The importance of nuclear spin in the order-disorder phase transitions of solid hydrogen

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Introduction

- Phase diagram of hydrogen
  - Pressure
  - Temperature
  - Ortho-para ratio
- Review articles:
  - I. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).
  - H.-K. Mao and R. J. Hemley, *Rev. Mod. Phys.* **66**, 671 (1994).
  - A. Brooks Harris and H. Meyer, *Can. J. Phys.* **63**, 3 (1985).

Phase diagram

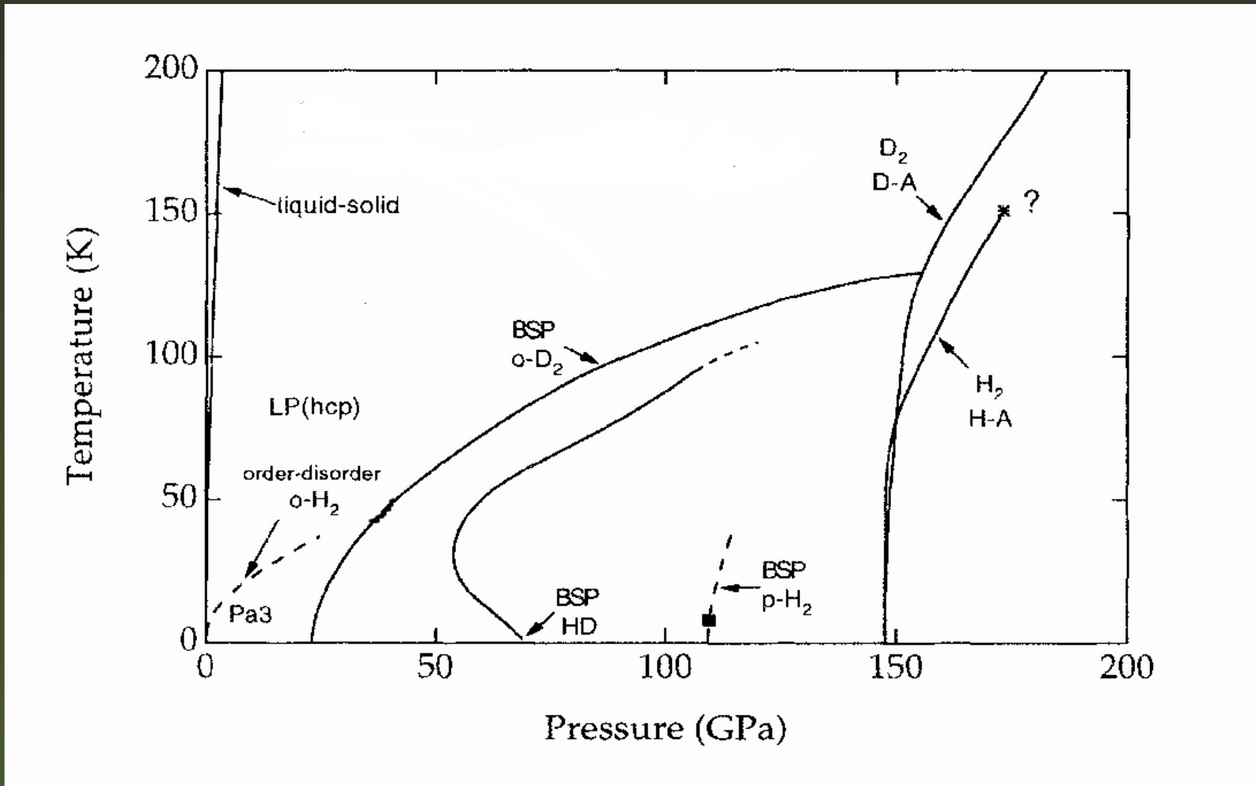


Figure 1: Phase diagram of solid hydrogens at high pressure (Cui *et al.*, 1995)

Hydrogen molecules

- H_2 molecule
  - Each nucleus consists of one proton
  - Total nuclear spin: I = 1 {I_z=-1,0,1} ; I=0 {I_z = 0}
  - Rotational consant $B = 85.5K$
- D_2 molecule
  - Each nucleus consists of one proton and one neutron:
  - Total nuclear spin: I = 2 {I_z = -2,-1,-1,0,1,2} ; I = 1 {I_z=-1,0,1} ; I=0 {I_z = 0}
  - Rotational consant $B = 42.8K$

The H_2 molecule

- H_2 molecule
  - Ortho-para distinction results from the requirement that the total wavefunction

$$\Psi = \Psi_{spin}\Psi_{spatial},$$

    must be **anti-symmetric** with respect to exchange.
  - The spin states (I = 1 {I_z=-1,0,1} ; I=0 {I_z = 0}) can be combined to give **three symmetric states** and **one anti-symmetric states**.
  - As exchange corresponds to a rotation by π, **anti-symmetric(symmetric) spatial functions** correspond to **odd-J(even-J) states**.

The D_2 molecule

- D_2 molecule
  - Ortho-para distinction results from the requirement that the total wavefunction

$$\Psi = \Psi_{spin}\Psi_{spatial},$$

    must be **symmetric** with respect to exchange.
  - The spin states (I = 2 {I_z=-2,-1,0,1,2} ;I = 1 {I_z=-1,0,1} ; I=0 {I_z = 0}) can be combined to give **six symmetric states** and **three anti-symmetric states**.
  - As exchange corresponds to a rotation by π, **anti-symmetric(symmetric) spatial functions** correspond to **odd-J(even-J) states**.

Orientational glass

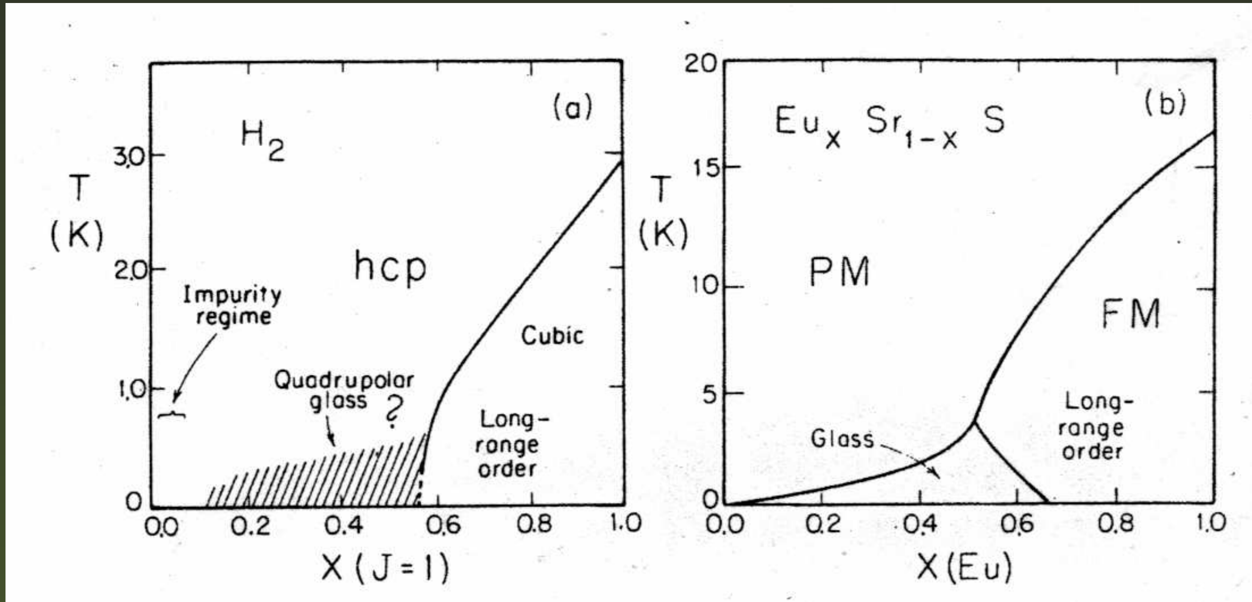


FIG. 1. (*a*) The phase diagram for solid $(ortho\text{-}H_2)_X(para\text{-}H_2)_{1-X}$ mixtures showing the transition lines from the cubic-to-hcp, $T_{ch}(X)$. (*b*) The phase diagram for $Eu_X Sr_{1-X} S$ mixtures (from Maletta, ref. 6).

Figure 2: Phase diagram of solid hydrogens as a function of temperature and ortho fraction (Brooks Harris and Meyer, 1985)

Intermolecular interaction

- Angular part: electrostatic quadrupole-quadrupole interaction:

$$V(\Omega_1, \Omega_2) = \frac{K}{2}\left(\frac{R_0}{R_{ij}}\right)^5 \sum_{m,n} C(224; mn)$$

$$\times Y_{2m}(\Omega_i) Y_{2n}(\Omega_j) Y^*_{4m+n}(\Omega_{ij})$$

- Two-dimensional model (anisotropic term only):

$$H = K \sum_{\langle i,j \rangle} \cos(2\phi_i + 2\phi_j - 4\phi_{ij})$$

Model Hamiltonians

- Two-dimensional model (QAPR):

$$H = -B \sum_i \frac{\partial^2}{\partial \phi_i^2} + K \sum_{\langle i,j \rangle} \cos(2\phi_i + 2\phi_j - 4\phi_{ij})$$

- Three-dimensional model:

$$H = B \sum_i L_i^2 + \sum_{i<j} V(\Omega_i, \Omega_j)$$

- Mean-field solutions:
  - QAPR, Martonak *et al.*: predicts reentrance for "HD" system
  - 3D rotors, Freiman *et al.*: predicts qualitative features of the experimental phase diagram

Reentrance in QAPR

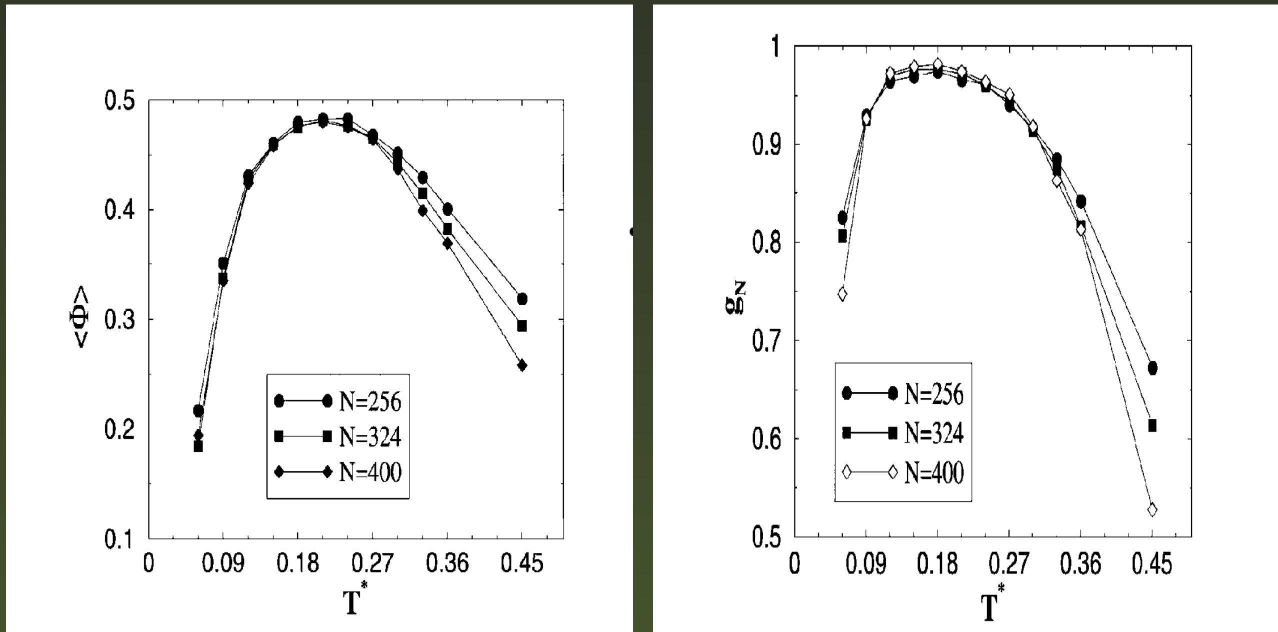


Figure 3: Quantum Monte Carlo simulation of the QAPR model at K = 1.571 (BH, M.H. Müser, and B.J. Berne, 1999).

Mean-Field solution for hydrogen

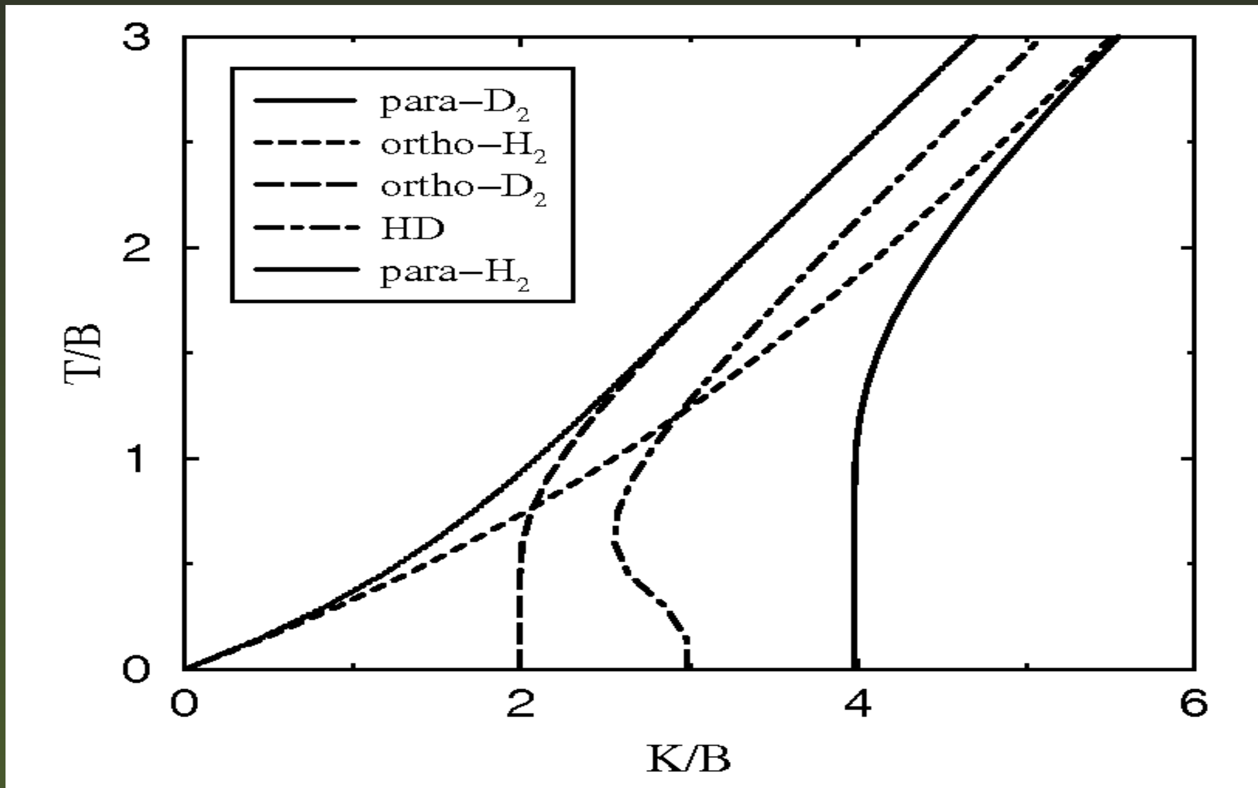


Figure 4: Mean-field solution for various hydrogen isotopes.

Mean-Field solution for hydrogen

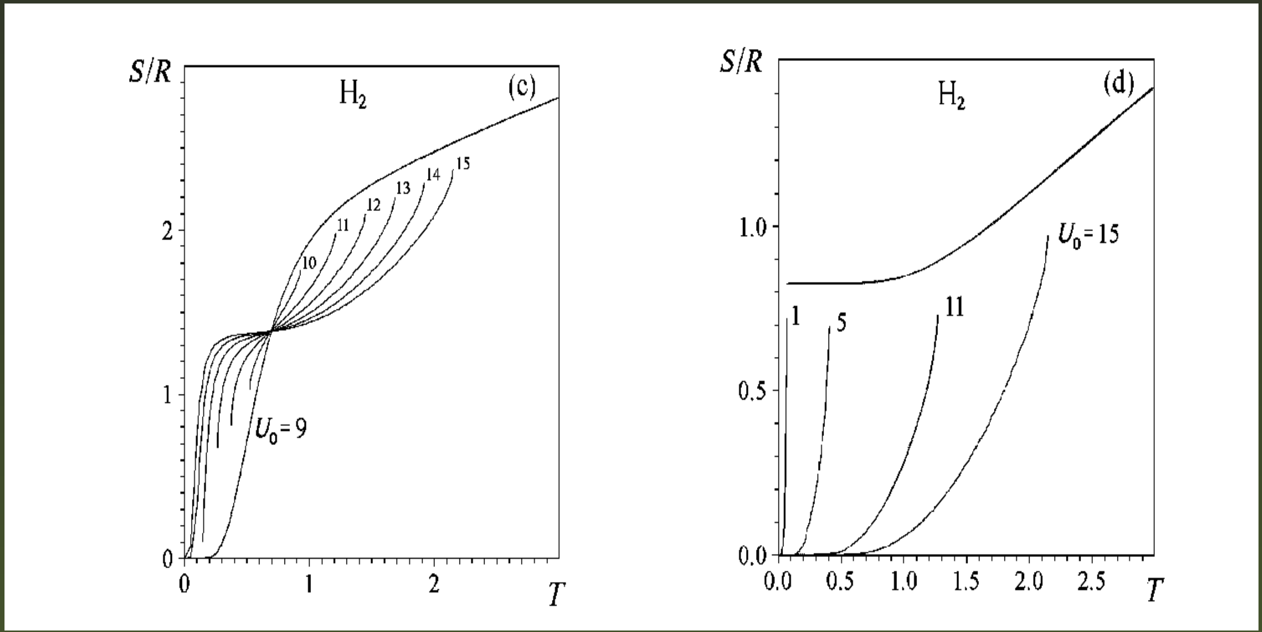


Figure 5: Entropy of the equilibrium (left) and fixed ortho concentration (right) systems at fixed values of the order parameter (Freiman *et al.*, 2005).

MOP-MFT for ortho-para mixtures

- Lattice where each molecule is ortho or para (not averaged out)
- Rewrite Hamiltonian as

$$H_0 = B \sum_i L_i^2 + \sum_{i<j} \frac{K}{2} \left(\frac{R_0}{R_{ij}} \right)^5 \sum_{m,n} C(224; mn)$$

$$\times Y_{2m}(\Omega_i) \gamma_j Y^*_{4m+n}(\Omega_{ij})$$

with

$$\gamma_j = \langle Y_{2n}(\Omega_j) \rangle .$$

MOP-MFT for fixed ortho conc.

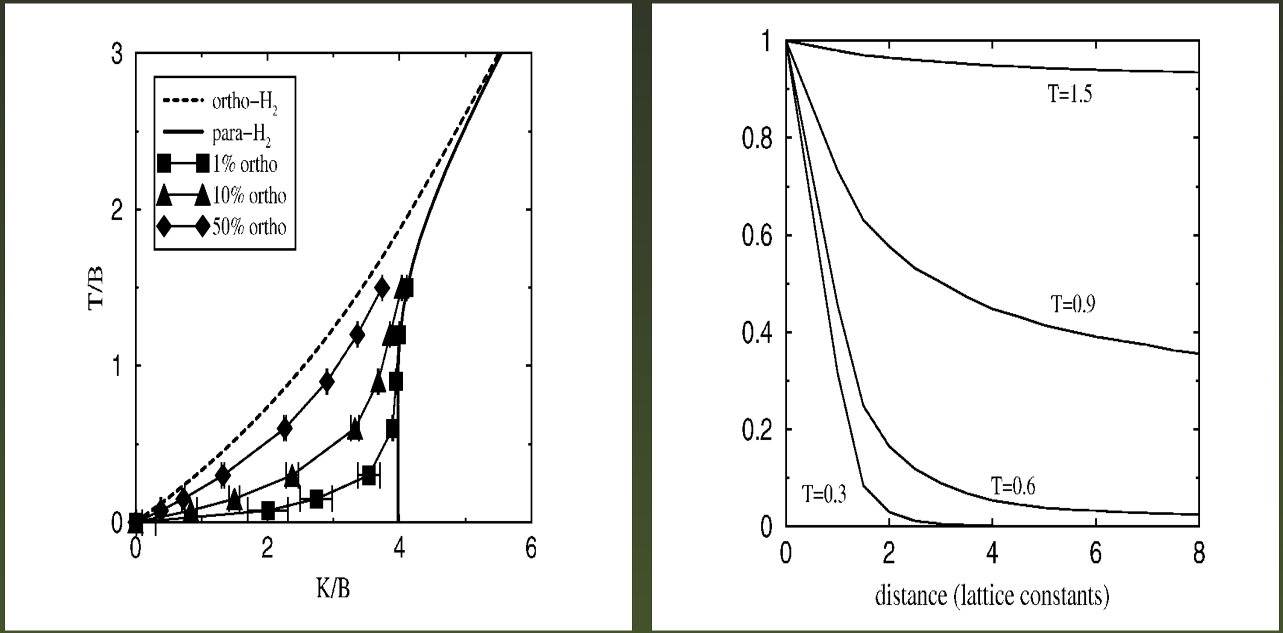
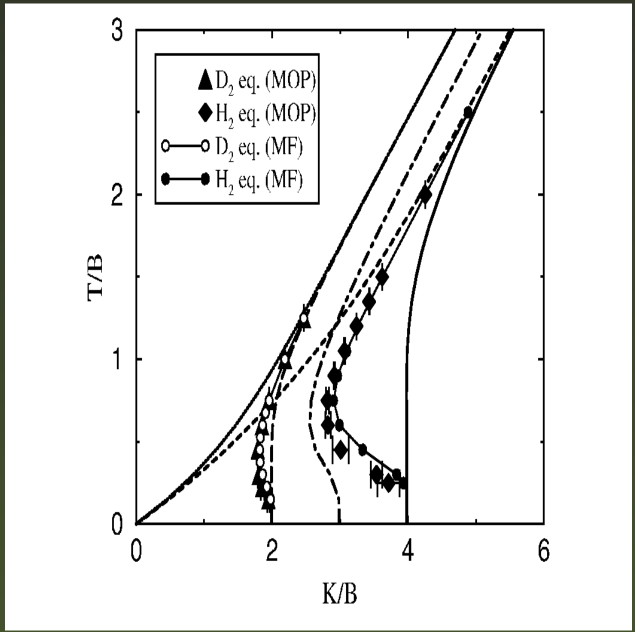


Figure 6: Phase diagram for fixed ortho concentrations (left), $\langle[\gamma(0)\gamma(r)]^2\rangle$ for a system with 10% ortho fraction along the phase boundary (right).

MOP-MFT at thermal equilibrium



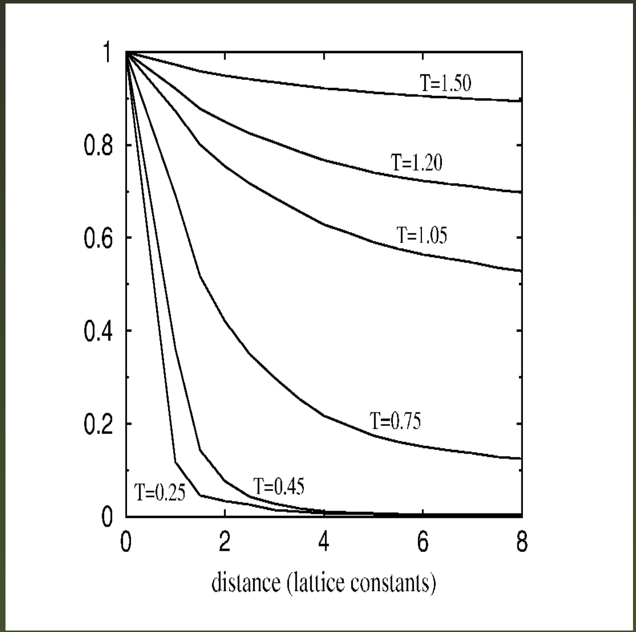


Figure 7: Phase diagram for ortho-para systems at thermal equilibrium (left), $\langle[\gamma(0)\gamma(r)]^2\rangle$ along the phase boundary (right).

Experimental results (D_2)

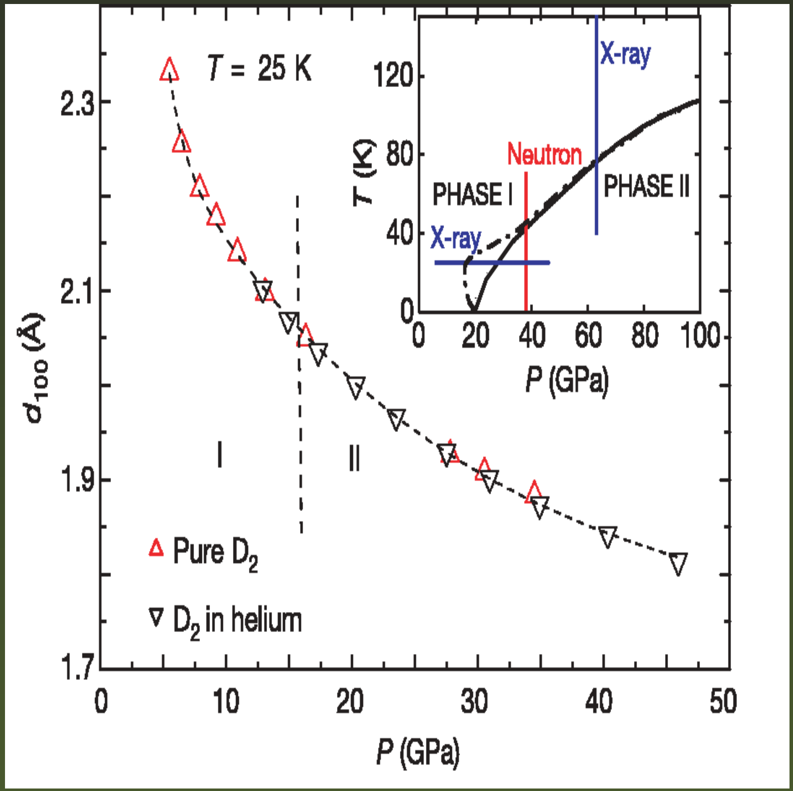


Figure 8: X-ray and neutron diffraction measurements of (Goncharenko and Loubeyre, 2005).

Conclusions

- Mean-field and multi-order parameter mean-field theories predict an anomalous reentrant phase transition for the homonuclear solid hydrogens at thermal distribution.
- For arbitrary ortho concentrations the qualitative picture provided my both theories agrees with experiment. The multi-order parameter mean-field theory predicts short range ordering at lower ortho concentrations.
- Future directions: study ortho-para mixtures with path-integral Monte Carlo methods.

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