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COMPRESSION AND PHASE TRANSITIONS OF SOLID

HCl, HBr, SiH<sub>4</sub>, AND SF<sub>6</sub>\*

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Abstract

Isothermal PV curves for solid HCl, HBr, SiH<sub>4</sub>, and SF<sub>6</sub> have been determined by the direct piston displacement method up to pressures of 20,000 kg/cm<sup>2</sup> at various temperatures between 50°K and 190°K. Relative volume changes (and in some cases molar volumes) and compressibilities have been calculated for each substance. Phase transitions have been observed as discontinuities in the piston motion. First order transitions have been observed in solid HCl, SiH<sub>4</sub>, and SF<sub>6</sub>. Phase diagrams are included. The expected second order transition in solid HBr was not noted, probably because of impurities in the samples. The approximate volume changes accompanying the observed transitions have been determined. Their consistency with other data has been checked by means of the Clausius-Clapeyron equation.

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## I. Introduction

Previously described<sup>1, 2</sup> techniques have been utilized to apply high pressure to samples of solid HCl, HBr, SiH<sub>4</sub>, and SF<sub>6</sub>. PV isotherms and phase transition parameters to 20,000 kg/cm<sup>2</sup> have been observed for various low temperatures. The piston displacement technique<sup>1</sup> was employed throughout. Samples of each gas were condensed directly into the sample holder, and uniaxial compression applied with a piston. The validity of the PVT data thus obtained depends upon the plasticity of the solid. The samples must exhibit plastic behavior, as opposed to brittleness, and must have low shear strength. These conditions appear to be met for these four solids in the temperature ranges considered here. The present results are apparently the first high pressure data which have been obtained for these substances in their solid states.

The HCl, HBr, and SF<sub>6</sub>, obtained from Matheson lecture bottles, were of unknown relatively high purity. The silane was from a sample supplied to the author through the kindness of Dr. R. M. Joyce of the duPont Experimental Station, Wilmington, Delaware. HCl and HBr appeared to be of special interest on account of the phase transitions which occur at atmospheric pressure. Very little work of any kind had previously been done with solid SiH<sub>4</sub> and SF<sub>6</sub>. These four substances bring to twenty-two the total number of solidified gases for which compressibility and phase transition data have been determined by the present techniques<sup>1,2,3,4,5</sup>.

The apparatus used in the current investigation was that previously employed<sup>2</sup> for similar studies of solid NH<sub>3</sub>, SiF<sub>4</sub>, H<sub>2</sub>S, and CF<sub>4</sub>. The details of the experimental manipulation and reduction of data were similar. A search was made for solid-solid transitions in each of the



substances investigated. HCl, SiH<sub>4</sub>, and SF<sub>6</sub> each showed one first order transition, while none was found in solid HBr. The volume changes of the first order transitions were measured and correlated with the experimentally observed slopes of the transition lines. This correlation proves to be quite inaccurate because the inevitable friction and the low but finite concentration of impurities in the solid samples tend to smear out the transitions over a wide pressure range. It is believed that the pressure at which such a transition runs in thermodynamic equilibrium at a given temperature can be determined by the present technique to within 5 to 10 per cent. The accuracy of  $\Delta (\Delta V/V_0)$  at transitions is considerably poorer than this.

## II. Experimental Technique and Calculations

A detailed description of the experimental methods<sup>1, 2</sup> will not be repeated here. In brief, the procedure was as follows. After initial compaction of the loosely frozen solid, the change of length of the sample was observed as a function of monotonically increasing and decreasing pressure. Weights were added to and removed from the pan of the dead weight gauge in sequence, and the piston position observed each time. The values of  $\Delta V/V_0$  were determined by the method originally proposed and used by Bridgman<sup>6</sup>. Correction had to be made for the appreciable distortion of the press members and the small dilation of the sample holder under internal pressure<sup>2</sup>.

Transitions appeared as finite breaks in the volume versus pressure curves. In the present investigation only first order transitions

were observed. The difference in the apparent pressures at which a transformation runs with monotonically increasing and decreasing pressure is equal to twice the sum of the effective friction in the apparatus and the overpressure ("region of indifference") which must be applied to induce the transition to run. The latter is increased in width by impurity in the sample. Thus, the greater the contamination, the less accurately can one determine the actual transition pressure and the accompanying volume change.

The sample temperature was adjusted to the desired value and maintained constant in a variable temperature cryostat of the type designed by Swenson<sup>7</sup>. Liquid nitrogen was the coolant for  $77^{\circ}\text{K} < T < 200^{\circ}\text{K}$ , while liquid helium was used for the single run on  $\text{SiH}_4$  at  $54^{\circ}\text{K}$ . The temperature was measured and monitored by means of a resistance coil of extruded 99.999% pure indium<sup>8</sup> wire mounted in close thermal contact with the outside of the pressure cylinder<sup>9</sup>. By manual adjustment of the flow rate of the coolant by means of a valve, the temperature could be held constant to within about one degree Kelvin for periods of four hours or longer.

After the total compression of a sample,  $-\Delta V/V_0$ , had been obtained as a function of pressure, fit was made to a Murnaghan<sup>10</sup> relation of the form

$$P = \frac{3}{2\beta_0} \left[ y^7 - y^5 \right] \left[ 1 - \xi (y^2 - 1) \right] \quad (1)$$

$\beta_0$  is the compressibility at zero pressure,  $y^3 = V_0/V$  with  $V_0$  the volume at zero (atmospheric) pressure and  $V$  the volume at pressure  $P$ .  $\xi$  is an



adjustable constant whose value depends upon the relative importance in the compressional energy of strain terms higher than quadratic. The fit was in all cases at least as good as the experimental accuracy of the  $\Delta V/V_0$  data - roughly  $\pm 5$  per cent. Equation (1) is useful only for pressures between atmospheric and that of a transition. At a transition  $\xi$  and  $\beta_0$  assume different values in a manner which is difficult to interpret. A new fit can be made for the pressure range above a transition, but this is not particularly meaningful.

The "instantaneous" compressibilities,  $\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  were determined by analytic differentiation of (1). This yields

$$K = \frac{1}{\beta} = \frac{1}{2} K_0 y^5 \left[ -9 \xi y^4 + (7 + 14\xi) y^2 - (5 + 5\xi) \right] \quad (2)$$

where  $K$  is the instantaneous bulk modulus. This gives smoothed values of the compressibility which are more accurate than one can obtain graphically from the original data.

As yet there is no basis for comparison between the experimental data for these substances and a theoretically calculated PVT surface. So far such detailed calculations are possible only for the simplest solids, such as the solidified rare gases<sup>11</sup> and the alkali metals<sup>12</sup>. The theoretical calculation of pressure as a function of temperature for solid-solid transitions represents an even more difficult problem. No final solution based upon microscopic theory has been found for any substance.

### III. Detailed Results and Discussion

In Table I is presented a summary of the PVT results at one selected temperature for each of the four substances under consideration. Detailed discussion of each follows.

#### HCl

This has been investigated over the temperature range  $77^{\circ}\text{K}$  -  $152^{\circ}\text{K}$ . Twenty-four separate determinations of volume as a function of pressure were made at different temperatures and in three sizes of sample holder. In general, three to five runs were made with each sample. Where direct comparison could be made, reproducibility of  $\Delta V/V_0$  was within 5%.

HCl gas was condensed into the steel sample holder with liquid nitrogen. A current of approximately 3 amperes was passed through the 0.031" i.d. stainless steel filling capillary to prevent blockage by solid. Little difficulty was experienced in filling the sample holders.

It is well known that solid HCl exhibits a first order transition at  $98.4^{\circ}\text{K}$  at atmospheric pressure<sup>13</sup>. The latent heat of the transition is 284 calories per mole<sup>13</sup> (7.8 calories per gram). We have observed this same transition under pressure at temperatures between  $101^{\circ}\text{K}$  and  $125^{\circ}\text{K}$ . The transition always was quite sharp, appearing equally clearly under increasing and decreasing pressure. All but two of the observed points lie closer than experimental error to the smoothed PT curve (Fig. 1). This curve extrapolates very nearly to  $98.4^{\circ}\text{K}$  at  $P = 0$ ; the lowest transition pressure observed was  $1,630 \text{ kg/cm}^2$ .

At  $105^{\circ}\text{K}$  the observed  $\Delta (\Delta V/V_0)$  for the transition is 0.7%, so  $\Delta V = 0.18 \text{ cm}^3/\text{mole}$ . We observe  $dP/dT = 430 \text{ kg/cm}^2 \text{ }^{\circ}\text{K}$ , and from the



Clausius-Clapeyron equation  $dP/dT = L/T\Delta V$ , one finds that  $L_{105} = 190$  calories per mole. This is to be compared with Giaque's value<sup>13</sup> of 284 calories per mole at 98°K. On account of the smearing out of the transition there is no doubt that our value of  $\Delta (\Delta V/V_0)$  is too small. If we neglect the (small) change of  $L$  between 98°K and 105°K and use Giaque's<sup>13</sup> value, we obtain a calculated  $\Delta (\Delta V/V_0)$  of 1.0%. Actually this is consistent with the current experimental data. The uncertainty is great enough so that one could easily draw the original  $V$  vs  $P$  curve with a relative discontinuity of 0.010 in  $\Delta V/V_0$ , instead of 0.007. Except for the most plastic of the solidified gases, friction and non-hydrostatic stress components are too great for precise measurement of volume discontinuities to be possible. Sample purity is also a factor. The relative accuracy of the overall volume changes at high pressure is considerably greater.

The value of the density of solid HCl, 1.469 gram/cm<sup>3</sup> (107°K) used in the above calculation and upon which was based the determination of the molar volumes in Table I, was obtained by means of a pycnometer by Simon and Simson<sup>14</sup>. This is the only reliable measurement of the density above the transition temperature. There has been no satisfactory direct measurement of the density change of the solid at the transition at atmospheric pressure. The various density measurements which have been reported<sup>15,16,17</sup> at different temperatures are not wholly self-consistent.

The crystal structures of the two modifications of HCl have been determined by X-ray diffraction<sup>14,15,17</sup> and confirmed by infra-red



spectrum<sup>18</sup> and nuclear magnetic resonance<sup>19</sup> studies. The current consensus of opinion<sup>20</sup> is that the high temperature phase I is face-centered cubic (isotropic) and the low temperature phase II is face-centered orthorhombic (anisotropic). It is now definitely known that this is not a rotational transformation of the methane type<sup>5</sup>. The current high pressure data are of no assistance in determining the crystal structure. It can be stated that there is apparently only this one transition in the pressure-temperature domain bounded by 77°K, 152°K, atmospheric pressure, and approximately 17,000 kg/cm<sup>2</sup>. Because of friction, transitions occurring just below the upper limit of 20,000 kg/cm<sup>2</sup> cannot be ruled out.

#### HBr

This substance might be expected to be analogous to HCl. However, its behavior at atmospheric pressure was observed by Giaque and Wiebe<sup>21</sup> to be quite different. Instead of a single first order transition as in HCl, three apparently second order transitions were observed, at 89.7°K, 113.6°K, and 116.9°K. Later work has confirmed this multiplicity. The phase diagram of solid HBr is thus quite complicated. In the case of DBr<sup>22</sup>, the two upper transitions coalesce into one, which is still second order. Giaque<sup>21</sup> and Alpert<sup>19</sup> report that the HBr transitions show much more temperature hysteresis than does the HCl transition.

Somewhat surprisingly, in the present investigation no transitions of any kind were observed in solid HBr. On account of the fact that the transitions are second order, one would not expect a volume discontinuity such as is observed in HCl. However, differing compressibilities of the two phases should be revealed by a break in the slope of

the volume vs pressure curves<sup>5</sup>. It is extremely unlikely that all four of the expected phases of HBr would have the same compressibility. Some of the modifications might have a limited domain of existence in the PT plane. No such break was observed in fourteen runs covering a temperature range of 89°K - 173°K, and the pressure range 1 - 20,000 kg/cm<sup>2</sup>.

The probable explanation of this negative result is that it was never possible to fill a sample holder more than one-third full of solid HBr. Condensation always stopped prematurely, and no amount of manipulation of the sample holder temperature could induce more gas to condense. When the sample holder was warmed above the melting point of HBr the entire contents invariably evaporated. This difficulty at first appeared to be similar to that experienced earlier with H<sub>2</sub>S<sup>2</sup>. The use of a large bore capillary in the cold region, coupled with electrical heating and the use of a silica gel drying tube (measures which had solved the problem for H<sub>2</sub>S) unfortunately proved to be of no benefit in the case of HBr. Furthermore, to remove possible traces of Br<sub>2</sub>, the HBr gas was also passed over finely divided silver. There was little tarnishing of the silver, so that this contaminant could not have been present in any great degree. In addition, the cylinder of HBr was immersed in a dry-ice acetone mixture in order to freeze out possible non-volatile impurities. The nature of the impurity responsible for the apparent blocking of the filling line is not known. Possibly it is a strongly bonded hydrate such as HBr•H<sub>2</sub>O with a freezing point below room temperature, but considerably above that of HBr.



The shortness of the samples impaired the relative accuracy of the compressibility data. In these cases, the distortion correction for the press and cylinder amounted to over 60% of the total effect observed. This correction must be subtracted from the raw data. Thus the HBr  $\Delta V/V_0$  data in Table I are certainly less accurate than those for HCl. Had it been possible to obtain samples of normal size, it is conceivable that the expected transitions would have been observed. However, relatively large hysteresis is to be expected in view of the observations of Giauque<sup>21</sup> and Alpert<sup>19</sup> mentioned earlier, while the effects being sought are probably small compared to that in HCl.

The value of the density of solid HBr at 150°K,  $2.55 \pm 0.1$  gram/cm<sup>3</sup> used in calculating the molar volumes in Table I is based upon interpolation between several rather uncertain experimental values<sup>17,23,24</sup>. There have apparently been no more recent determinations.

Evidently<sup>25</sup>, the crystal structures of the highest and lowest temperature modifications of solid HBr are similar to those of the two HCl phases. On the other hand, the details of the transition mechanism from one to the other must be quite different.



This substance offers an interesting comparison with CH<sub>4</sub>. However, as occurs frequently when compounds containing analogous elements in the periodic table are compared, the phase transitions are found to be qualitatively different. Clusius<sup>26</sup> observed a first order

transition at  $63.5^{\circ}\text{K}$  with a latent heat of 147 calories per mole (4.58 calories per gram). This is completely unlike the methane transition<sup>5</sup> ( $20.5^{\circ}\text{K}$ ) which is unmistakably second order.

At high pressure (nine determinations) we have observed a single first order transition. This could be traced only to  $4,000 \text{ kg/cm}^2$  (Fig. 2), at which pressure the transition occurs well above the melting point at atmospheric pressure. Attempts to follow the transition to higher pressure failed because of loss of the samples. The observed transition curve is linear, and extrapolates closely to  $63.5^{\circ}\text{K}$  at atmospheric pressure.  $dP/dT$  is found to be  $91 \text{ kg/cm}^2 \text{ }^{\circ}\text{K}$ , and the  $\Delta (\Delta V/V_0)$  for the transition ( $80^{\circ}\text{K}$ ) is 2.4%. The transition is sharp and the hysteresis slight. Thus the experimental value of  $\Delta (\Delta V/V_0)$  should not be too small as it may be for broad transitions.

There appears to have been no reliable determination of the density of solid silane. One, therefore, cannot check consistency of the transition data by means of the Clausius-Clapeyron equation. However, if we assume the same value of  $\Delta (\Delta V/V_0)$  at atmospheric pressure as observed at  $1,500 \text{ kg/cm}^2$ , we can calculate the density at  $63.5^{\circ}\text{K}$ ,  $\rho_0$ , to be  $0.71 \text{ gram/cm}^3$ . This appears to be a bit low. There is one observation<sup>27</sup> of the density of liquid silane at the melting point -  $0.68 \text{ gram/cm}^3$ . Thus one might expect the density of the solid at the transition temperature to be in the neighborhood of  $0.75$  to  $0.80 \text{ gram/cm}^3$ . It is possible that either the latent heat or our  $\Delta (\Delta V/V_0)$  could have a 10% error. The agreement between the observed and calculated  $\Delta (\Delta V/V_0)$  is much closer for  $\text{SiH}_4$  than for  $\text{HCl}$ , where the hysteresis effects are greater.



The preparation of adequately large samples of solid  $\text{SiH}_4$  offered no fundamental difficulty. The only problem was that, since silane ignites spontaneously in the atmosphere to form a "snowstorm" of fine particles of silica, traces of air in the filling system led to clogging of the valve seats. After each run it was necessary to remove the valve stems and purge the system with dry nitrogen. On each occasion clouds of silica were seen to emerge. Particles of inert  $\text{SiO}_2$  embedded in the solid  $\text{SiH}_4$  samples should not cause smearing out of the transitions.

The nine runs which were made covered the ranges  $54^\circ\text{K} - 108^\circ\text{K}$  and  $1 - 20,000 \text{ kg/cm}^2$ . For the runs above the melting point ( $88.5^\circ\text{K}$ ) it was not possible to lower the pressure to zero lest the sample escape. In all cases with this substance friction was unusually small. It appeared to be quite plastic.

The crystal structures of the two phases of solid  $\text{SiH}_4$  have apparently never been determined. Clusius<sup>26</sup> observed that phase I (between  $63.5^\circ\text{K}$  and the melting point) is weakly doubly refracting, while the low temperature phase II was found to be strongly birefringent, showing considerable anisotropy. The transition appears to be of the ordinary crystallographic type. No evidence has been found for the existence of rotational transformations analogous to those in solid  $\text{CH}_4$  and  $\text{CD}_4$ .

SF<sub>6</sub>

We have made a total of sixteen runs with solid SF<sub>6</sub>, covering the ranges 81°K - 190°K and 1 - 20,000 kg/cm<sup>2</sup>. A single first order transition was observed at twelve different pressures (Fig. 3). The transition is apparently linear in the PT plane. Our transition line extrapolated to atmospheric pressure gives excellent agreement with the transition studied at 94°K by Eucken and Schroder<sup>28</sup>. They concluded that the transition was first order, with a latent heat of 384 calories per mole (2.63 calories per gram).

The observed value of  $\Delta (\Delta V/V_0)$  for this transition is 2.6% at 182°K and 7,300 kg/cm<sup>2</sup>. Hysteresis and friction were small, so that this is a relatively accurate value. The transition occurred rapidly for both increasing and decreasing pressure and so could be located quite precisely. As is the case with Figures 1 and 2, the error bars on the points in Figure 3 correspond to the size of the pressure increments used.

The density of solid SF<sub>6</sub> has been measured at very low temperature and at the melting point by Klemm and Henkel<sup>29</sup>. At 182°K the value 2.55 grams/cm<sup>3</sup> has been obtained by interpolation, with account taken of the discontinuous density change at the transition. This value was used to determine the molar volumes in Table I.

If we use the observed  $dP/dT$  (82.8 kg/cm<sup>2</sup> °K) and  $L$  at 94°K, we find from the Clapeyron equation  $\Delta V = 2.10$  cm<sup>3</sup>/mole. The interpolated density<sup>30</sup> at 94°K is 2.70 gram/cm<sup>3</sup>, giving a molar volume of 54.1 cm<sup>3</sup>.



Thus  $\Delta (\Delta V/V_0)_{94} = 3.9\%$ , which agrees reasonably well with the value of 2.6% observed in the current investigation at 182°K. Inasmuch as the latent heat of transformation might be expected to vary considerably over a large range of temperature, there is no basis for a direct comparison at 182°K and 7,300 kg/cm<sup>2</sup>. If  $L$  and  $dP/dT$  both remained the same between 94°K and 182°K, then at the latter temperature  $\Delta (\Delta V/V_0)$  would be only 2.0% which is definitely smaller than indicated by the current observations.

No data appear to be available on the crystal structure of solid SF<sub>6</sub>. The transition has all the characteristics of an ordinary crystallographic one.

Because of blockage of the filling capillary, it was impossible to obtain large samples of solid SF<sub>6</sub>. After it was found that it had no observable effect, the use of the silica gel drier in the line was discontinued. On account of the lack of friction and the sharpness of the observed transition, it is believed that the blockage was by solid SF<sub>6</sub> itself rather than by impurities. SF<sub>6</sub> has a high triple point pressure, 1,700 mm Hg, so that the gas must be continuously supplied at a pressure above 19 psig in order to permit condensation to the liquid rather than sublimation to the solid. Under these conditions blockage readily occurs. It is not felt that the shortness of the SF<sub>6</sub> samples significantly affected the accuracy of the results.

IV. Acknowledgments

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TABLE I. COMPRESSION OF SOLID HCl, HBr, SiH<sub>4</sub>, AND SF<sub>6</sub>

Pressure Kg/cm <sup>2</sup>	HCl M.P. 159°K			HBr M.P. 186°K			SiH <sub>4</sub> M.P. 88.5°K		SF <sub>6</sub> S.P. 210°K		
	T = 130°K			T = 150°K			T = 80°K		T = 182°K		
	Molar Vol. cm <sup>3</sup>	$-\frac{\Delta V}{V_0}$	$\beta \times 10^{-5}$ cm <sup>2</sup> /kg	Molar Vol. cm <sup>3</sup>	$-\frac{\Delta V}{V_0}$	$\beta \times 10^{-5}$ cm <sup>2</sup> /kg	$-\frac{\Delta V}{V_0}$	$\beta^a \times 10^{-5}$ cm <sup>2</sup> /kg	Molar Vol. cm <sup>3</sup>	$-\frac{\Delta V}{V_0}$	$\beta \times 10^{-5}$ cm <sup>2</sup> /kg
0	25.3	0	3.60	31.7	0	3.65	0	3.1	57.3	0	2.93
1,500	-	-	-	-	-	-	.080	-	-	-	-
1,500	-	-	-	-	-	-	.104	-	-	-	-
2,000	23.9	.057	2.34	29.7	.063	2.37	.116	-	54.5	.050	2.15
4,000	22.9	.096	1.80	28.6	.099	1.86	160	2.0	52.4	.086	1.72
6,000	22.2	.125	1.47	27.7	.128	1.53	.194	-	50.8	.114	1.45
7,300	-	-	-	-	-	-	-	-	49.9	.129	-
7,300	-	-	-	-	-	-	-	-	48.4	.155	-
8,000	21.6	.148	1.26	26.9	.151	1.33	.220	-	-	-	-
10,000	21.1	.168	1.10	26.3	.171	1.18	.241	1.3	47.0	.180	-
12,000	20.7	.184	.99	25.8	.187	1.05	.257	-	46.1	.196	-
14,000	20.3	.199	.90	25.3	.202	.96	.271	-	45.4	.208	-
16,000	20.0	.212	.82	24.9	.216	.87	.283	-	44.8	.219	-
18,000	19.6	.225	.76	24.5	.229	.80	.293	-	44.3	.228	-
20,000	19.3	.238	.70	24.1	.241	.74	.303	-	43.8	.236	(0.55) <sup>b</sup>
	No transition (at 130°K)			No transition			I-II transition at 1,500 kg/cm <sup>2</sup>		I-II transition at 7,300 kg/cm <sup>2</sup>		
	$\xi = -2.8 \pm 0.2$			$\xi = -2.4 \pm 0.2$			$\xi^a = -0.5 \pm 0.2$		$\xi = -1.8 \pm 0.2$		

- a  $\xi$  and  $\beta$  are evaluated at 54°K where solid SiH<sub>4</sub> is somewhat brittle. These values are not as reliable as those for the other substances. At 80°K the transition occurs at  $P = 1,500$  Kg/cm<sup>2</sup>, giving too short a range of pressure for a satisfactory Murnaghan fit of Phase I data.
- b Estimated from slope of volume vs pressure plot.

References

1. J. W. Stewart. *J. Phys. Chem. Solids* 1, 146 (1956).
2. J. W. Stewart. *J. Chem. Phys.* 33, 128 (1960).
3. J. W. Stewart. *Phys. Rev.* 97, 578 (1955).
4. J. W. Stewart, R. I. LaRock. *J. Chem. Phys.* 28, 425 (1958).
5. J. W. Stewart. *J. Phys. Chem. Solids* 12, 122 (1959).
6. P. W. Bridgman. *Proc. Am. Acad. Arts and Sci.* 74, 425 (1942).
7. C. A. Swenson, R. Stahl, *Rev. Sci. Instr.* 25, 608 (1954).
8. G. K. White, S. B. Woods. *Rev. Sci. Instr.* 28, 638 (1957).
9. J. W. Stewart. *Rev. Sci. Instr.* 30, 949 (1959).
10. F. Birch. *J. Geophys. Res.* 56, 227 (1952).
11. N. Bernardes. *Phys. Rev.* 112, 1534 (1958).
12. H. Brooks, F. S. Ham. *Phys. Rev.* 112, 344 (1958).
13. W. F. Giaque, R. Wiebe. *J. Am. Chem. Soc.* 50, 101 (1928).
14. F. Simon, C. Simson. *Zeit. Physik* 21, 168 (1924).
15. G. Natta. *Nature* 127, 235 (1931).
16. C. P. Smyth, C. S. Hitchcock. *J. Am. Chem. Soc.* 55, 1830 (1933).
17. G. Natta. *Gazz. chim. Italia* 63, 425 (1933).
18. D. F. Hornig, W. E. Osberg. *J. Chem. Phys.* 23, 662 (1955).
19. N. L. Alpert. *Phys. Rev.* 75, 398 (1949).
20. G. L. Hiebert, D. F. Hornig. *J. Chem. Phys.* 27, 1216 (1957).
21. W. F. Giaque, R. Wiebe, *J. Am. Chem. Soc.* 50, 2193 (1928).
22. T. J. Krieger, H. M. James. *J. Chem. Phys.* 22, 796 (1954).
23. A. Reis. *Zeit. Physik* 1, 299 (1920).
24. W. Herz. *Zeit. anorg. allgem. Chem.* 119, 221 (1921).
25. J. G. Powles. *Trans. Faraday Soc.* 48, 430 (1952).



26. K. Clusius. Zeit. phys. Chem. B22, 213 (1933).
27. Stock Somieski Ber. der deutschen chemischen Gesellschaft 49, 111 (1916).
28. A. Eucken, F. Schroder. Zeit. phys. Chem. B41, 307 (1938).
29. W. Klemm, P. Henkel. Zeit. anorg. allgem. Chem. 207, 73 (1932).

Compression and Phase Transitions of Solid HCl, HBr,  
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Figure Captions

- Figure 1 - Phase Diagram for Solid HCl.  
Figure 2 - Phase Diagram for Solid SiH<sub>4</sub>.  
Figure 3 - Phase Diagram for Solid SF<sub>6</sub>.



PHASE TRANSITION IN SOLID HYDROGEN CHLORIDE

