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Pressure Studies on the Nuclear Magnetic Resonance of Solid Hydrogen between 1.2° and 14°K*

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The nuclear magnetic resonance spectrum of solid hydrogen (75% *ortho*) has been studied as a function of temperature from 1.2°K to 14°K and of pressures from one to three hundred atmospheres. At 10°K the absorption signal broadens from less than one gauss to 5.3 gauss between slope extrema as the temperature is lowered and self-diffusion ceases. When pressure is applied, this broadening is shifted to higher temperatures by a sizable amount. With 230 atmospheres, a shift of 3.2°K was observed. Correlation times and activation energies of self-diffusion have been computed for each of the transitions at various pressures. The activation energies are linearly dependent upon the transition temperatures. The lower transition at 1.5°K in which some rotational degeneracy is removed was also investigated with various pressures. Pressures up to 216 atmospheres did not shift the transition temperature to any observable extent. Pressures up to 337 atmospheres had no effect on line shape below 1.5°K.

INTRODUCTION

THE nuclear magnetic resonance (NMR) of solid normal hydrogen was first investigated by Hatton and Rollin[1] soon after NMR was developed as a useful tool for investigation of the solid and liquid states.[2,3] Hatton and Rollin observed two line-shape transitions in the solid—one at about 10°K where the line broadened from less than 1 gauss to 6 to 8 gauss as the temperature was lowered, and the second at 1.5°K where side peaks of 40-gauss separation appeared with decreasing temperature. The first transition or line broadening is associated with the self-diffusion of the H_2 molecules in the solid. The 1.5°K transition is assigned to proton-proton interaction in an *ortho*-molecule and to spin-rotational interactions. Hill and Ricketson[4] found at 1.6°K an anomaly in the specific heat of solid hydrogen which they associated with the removal of the threefold degeneracy of the lowest rotational state of the *ortho*-molecules. As the *ortho*-molecules fall into their lowest rotational state, the proton-proton interactions are no longer averaged to zero by the rotational motion and hence the effect of these interactions appears in the magnetic resonance signals. Reif and Purcell[5] examined the lower NMR transition more precisely and were able to explain quantitatively the line shape at temperatures below 1.5°K. Tomita[6] has considered the theory of this transition as a cooperative phenomenon. Sugawara *et al.*[7] have measured the temperature of appearance of the side peaks for various *ortho*-concentrations. Their data are in good agreement with the specific heat anomaly data of Hill and Ricketson,[4] and of Hill, Ricketson, and Simon.[8]

Rollin and Watson[9] have studied the upper NMR line-width transition carefully in order to determine activation energies and correlation times for the self-diffusion process which averages out intermolecular interaction and thus narrows the resonance line. Bloom[10] has used the method of spin echo to obtain the activation energy with greater precision. His results agree well with those of Rollin and Watson.

The present work was undertaken to determine the effect of pressure on the nuclear resonance of solid hydrogen from about 1.2°K to the melting point. Since solid hydrogen has a large compressibility,[11] we felt that with modest pressures we might be able to detect changes in line shape which would shed further light on the nature of the "rotation-libration" transition at 1.5°K and on the self-diffusion transition.

EXPERIMENTAL APPARATUS AND METHODS

The spectrometer used was a Pound-Watkins[12] type, manufactured by the Nuclear Magnetics Corporation. In the region of 1.2°K to 4.2°K line widths and shapes were studied in two ways. The absorption signal could be observed visually and photographically on a DuMont 304-A scope equipped with calibration for comparison of areas under absorption signals at various temperatures. In addition a lock-in amplifier allowed us to trace the derivative of the absorption signal on a Varian G-10 recording meter. From 4.2°K to 14°K only the absorption signal was observed.

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* Supported by a grant from the Robert Welch Foundation.

[1] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) **A199**, 222 (1949).

[2] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948) (referred to as BPP).

[3] F. Bloch, Phys. Rev. **70**, 460 (1946).

[4] R. W. Hill and B. W. A. Ricketson, Phil. Mag. **45**, 277 (1954).

[5] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

[6] K. Tomita, Proc. Phys. Soc. (London) **A68**, 214 (1955).

[7] Sugawara, Masuda, Kanda, and Kanda, Sci. Repts. Research Inst. Tôhoku Univ. **7**, 67 (1955).

[8] Hill, Ricketson, and Simon, *Conférence de Physique des Basses Temperatures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), No. 76.

[9] B. V. Rollin and E. Watson, *Conférence de Physique des Basses Temperatures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), No. 63.

[10] M. Bloom, Physica **23**, 767 (1957).

[11] H. Megaw, Phil. Mag. **28**, 129 (1939).

[12] G. D. Watkins, thesis, Harvard University, 1952 (unpublished).

The cryogenic equipment consisted of the usual concentric helium and nitrogen Dewars with tails tapered to fit between the magnet pole faces. A Varian 6-inch electromagnet, powered by a bank of 12-volt batteries, supplied fields of the order of 3000 gauss. An rf frequency of 12.4 Mc was used. The external field could be modulated from 0.1 to 70 gauss at frequencies of 30, 60, or 280 cps.

The sample chamber and pressure system are shown schematically in Fig. 1. Hydrogen was admitted from a cylinder to the sample chamber through a catalytic deoxygenator and a nitrogen trap. The hydrogen was sucked into the sample chamber when liquid helium was admitted to the inner Dewar. Vertical forces were applied by resting weights on a stainless steel rod which pressed on the solid hydrogen. The considerable compressibility of solid hydrogen allows us to regard the specimen as being under an equivalent hydrostatic pressure.[13] A slight overpressure of helium prevented air from being pulled through the gasket system which was lossened to allow the stainless steel rod to move freely.

In order to observe the NMR line between 4.2°K and 1.2°K, a bath of liquid helium around the Pyrex sample tube was used. Reif[14] has indicated that the sample temperature follows changes of bath temperature quite readily in such a situation even though the heat conductivity of glass is comparatively small. Temperatures were determined from the bath pressure and from carbon resistance thermometers calibrated against the bath in the liquid helium region.[15]

The 10°K line-width transition was observed by allowing the system to warm slowly from liquid helium temperatures to about 14°K. By use of helium-saturated activated charcoal[16,17] around the lower assembly, the rate of temperature rise was held to any desired value by pumping the gas off the charcoal. In most of the runs, warmup was completely stopped at various temperatures where line shapes were photographed for different pressures.

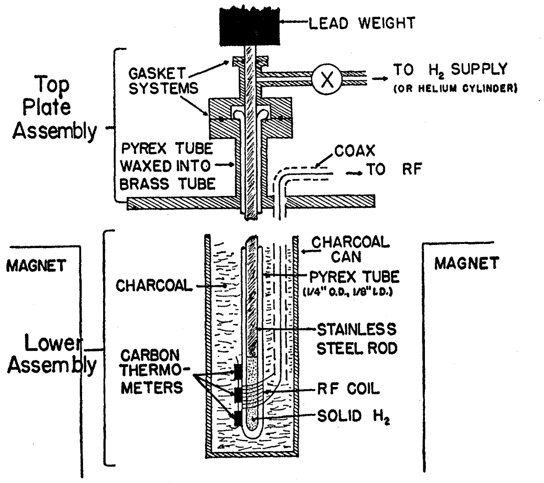

FIG. 1. Schematic diagram of the sample chamber and pressure system. The Pyrex tube extends about 40 inches below the top plate while the charcoal can is 12 inches long.

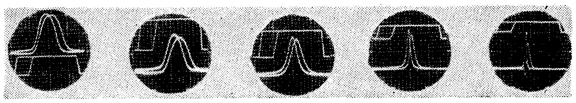

FIG. 2. Change in line shape of the solid hydrogen NMR absorption signal at the self-diffusion transition. The line narrows with increasing temperature. The square wave form is a calibration signal.

The self-diffusion transition was studied from photographs of the solid-hydrogen line at various temperatures between 4.2°K and 14°K. The procedure used was to obtain a constant temperature by regulating the pumping rate on the helium adsorbed by the charcoal and then to photograph the absorption signal on the scope for pressures of 1, 74, 130, and 230 atmospheres. The carbon resistance thermometer readings were made simultaneously. Signal areas were normalized by use of the scope calibrator. The same value of rf field was used for all runs. The magnitude of the modulation field, large enough to display the whole line, was constant throughout each run.

RESULTS

A. Self-Diffusion Transition

Since the absorption signal was observed, the line width determined was that at half-maximum signal strength $(\Delta H)_{\frac{1}{2}}$. By examining the ratio of the line width at half-maximum to the line width between slope maxima $(\Delta H)_{\text{s.m.}}$ as determined crudely for absorption signals at various intervals through the transition, we found that the line shape changes from a roughly Gaussian one to a Lorentzian one as temperature increases through the transition. This shape change can be seen in Fig. 2. The change of shape is in agreement with the theory of Kubo and Tomita.[18] Studies of about 20 derivative curves for $T<4.2$°K agreed with the conclusion that the absorption signal is approximately Gaussian below 8°K.[2]

The method used for presenting the data was to plot $(\Delta H)_{\frac{1}{2}}$ as a function of temperature for $P=1$, 74, 130, and 230 atmospheres. The line widths for all pressures were the same below the transition and are constant from 4.2°K to 8°K. The value of $(\Delta H)_{\text{s.m.}}$ at 4.2°K, as found from the derivatives of the absorption signals, is 5.3 gauss. Our line-width data for all pressures were normalized at 4.2°K to the corresponding value of $(\Delta H)_{\frac{1}{2}}$ for a Gaussian line, 6.25 gauss. The raw

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[13] J. W. Stewart, Phys. Rev. **97**, 578 (1955).

[14] F. Reif, thesis, Harvard University, 1953 (unpublished).

[15] J. Nicol and T. Soller, Bull. Am. Phys. Soc. Ser. II, **2**, 63 (1957).

[16] F. Simon, Physica **4**, 879 (1937).

[17] A. C. Rose-Innes and R. F. Broom, J. Sci. Inst. **33**, 31 (1956).

[18] R. Kubo and K. Tomita, J. Phys. Soc. (Japan) **9**, 888 (1954).

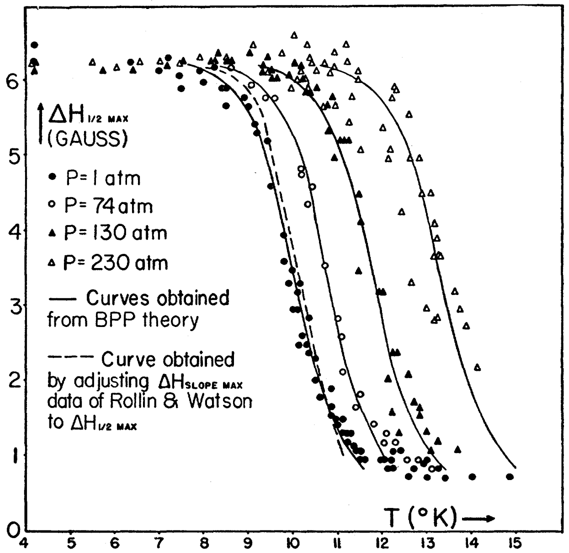

FIG. 3. The line width of solid hydrogen for $P=1$, 74, 130, and 230 atmospheres in the temperature range from 4 to 15°K. $\Delta H_{\frac{1}{2}\,\mathrm{max}}$ is labeled $(\Delta H)_{\frac{1}{2}}$ in the text, and $\Delta H_{\mathrm{slope\,max}}$ is called $(\Delta H)_{\mathrm{s.m.}}$.

line-width data thus normalized are shown in Fig. 3. The heavy lines are theoretical curves explained in a later section. The dashed line for $P=1$ represents the $(\Delta H)_{\mathrm{s.m.}}$ data of Rollin and Watson[9] normalized to our data and adjusted to $(\Delta H)_{\frac{1}{2}}$ in accordance with the line-shape change. It can be seen that our one-atmosphere data agree well with those of Rollin and Watson. In Fig. 4 is plotted the dependence of the shift upon pressure. We arbitrarily chose to plot the temperature at which the width $(\Delta H)_{\frac{1}{2}}=3.54$ gauss. This corresponds to $(\Delta H)_{\frac{1}{2}}/B=\Delta=0.556$ where B is the value of $(\Delta H)_{\frac{1}{2}}$ below the transition. B is thus the rigid lattice line width. For high enough pressures the shift is linearly dependent upon P. It was possible to increase and decrease the line width at will in the region of transition by changing the pressure.

In Fig. 5 are shown the normalized signal areas (A) multiplied by T *versus* temperature. For constant density, Curie's law would require a constant value for (AT). The scatter is quite bad, particularly in the region of the transition for each curve. It can be seen from Fig. 5 for $P=1$ atmosphere that the Curie law is obeyed fairly well from 4°K to 9°K. Thus apparently no changes larger than a few percent occur in the density (and hence in the expansivity).

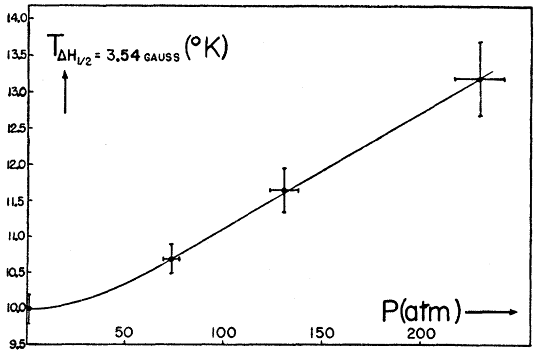

FIG. 4. Effect of pressure on the transition temperature for the self-diffusion transition. Similar curves hold for temperatures corresponding to other values of $(\Delta H)_{\frac{1}{2}}$.

In Fig. 6 data on the temperature dependence of the density of solid and liquid hydrogen are shown. The data of Dewar[19] have been corrected in two ways. Using the values of vapor pressure given by Dewar, the temperatures were adjusted to values more consistent with recent vapor-pressure tables for hydrogen. In addition his data are normalized so that the liquid values agree with those of Onnes[20] and of Scott and Brickwedde.[21] The value of density for the solid at 14°K is obtained from the molar volume calculated by means of the Clapeyron equation as explained by Woolley *et al.*[22] Since our NMR work indicates that the density is constant from 4.2°K to 9°K, we extend the value of Megaw[11] to cover that range. The wide variance of the solid density data indicates the need for accurate

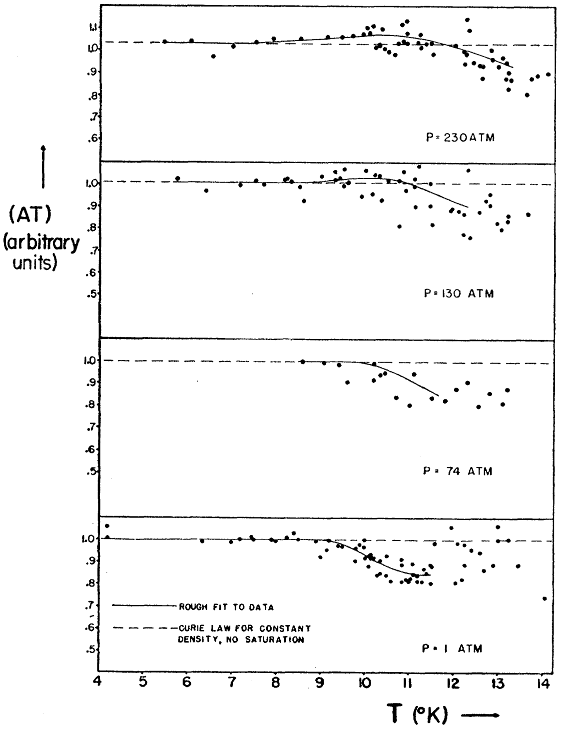

FIG. 5. (AT) *versus* temperature for $P=1$, 74, 130, and 230 atmospheres.

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[19] J. Dewar, Proc. Roy. Soc. (London) **A73**, 251 (1904).

[20] H. K. Onnes, Commun. Phys. Lab. (Leiden) **137a** (1913).

[21] R. B. Scott and F. G. Brickwedde, J. Chem. Phys. **5**, 736 (1937).

[22] Woolley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).

determinations of that quantity over the range of temperatures up to 14°K.

From the change with pressure in the value of the normalized area at a given temperature, we hoped to compute the change in density and hence the compressibility k. Experimental scatter prevented any accurate calculations of the compressibility, although a slight increase of k seemed indicated just below the transition region. Between 6°K and 9°K, using the values of AT for $P=230$ atmospheres and $P=1$ atmosphere, we obtained approximately $k=[1-(AT)_0/(AT)_{230}]/\Delta P=-2\times10^{-4}$ atmos^{-1} at 230 atmospheres. Stewart[13] gives a value of $\sim-3\times10^{-4}$ atmos^{-1} for $P=200$ atmospheres at 4.2°K. We may conclude from our results that k does not change appreciably between 4.2°K and 9°K. In the region of each transition, saturation effects render our results for (AT) invalid as a measure of density. This is discussed in a later section.

B. Results below 4.2°K

Accurate line widths were determined by use of the lock-in amplifier and Varian meter which recorded the derivatives of the absorption curves. Our results on line shape below the 1.5°K transition agree well with those of Reif and Purcell[5] and of Sugawara.[7] Table I summarizes the line-width data for the complex line shape shown in Fig. 7. Also tabulated are line-width results for 73% *ortho* and 50% *ortho* between 1.3°K and 4.2°K.

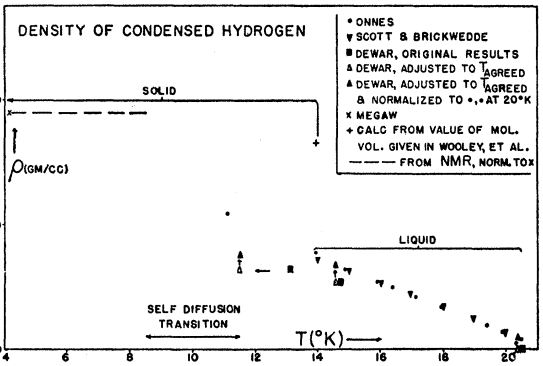


FIG. 6. The density of solid and liquid hydrogen as determined by various workers.

Pressures up to 337 atmospheres had no effect on the line widths or shapes below the transition, and a pressure of 216 atmospheres did not change the temperature of the disappearance of side peaks (1.57°K).

DISCUSSION

The data of Fig. 3 were fitted by means of the BPP formula:

$$\left(\frac{1}{T_2}\right)^2=\left(\frac{1}{T_2^*}\right)^2\frac{2}{\pi}\tan^{-1}\left(\frac{2\pi\alpha\tau_c}{T_2}\right), \tag{1}$$

TABLE I. Nuclear magnetic resonance line-width parameters for solid hydrogen of 73% and 50% *ortho*-concentrations. See Fig. 7.

A. Normal H_2, $T<1.5$°K

Reference	ΔH_c (gauss)	ΔH_s (gauss)	ΔH_h (gauss)
Reif and Purcell	4.6±0.1	40.0±0.1	77.1±0.2
Sugawara *et al.*	4.9	39.5±0.5	75.7±0.9
Present work ($P=0$ to $P=337$ atmos)	5.5±0.7	39.6±0.6	76.1±1

B. Normal H_2, $(\Delta H)_{\mathrm{s.m.}}$, present work, $P=0$ to $P=40$ atmos

T (°K)	4.2	3.15	2.35
$(\Delta H)_{\mathrm{s.m.}}$ (gauss)	5.3±0.4	5.8±0.35	5.9±0.2

C. ~50% *Ortho* H_2, $(\Delta H)_{\mathrm{s.m.}}$ in gauss

Reference	$T=4.2$°K	$T=1.35$°K
Sugawara *et al.*	5.0	5.0
Present work	4.9±0.2	6.5±0.3

where T_2 is the spin-spin relaxation time, roughly inversely proportional to the line width, T_2^* is the value of T_2 for the rigid lattice, α is a constant of the order of 1 and in fact equal to $(8\ln2)^{-1}$ from the theory of Kubo and Tomita,[23] and τ_c is the correlation time—roughly the average time an *ortho*-molecule spends on a lattice site during the self-diffusion process. Ignoring line-shape changes, and letting $1/T_2=\frac{1}{2}\gamma(\Delta H)_{\frac{1}{2}}$ (which is true for a Lorentzian line), we have

$$(\Delta H)_{\frac{1}{2}}^2=B^2(2/\pi)\tan^{-1}[\pi\tau_c\alpha\gamma(\Delta H)_{\frac{1}{2}}], \tag{2}$$

where γ is the gyromagnetic ratio defined by $\omega=\gamma H$ and B is the rigid lattice line width. Using Eq. (2), we evaluated τ_c for $(\Delta H)_{\frac{1}{2}}<B$. τ_c then obeys the relation

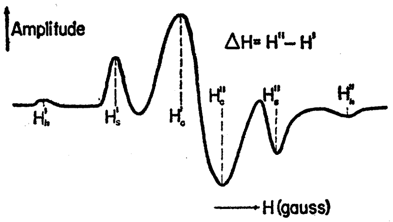
$$\tau_c=\tau_0\exp(E/RT). \tag{3}$$

The line narrows when τ_c is of the order of $(\gamma\Delta H)^{-1}$.

By plotting our experimentally determined values of $\ln\tau_c$ aganist $1/T$, we found values of E, the activation energy for the self-diffusion. The uncertainty involved in these determinations is large [of the order of some 50 cal/mole] because of the small temperature range of the transition and the large experimental scatter. The values found for τ_c are only order-of-magnitude ones because of the approximate nature of Eq. (1) and because we ignore line-shape changes. The results for τ_c and E thus found are given in Table II.

Reversing the above process and evaluating τ_c as a function of T for the best value of E, we found the theoretical curves shown in Fig. 3. The line-width

FIG. 7. The derivative of the solid normal hydrogen nuclear-magnetic-resonance signal at $T=1.2$°K. The sweep was large enough to include only one of the humps.



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[23] G. E. Pake, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 71.

TABLE II. Activation energies and correlation times for self-diffusion in solid hydrogen. The present results are calculated from Eq. (2) using line width at half-maximum.

P (atmos):	1	74	130	230
E (cal/mole) [from $(\Delta H)_{\frac{1}{2}}$]	230	260	295	370
τ_c (sec) at $T=10°\mathrm{K}$ [from $(\Delta H)_{\frac{1}{2}}$]	0.1×10^{-4}	0.2×10^{-4}	0.85×10^{-4}	9.5×10^{-4}
E (Rollin and Watson) [from $(\Delta H)_{\text{s.m.}}$]	350	···	···	···
E (Bloom) spin echo	380 ± 20	···	···	···

transitions can all be well represented as a function of temperature by the same theoretical curve displaced laterally. For this reason the activation energy is linearly dependent upon the transition temperature.

It will be noted that our value of E for $P=1$ atmosphere is considerably below that of Bloom, and of Rollin and Watson. The reason for this is that we measured $(\Delta H)_{\frac{1}{2}}$ rather than $(\Delta H)_{\text{s.m.}}$. Since $(\Delta H)_{\text{s.m.}}$ decreases more rapidly than $(\Delta H)_{\frac{1}{2}}$ during the line-width transition, values of E found from the former are higher than those found from the latter. The activation energies derived using $(\Delta H)_{\text{s.m.}}$ in Eq. (2) give results in better agreement with those of Bloom than those from $(\Delta H)_{\frac{1}{2}}$. Because our line-width data for $P=1$ atmos agree with those of Rollin and Watson[9] when adjusted for shape changes, we derived, for the $P=74$-, 130-, and 230-atmosphere transitions, values of E appropriate to $(\Delta H)_{\text{s.m.}}$ by adjusting our line-width data to $(\Delta H)_{\text{s.m.}}$. The corrected values of E are given in Table III.

ERRORS

Several sources of heating contribute to any errors in temperature determination. Ortho-para conversion produces heating, and heat is conducted down the pressure rod. The poor thermal conductivity of glass contributed to the isolation of the sample from the bath so that the temperature of the hydrogen may have been some 0.2°K higher than that of the carbon thermometer at low pressures. Because of the good reproducibility of the 1-atmosphere and the 74-atmosphere data, we feel that the error is no larger for these pressures. In particular the 1-atmosphere data agrees with that of Rollin and Watson to within 0.1°K. The highest temperature (as determined by the carbon thermometer) at which the hydrogen would support a pressure of 230 atmospheres was 14.5°K. This temperature is 5.5°K below the known melting temperature of solid hydrogen for that pressure.[20] Temperature data from the carbon thermometers indicated that a thermal gradient of the order of a degree existed between the lower end of the pressure rod and the center of the rf coil (a distance of about one inch). At temperatures of the order 14°K, it was no longer possible to maintain a constant temperature by pumping on the charcoal since the helium gas had become almost entirely depleted. As a result the sample warmed up very rapidly. The temperature gradient between the rod end and sample center, together with the poor thermal conductivity of the glass, combined to cause the carbon thermometer to lag the temperature at the end of the pressure rod by several degrees, when the nonequilibrium conditions of very rapid warmup existed. Since all of our line-width data were taken under fairly good equilibrium conditions, the temperature error should be no larger than the experimental scatter or about ±0.3°K for $P=130$ atmos and ±0.5°K for $P=230$ atmos. The increased scatter for the higher pressures is due to the poorer equilibrium conditions.

The decrease in AT at each transition, as seen in Fig. 5, can be ascribed to saturation as T_2 increases during line narrowing. T_1 remains practically constant.[10] A crude calculation indicated that H_1 should be of the order of 10^{-2} gauss to produce the amount of saturation observed. A rough measurement gave $H_1\approx3-6\times10^{-2}$ gauss. Because of this saturation, the compressibility results as calculated in our preliminary report[24] are incorrect.

Errors in the line width above 4.2°K depend upon several factors. The correctness of the absolute magnitude of $(\Delta H)_{\frac{1}{2}}$ is determined by the validity of the assumption of a Gaussian line at 4.2°K. Another possible source of error is the fact that one signal on the scope was always somewhat wider than the other (see Fig. 2) and that $(\Delta H)_{\frac{1}{2}}/B$ was found from the average of the two. We have been unable to determine the cause of the difference in width of the two traces. The saturation at each transition may have produced a less rapid narrowing of the line by increasing $(\Delta H)_{\frac{1}{2}}$ for extremely narrow lines by about 15% over the unsaturated values. This increase is considerably less for the broader lines and the net effect on the transition is negligible compared with the scatter. The error in determining $(\Delta H)_{\frac{1}{2}}/B$ should be no more than 5%, while the error in the absolute magnitude of $(\Delta H)_{\frac{1}{2}}$ could be as large as 15%.

Scatter in signal area (Fig. 5) below each transition is due to the fact that a broad line requires a large gain to give adequate signal height on the scope and as a result pickup from the sweep field is magnified, making it difficult to find the base line on the scope trace. The error here is estimated at 5%. In the region of line narrowing and of increased temperature, the area

TABLE III. Activation energies and correlation times from line width at maximum slope of the absorption signal used in Eq. (2) of the text.

P (atmos):	1	74	130	230
E (cal/mole) ±50 cal/mole	350	400	450	560
τ_c (sec) at $T=10°\mathrm{K}$	0.02×10^{-4}	0.1×10^{-4}	0.7×10^{-4}	23×10^{-4}

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[24] G. W. Smith and C. F. Squire, *Reports of Fifth Internation Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957* (to be published).

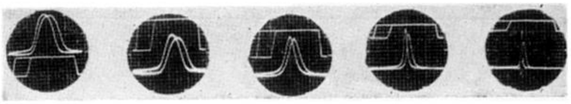
becomes smaller and more difficult to determine accurately.

Error in the value of the pressure was introduced by the fact that hydrogen tended to collect along the Pyrex tube walls after several runs. This produced a binding effect on the pressure rod so that the amount of pressure transmitted to the solid may have fluctuated from one pressure application to another. It was found necessary to free the pressure rod when reducing the pressure from 230 atmospheres to 1 atmosphere, since the binding effect "locked-in" a pressure of the order of 25–50 atmospheres upon removal of the weights. We were careful to remove this locked-in pressure for the 1-atmosphere results, but the effect may have tended to decrease the pressure for higher pressures. We estimate any errors in pressure to be about ±5%.

CONCLUSIONS

From our work on solid hydrogen we may conclude that pressures up to several hundred atmospheres do not affect the rotation-libration transition at 1.5°K, but modest pressures produce sizable shifts of the self-diffusion transition at 10°K. This latter result for increasing pressure is not surprising, for one would expect increased interactions between the molecules to necessitate larger thermal energy of the hydrogen molecules in order to overcome the barrier to self-diffusion. One would also expect the decreased separation of the hydrogen molecules to be reflected by an increase of the rigid lattice line width. Although such an increase just below the transition for $P=230$ atmospheres is possible (see Fig. 3), experimental scatter prevents any definite conclusion from being reached.

Further studies on the *ortho*-concentration dependence and the pressure dependence of the self-diffusion transition, coupled with accurate data on the compressibility and density of solid hydrogen, could yield valuable information on the nature of the intermolecular potential and greater understanding of the relation of the self-diffusion transition to the melting phenomenon. Measurements of the pressure and concentration dependence of the spin-lattice relaxation time T_1 in the region of self-diffusion would also be valuable.



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