Orientational Ordering in Solid Hydrogen: Dependence of Critical Temperature and Concentration on Density

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The orientational ordering phase transition in solid hydrogen has been studied as a function of para concentration and pressure up to 6 kbar. Measurements are consistent with the *Pa*3 structure for all densities and high ortho concentration. The density dependence of the critical temperature is consistent with that for the electric quadrupole-quadrupole interaction. When doped with p-H_2, with increasing density the critical concentration decreases anomalously below the zero-pressure value of 0.56.

Solid orthohydrogen (molecules in the $J=1$ rotational state) has an orientational disorder-order transition at $T_{do} \simeq 3$ K and pressure $P=0$. The transition is driven by the electric quadrupole-quadrupole (EQQ) interaction, V_{EQQ}. In the ordered state the symmetry axes of the EQ bearing $J=1$ molecules align along the body diagonals of an fcc lattice to give the *Pa*3 structure.[1] Doping the solid with spherical p-H_2 ($J=0$ state) dilutes the interaction and at a critical concentration of $J=1$ molecules of $x_{1c}=0.56$,[2] ordering in the *Pa*3 structure is no longer observed for $T\to 0$. We have studied the critical line as a function of density of the solid and ortho concentration. We find that the critical concentration x_{1c} unexpectedly shifts to a lower value of x_1. If the interaction is still dominated by V_{EQQ} at higher densities, then x_{1c} is expected to remain unchanged. A careful study of T_{do} for $x_1 \to 1$ and $\rho/\rho_0 > 1$ shows that V_{EQQ} remains dominant leaving this new result unexplained.

In this Letter we report on far-infrared spectroscopic studies of the ordered phase in hydrogen for ortho concentrations $0.40 < x_1 < 0.98$, temperatures $T \geq 1$ K and pressures up to 6 kbar, corresponding to a relative increase in zero-pressure density ρ_0 of $\rho/\rho_0 = 1.7$. Additional results are summarized as follows: (1) The spectra are consistent with ordering in the *Pa*3 structure for all densities; (2) the temperature dependence of the order parameter, $\sigma = [(4\pi/5)^{1/2}/N x_1] \sum_i \langle Y_{20}(\omega_i)\rangle$, is much more gradual at low x_1 than at high x_1 (here, N is the number of molecules and Y_{20} a spherical harmonic with argument ω_i representing the deviation of the molecular axis from the direction of quantization); (3) hysteresis in the transition which exists at $P=0$ is present for all x_1 and ρ studied,[3] i.e., $T_{od} - T_{do} \neq 0$ (T_{od} is associated with the orientational order-disorder transition); the hysteresis decreases with thermal cycling. For $P=0$, $x < x_{1c}$ and $T \lesssim 0.3$ K another phase occurs which has been speculated to be a quadrupolar glass.[4] However, all of our measurements were carried out at higher temperatures where this phase is not expected to occur.

Critical phenomena are governed by the properties of the partition function $Z = \mathrm{Tr}\exp(-H/kT)$. Orientational ordering is driven by the anisotropic interactions between molecules. We can restrict our attention to $H = H_{anis} + H_{rot}$ where H_{anis} is well approximated by a sum over pair interactions strongly dominated by V_{EQQ} at low densities, although there are much smaller terms.[5] $H_{rot} = B\vec{J}^2$ ($B = 39.339$ cm^{-1}) can usually be ignored as rotational states other than $J=0$ or 1 are not thermally populated. The effective (phonon-renormalized) EQQ interaction in the solid is

$$V_{eff} = (20\pi/18)(70\pi)^{1/2}\Gamma_{eff} \sum_{\substack{i,j\\M,N}} C(224;MN)Y_{2M}(\Omega_i)Y_{2N}(\Omega_j)[Y_{4,M+N}^*(\Omega_{ij})\Gamma_{ij}/\Gamma_0], \qquad (1)$$

where $\Omega_i \equiv (\theta_i,\varphi_i)$ specifies the orientation of a molecule with respect to the crystal axes, $C(224,MN)$ is a Clebsch-Gordan coefficient and $\Gamma_{ij} = 6e^2Q^2/25R_{ij}^5$ is the EQQ coupling parameter. Here Q is the EQ moment and $\vec{R}_{ij}$ is the vector separating molecules i and j; the orientation of this vector is specified by Ω_{ij}. The factor $\Gamma_{eff} = \xi_{54}(R)\Gamma$ accounts for the renormalization of the nearest-neighbor interactions due to the large zero-point motion as discussed by Harris[6]; Γ is the value of Γ_{ij} evaluated at the nearest-neighbor distance R. The reduction factor ξ_{54} is weakly density dependent having a value of 0.91 at the zero-pressure volume of 22.68 cm^3/mole and approaching 1 with increasing density ($\xi_{54} \simeq 0.96$

at 10 cm^3/mole).[7] Equation (1) is strictly correct for nearest-neighbor interactions only, as $\xi_{54} \simeq 1$ for further neighbors.

With these restrictions we can define a scaled temperature $T^* = kT/\Gamma_{\mathrm{eff}}$ and the critical temperature scales as Γ_{eff}. Thus for $H_{\mathrm{anis}} = V_{\mathrm{EQQ}}$ with J as a good quantum number, we have

$$T_{od} = \xi_{54}(\rho)/\xi_{54}(\rho_0)(\rho/\rho_0)^{5/3} T_{od}(\rho_0). \qquad (2)$$

However, the anisotropic interactions will increasingly mix higher rotational states into the $J=1$ state as density is increased.[8,9] This leads to the result that diagonal energy levels (in Z) no longer scale as Γ_{eff}. In a rough approximation (for $x_1 = 1$) we can assume that T_{od} scales as the mean libron (gap) energy per molecule, E_g. Harris, Berlinsky, and Meyer[10] have shown that mixing of the $J=3$ state reduces E_g, so that

$$E_g = 21.2\Gamma + 45.21\Gamma^2/B. \qquad (3)$$

By taking this into account and renormalizing only the first term in Eq. (4), the $(\rho/\rho_0)^{5/3}$ term in Eq. (2) becomes

$$[(\rho/\rho_0)^{5/3} + 0.024(\rho/\rho_0)^{10/3}]/1.024. \qquad (4)$$

If the interaction remains EQQ at high pressure, we expect the critical concentration to be a geometric factor and remain constant with density,[11] i.e., $x_{1c}(\rho) = x_{1c}(\rho_0)$. We mention here that the critical concentration $x_{1c} = 0.56$ in H_2 is very high and unexplained. The percolation limit for the site-diluted fcc lattice is 0.195 for nearest-neighbor interactions; further-neighbor interactions only reduce this value. The high value of x_{1c} may be a result of the fact that in the $Pa3$ structure the bond energy does not minimize the pair energy which can be reduced by about a factor of 4 if the molecules are oriented orthogonal to each other as in the letter T. An ordering where all molecules are in mutual T configurations will not fit on an fcc lattice. As the lattice is diluted with spherical molecules, fluctuations which favor the T configuration could be responsible for the early loss of long-range order.

We have studied the phase diagram by means of far-infrared spectroscopy using a computer controlled Michelson interferometer. The sharp transverse phonon, T_u^t, of the $Pa3$ structure is infrared active and the integrated absorption coefficient is proportional to the square of the order parameter.[12] The disordered phase, which can be either hcp or fcc or a mixture, has no first-order ir phonon absorption. A high-pressure cell made of Berrylco-25 with a vertical sample length of 80 mm was used. Enriched o-H_2 was condensed in the cell to form zero-pressure samples of length 5–10 mm at 4.2 K. Pressure was applied by filling the remaining sample path with liquid helium which performed as a liquid piston. To reach higher pressures with liquid helium, the cell was warmed above the helium melting temperature. Since the H_2 melt line is always much lower than that of helium, the H_2 remained solid. Care was taken to keep the temperature as low as possible to inhibit He diffusion into the sample; however, the density dependence of the diffusion temperature is not well known. We saw no identifiable signs of He impurity effects in our spectra. After pressurizing, the cell was cooled which resulted in a solid He-H_2 cylinder of rather hydrostatic pressure. The pressure on the sample was determined from the helium isochores of Spain and Segall[13] and the H_2 density from the tables of Driessen, de Wall, and Silvera.[14] Different concentrations, x_1, were obtained by allowing the sample to convert towards equilibrium (p-H_2) which takes place at a few percent per hour.[15] The concentration of the samples was determined from knowledge of the conversion rate at a given density and by Raman-scattering analyses before and after a run. Temperature was measured with a calibrated germanium thermometer. We always measured the phase line in warming the sample, thus T_{od}. This was generally determined by heating to a temperature just below T_{od}, holding the temperature constant and then allowing the sample to convert (aging) until the phonon intensity disappeared, providing a measure of T_{od} vs x_1. The accuracy in these determinations was about 0.01 K.

Selected results of T_{o} vs x_1 are shown in Fig. 1 for several densities. The values at $\rho = \rho_0$ are in good agreement with independent measurements. The dotted line shows the lower-temperature behavior which was outside of our range. The dashed lines are simply extensions of the linear behavior in the high-x_1 region. The most striking result is that as ρ increases, the critical concentration evidently decreases. For $\rho/\rho_0 = 1.69$ the sample remained in the ordered state for $x_1 = 0.45$ and $T = 1.01$ K. The interaction is expected to remain EQQ dominated at these densities. To check this we can extrapolate the data to $x_1 = 1$ to determine $T_{od}(x_1 = 1)$ vs ρ. These results are shown in Fig. 2 and compared to the rigid-lattice scaling ($\xi_{54} = 1$) as well as for the theoretical renormalized value for Eq. (2). The slight disagreement with experiment is improved by expression (4)

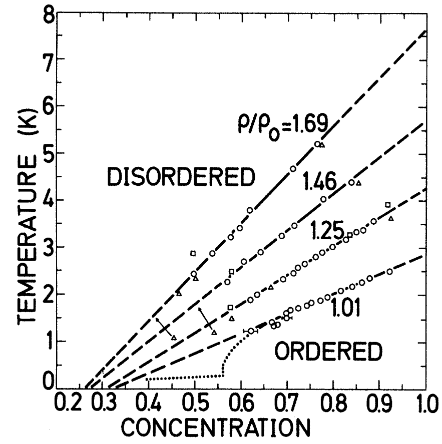

FIG. 1. Phase diagram of solid H_2. The symbols are as follows: circle, phase line; triangle, order state; square, disordered state. The dotted line for $\rho/\rho_0=1.01$ indicates the known behavior; the dashed lines are linear extrapolations, ρ_0 is the density of p-H_2 at $P=0$.

which increases $T_{od}(\rho)/T_{od}(\rho_0)$ by 3% at $\rho/\rho_0=1.7$. These results imply that the interaction is strongly dominated by V_{EQQ}, which has been accurately confirmed by Raman scattering in D_2.[16] Earlier results by Dickson and Meyer[17] of T_{od} vs ρ were of insufficient accuracy and too low of concentration x_1 to be useful here in an extrapolation to $x_1=1$.

In Fig. 3 we show the behavior of the order parameter as a function of temperature. At high concentrations, it changes sharply at T_{od}; for lower x_1, the temperature dependence is weaker.

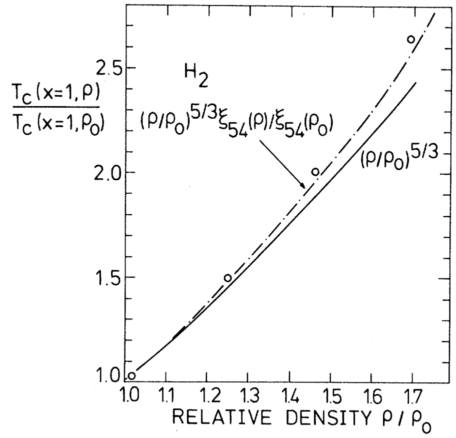

FIG. 2. Normalized transition temperature in solid H_2: circles, experimental results; solid line, $(\rho/\rho_0)^{5/3}$ behavior; dashed line, theoretical renormalized EQQ behavior for J a good quantum number using results of Goldman (Ref. 7); dash-dot line, correction from Eq. (5). Here, $T_c \equiv T_{od}$.

Finally, we mention that throughout the density regime of study, $T_{od}-T_{do} \lesssim 0.3$ K.

Measurements have also been carried out on D_2. In this case for technical reasons concerning the slow conversion rate and hysteresis it is more difficult to study the low-concentration region. For D_2, we did not observe any samples in the ordered state with $x_1(\rho) < x_{1c}(\rho_0)$.

These observations refocus attention on a longstanding theoretical problem, the high value of x_{1c}, and present a new aspect: its unexpected density dependence. Sullivan[18] has developed a theory for T_{od} vs x_1 which predicts the linear dependence of T_{od} on x_1 for large x_1. The theory remains valid for $P \neq 0$. He also predicts a high value of x_{1c} at $P=0$ comparable to the experimental value, but evidently the validity of the theory which he used breaks down at just these concentrations and does not seem useful for explaining the low-x_1 density dependence. We hope that further theoretical work will be stimulated by these experiments. We plan to extend the present observations with lower-temperature refrigeration.

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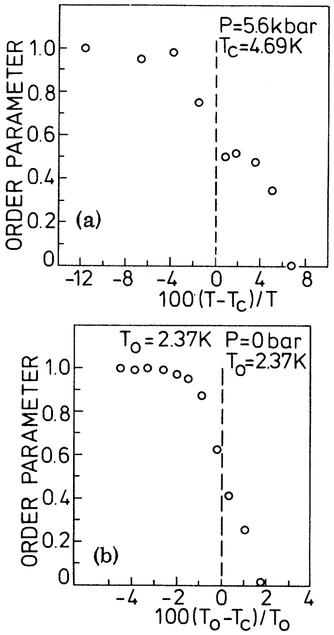

FIG. 3. Order parameter in H_2 for two pressures and (a) $x_1 \simeq 0.731$, $\rho=1.69\rho_0$; (b) $x_1=0.885$, $\rho=\rho_0$. For lower x_1, the transition is much broader in temperature. (a) is measured by temperature variation with $x_1 \simeq$ const. (b) is measured by aging at constant temperature T_0. In both (a) and (b), $T_c \equiv T_{od}$.

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Nuclear Magnetic Ordering in $PrCu_6$

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We have observed in $PrCu_6$ a sharp peak in the heat capacity and rapid change in the magnetization at 2.5 mK consistent with the occurrence of nuclear magnetic ordering below that temperature. Applying magnetic fields greater than 100 G rounds the transition. The behavior observed is similar to ferromagnetism in electronic systems, but other structures showing weak "ferromagnetism" are not ruled out.

We have observed the transition from the paramagnetic to a nuclear ordered state in $PrCu_6$ at 2.45 ± 0.05 mK. We believe this to be the first observation of this ordered state in a metal in which the complete system (magnetic moments, conduction electrons, and lattice) is in thermal equilibrium. The heat capacity and magnetization and their dependence on temperature and applied magnetic field unambiguously display the characteristics of such a transition. Precursors to such ordering have previously been observed, but the transition itself had not been traversed.[1]

The praseodymium in $PrCu_6$ and many other compounds has a singlet electronic ground state, the other eight states in the $^3H_4$ manifold usually being raised above 10 K in energy by the crystalline field. Thus, at low temperatures the Pr ions exhibits temperature-independent Van Vleck paramagnetism. The exchange is apparently too small to induce moments and magnetic ordering in the electronic system, as shown possible by Trammell[2] and Bleaney.[3] Such a state was first observed in fcc Pr metal by Bucher and co-workers[4,5] with a Curie temperature of approximately 20 K. In the absence of nuclear moments hyperfine coupled to induced electronic moments, singlet ground-state systems do not order at any temperature if the ratio $2\mathcal{J}z/\Delta$ of exchange to crystal-field splitting (z being the number of nearest magnetic neighbors) is less than a critical value of order unity.

With a hyperfine coupling $A\vec{I}\cdot\vec{J}$ of the nuclear moments to the $4f$ electrons, two important effects occur. First, the ordering behavior is modified.[6] If $2\mathcal{J}z/\Delta$ is less than, but close to, the critical value, then the presence of a large hyperfine interaction may be enough to induce an ordered state at a temperature lower than would be observed for electronic ordering alone. The transition to such an intermediate or mixed electronic-nuclear state has been observed in $PrCu_2$ at 54 mK[7] and in $PrCu_5$ at 24 mK.[8-10] A broad (Schottky-like) heat-capacity peak with a maximum below the magnetic ordering temperature