). The optical anisotropy of phase III observed by Kruis and Clusius[16] can, it is believed, be accounted for by a small (less than 1%) distortion of the basic cubic lattice.

CF₄

Some additional data have been obtained for solid CF_4. Figure 4 shows the first order transition at higher temperatures than previously.[2] This transition was first observed thermally at atmospheric pressure at 76.2°K by Eucken and Schroeder.[22] We have observed a volume change of 1.8 cm³/mole at 89°K, and, earlier,[2] 2.2 cm³/mole at 77.3°K. The experimental value of dP/dT is 97 kg/cm² °K. This and the latent heat of transition observed by Eucken and Schroeder[22] lead to a calculated ΔV of 2.0 cm³/mole for the transition at atmospheric pressure. The observed transition parameters thus appear to be consistent.

Evidently, the structure of neither phase of solid CF_4 has been determined experimentally. Wyckoff[23] makes no mention of this substance. The silicon atoms in SiF_4 occupy bcc sites, while in CBr_4, another similar compound, the structure is known to be similar to that of SnI_4 above 47°C, and monoclinic below 47°C. One can only speculate on the basis of the moderately large volume change (approximately 4%) that the low temperature modification of CF_4 is close packed, while phase I is not.

The I–II transition line may or may not intersect the melting curve. The variation of melting temperature with pressure for CF_4 has apparently never been determined. There do not appear to exist observations of the densities of liquid and solid at the melting point.

IV. ACKNOWLEDGMENTS

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