DENSITY CHANGES IN SOLID H_2

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The relative difference in molar volume between solid ortho- and para-H_2 is found to by $(V_p - V_o)/\bar{V} = (1.3 \pm 0.2)\,\%$ at 4.2°K. We also report the change in molar volume for a given ortho concentration as a function of temperature, in particular, upon the transition from hcp to fcc.

Mills and Schuch[1] recently reported the observation of a phase change from hcp to the fcc structure in solid H_2 at about 1.3°K for ~75% ortho concentration. This transition is accompanied by a quenching of the rotational motion[2] of the ortho molecules in the lattice of the fcc phase. We wish to report observation of the change of molar volume at this transition, too small to be measured by x-ray diffraction.[1] Furthermore, we report the change in molar volume when ortho-H_2 is converted into para-H_2.

The method uses a capacity strain gage to measure the pressure of a small quantity of solid H_2 confined in a tubular space (0.5 cm^3). The solid can expand by moving a thin 0.05-cm stainless-steel wall, one of the capacitor plates. This apparatus was previously used to measure[3] the thermal expansion of solid He^4. Extensive checks showed no hysteresis in the stainless-steel membrane.

The experiment consists in measuring the pressure in the cell as a function of temperature. Taking into account a small correction of the change in volume due to the displacement of the membrane, one obtains the pressure $P(T)$ at constant volume.

Solid H_2 with a nonzero ortho concentration converts slowly into para-H_2, and the pressure in the cell at a given temperature rises as a function of time t. This rise permits the determination of the relative difference in molar volume upon conversion. For this we assume (1) that the molar volume $V(x)$ of the sample is given by

$$V(x) = xV_o + (1-x)V_p, \tag{1}$$

where x is the ortho concentration, and V_o and V_p are, respectively, the molar volume of the ortho- and para-H_2; (2) that the isothermal compressibility k_T for ortho- and parahydrogen is the same and independent of pressure over a 20-bar range. We further use the familiar ortho-para conversion[4] rate $dx/dt = -Kx^2$. Then the pressure $P(t)$ in the cell as a function of time t is given by the relation

$$[P(t)-P(t=\infty)]^{-1} = [P(t=0)-P(t=\infty)]^{-1} + \frac{tK\bar{V}k_T}{(V_o - V_p)} \cdots, \tag{2}$$

where V, the average molar volume, is 22.3 cm^3/mole at these low pressures. In Fig. 1,

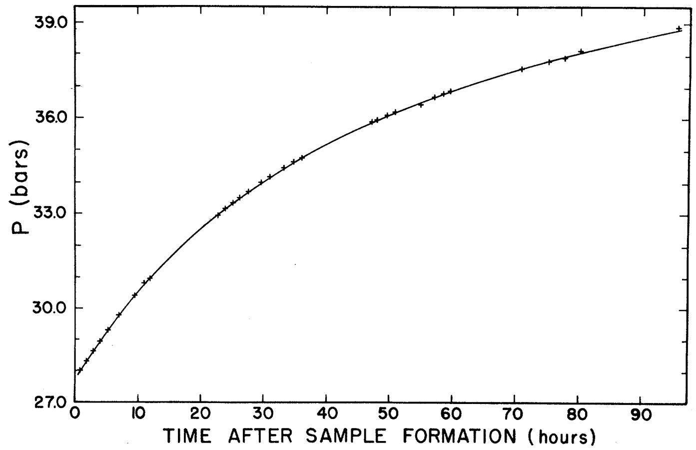

FIG. 1. The pressure in solid H_2 as a function of time at 4.27°K. Crosses, experimental points; solid line, fit using Eq. (2).

the measured time dependence $P(t)$ at 4.2°K is shown, as well as the fit to Eq. (3). We find $(V_p - V_o)/\bar{V} = (1.3 \pm 0.2)\%$ at this temperature, taking[5] $k_T = 0.50 \times 10^{-3}$ bar^{-1} and $K = 0.018$ h^{-1} from an analysis of the ortho concentration of the sample before and after the experiment. The uncertainty of the result is partly due to the inaccuracy in our knowledge of k_T at small pressures.

In the hcp phase, detailed measurements were made of the pressure in the cell for a given concentration as a function of temperature. The sample was cycled several times over the temperature range between 0.5 and 14°K, and it was possible by extrapolation and interpolation to select points at constant ortho concentration. The coefficient of thermal expansion α_p was then obtained from the P-T curve using the relation $(\partial P/\partial T)_V = \alpha_p/k_T$ and was found to increase sharply with ortho concentration at a given temperature. From the values of α_p it was then possible to estimate $(V_p - V_o)/\bar{V}$ in the hcp phase as a function of temperature. Extrapolation to 0°K (where this phase is not expected to be stable for ortho-H_2) is somewhat uncertain and should be of the order of $(V_p - V_o)/\bar{V} \approx 1.7\%$. Theoretical calculations of this volume change, based on the electric quadrupole interaction between ortho molecules,[6] are presently being carried out by Harris.

The phase transition hcp → fcc in solid H_2 has associated with it a sharp drop in pressure as the temperature is decreased. Representative transitions are shown in Fig. 2. The data presented here have already been corrected for the steady increase in pressure with time due to ortho-para conversion and represent the behavior at a given concentration. The pressure change on warming shows a hysteresis. The transition upwards is less sharp and occurs at higher temperature. If the sample is quickly recycled through the transition several times, the pressure change ceases to occur and the transition apparently disappears, as was observed by Ahlers and Orttung[7] from calorimetric measurements. Accordingly, in the process of taking data on one sample, the H_2 was annealed at the melting curve before every cooling through the transition. From the dependence of the transition temperature on pressure,[7,8] one obtains for 75% ortho at these low pressures $(dP/dT)_{\text{trans}} \approx 7\text{-}8 \times 10^2$ bar/deg. Hence for an observed pressure drop of 3 bar, the temperature interval should be approximately 4 mdeg, which is smaller than the measured width. The broadening could be due to inhomogeneities in the sample during the pressure drop.

The change in molar volume on transition can be calculated from the relation

$$\frac{V_{\text{hcp}} - V_{\text{fcc}}}{\bar{V}} = \frac{\Delta V}{\bar{V}} = -k_T \Delta P - \alpha_p \Delta T, \qquad (3)$$

where ΔP and ΔT are the pressure and temperature drop at constant volume at the transition. The second term in Eq. (3) is found to be much smaller than the first one and is neglected. For an ortho concentration of 73%, $\Delta V/\bar{V}$ up-

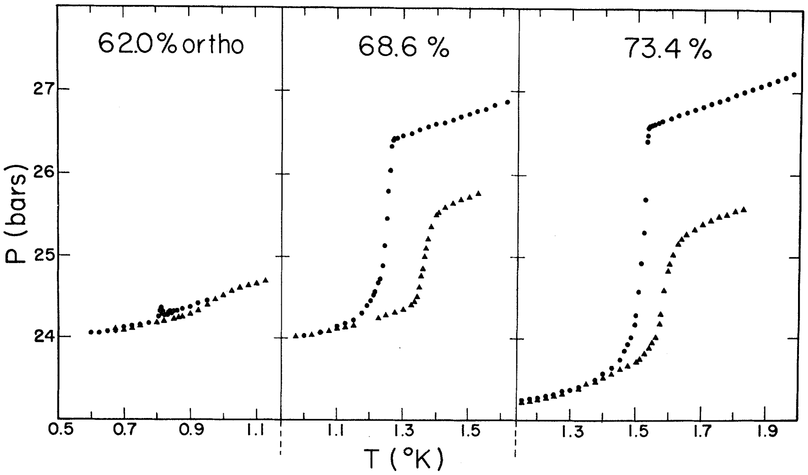

FIG. 2. Representative transitions hcp ⇄ fcc at three ortho concentrations in solid H_2. Circles, cooling; triangles, warming.

on cooling[9] is 0.15%. For the warming curve at this concentration, the relative volume change is only 0.08%. Ahlers and Orttung,[7] who measured the specific heat at zero pressure, found the entropy change for their first warming to be 1.65 J/mole deg. Taking this to be the entropy change for a smeared-out first-order transition with $(dP/dT)_{\mathrm{trans}} = 8 \times 10^2$ bar/deg, one finds from the Clapeyron equation $\Delta V/\bar{V} \approx 0.09\%$. The agreement with the present experimental value is satisfactory considering the appreciable uncertainties in $(dP/dT)_{\mathrm{trans}}$ and k_T. Figure 2 also shows the pressure drop upon cooling as a function of ortho concentration. In the region above 63%, $\Delta P/\Delta T$ is positive. In the region between 60 and 63%, there is some irregular behavior near 0.8°K, and some structure with maxima and minima appears in the curve of P vs T. Extrapolating the results up to 100% is uncertain, but we expect $\Delta V/\bar{V}$ to be not greater than 0.5% upon cooling.

In summary we feel that the direct measurement of $V_p - V_o$, too small to be detected by other techniques, permits study of a rather interesting type of interaction between molecules in a simple solid. The change in molar volume for a given ortho concentration makes it possible to study the gradual evolution of the phase transition with ortho concentration, to be reported in detail in the near future. Measurement of enriched ortho-H_2 and of D_2 samples are planned.

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[9] In the second half of Ref. 3, the change $\Delta V/\bar{V}$ was reported to be "about 0.3%." As this was only a very preliminary communication, no specific distinction was made between warming and cooling. Also a too large value of k_T was used to calculate ΔV.