H4. NEUTRON DIFFRACTION STUDY OF THE BROKEN SYMMETRY PHASE IN SOLID DEUTERIUM AT THE PRESSURE OF 38 GPa

I.N. GONCHARENKO[1] AND P. LOUBEYRE[2]

[1] Laboratoire Léon Brillouin (CEA-CNRS), CEA – Saclay, 91191 Gif-sur-Yvette, France
[2] Département Physique Théorique et Applications, CEA, 91680 Bruyères-le-Châtel, France

The solid hydrogen H_2, HD and D_2 exhibit intricate quantum phenomena, which have been the subject of numerous experimental and theoretical studies. Studying these phenomena is considered as essential to understand the quantum many-body effects of density. Various exciting scenarios have been suggested for high-pressure dense hydrogens, for example, room temperature superconductivity in monoatomic hydrogen or quantum melting at T=0K at the onset of the transition to the monoatomic state [1]. Despite enormous theoretical and experimental efforts, there was no unambiguous information on nature of the pressure induced phases in solid hydrogen. Optical probes detected a phase transition in solid D_2 at the pressure of 25 GPa and low temperatures [2]. A similar transition occurs in H_2 at much higher pressures of 70-100 GPa [3]. The giant isotopic effect reveals the quantum nature of the pressure-induced phase. The transition was interpreted as a transition to a rotationally ordered state. In the ground state at low temperature and low pressure, hydrogen molecules are in the J=0 spherical rotational states and exhibit a rotational disorder down to T=0 K. At high pressures, a trade-off between two tendencies, going higher in kinetic energy (that is, to $J\neq0$ rotational levels) and gaining a negative potential energy through a orientational ordering that minimizes electric quadrupole–quadrupole energy might lead to a breaking of the spherical symmetry and the stabilization of an orientationally ordered state (the so-called broken symmetry phase or BSP). In H_2, the contribution of the kinetic energy is higher than in D_2, which explains the isotopic effect on the pressure of the transition. The crystal structure of the quantum pressure–induced phases in solid hydrogen is a challenge for modern density-functional theory (DFT) and molecular dynamic simulations (MD). Various theoretical models proposed different crystal structures, most of them suggesting an orthorhombic lowering of symmetry in the basal plane of the initial h.c.p. lattice (see, for example Refs. 4,5). Until the present study, there was no direct evidence of the structural transition in high-pressure solid hydrogen, neither proof of its crystal structure. The optical data on vibron modes provides only indirect information on crystal structure. X-rays are scattered by electronic shells, and therefore almost insensitive to the orientations of hydrogen molecules having no internal electronic orbitals. Contrarily, neutrons are scattered by nuclei and therefore can "see" the orientations of the molecules. While the advantages of neutron techniques in studies of high-pressure hydrogen are obvious, such study is a challenge from an experimental point of view. At pressures above 25 GPa the sample volume is measured in small fraction (10^{-3}) of cubic millimetre. It seemed almost impossible to obtain high-quality structural information from such a small sample at the pressure of 38 GPa (the pressure was chosen well above the phase boundary) and low (down to 1.5K) temperatures. To carry out the study, we used a new approach, based on a combination of neutron and synchrotron probes. A high-quality single-crystal of D_2 was grown from He-D_2 mixture (Fig. 1). The crystal was surrounded by He pressure transmitting medium, which preserved it from shattering as pressure was increased to 38 GPa.

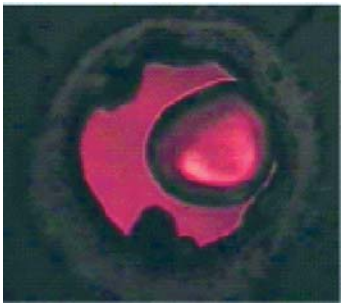

Figure 1. Single crystal of solid D_2 surrounded by He pressure transmitting medium.

New pressure cells (Fig.2) allowed to combine neutron and X-ray diffraction on the same sample. The quality and orientation of the crystal were checked at the ESRF (ID27 and ID9 beamlines) by X-ray diffraction. This saved many weeks of neutron time. Then the pressure cell was brought to the LLB and installed on the lifting-counter diffractometer 6T2, equipped by a He-flow cryostat. The neutron data on (100), (0-10), (-110), (110), (-210), (1-20) and (101) reflections were collected in the temperature range 1.5-70 K. The present study sets a new record for the maximal pressure in single-crystal neutron measurements.

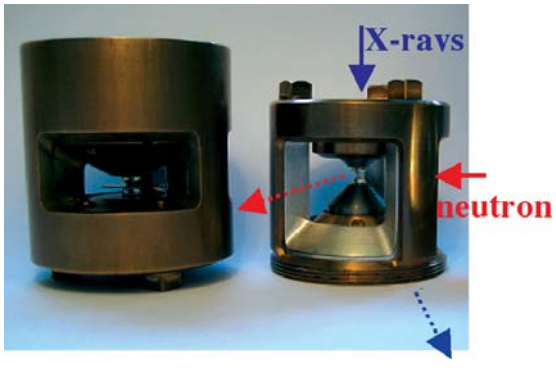

Figure 2. New "hybrid" low-temperature cells compatible with neutron and X-ray scattering at the LLB.

Fig. 3 and 4 show the first direct diffraction evidence of the BSP transition in solid D_2 under pressure. As temperature decreases, a small (~ 5%) decrease in intensity indicates a pressure-induced structural transition. The temperature (~45 K) of the transition exactly coincides with the temperature at which a shift in vibron modes was detected by optical spectroscopy and a tiny change in *c/a* ratio by X-ray scattering. The analysis of the obtained data revealed rather surprising results [6]. Firstly, we did not observe any significant difference (>5%) in the measured intensities from the reflections which are linked by the P-3 symmetry (and therefore equivalent) in the initial h.c.p. structure, but should become different in the orthorhombic cells predicted by theory. Secondly, the observed variation of intensities at the phase transition are much smaller than those predicted by the theoretical models [4,5].

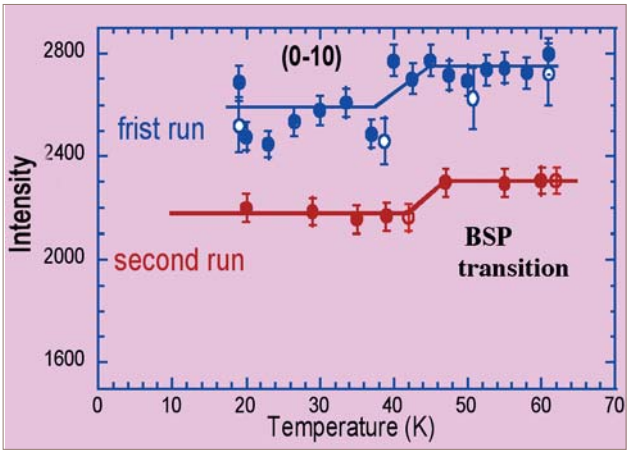

Figure 3. Integrated intensity of the (0-10) reflection versus temperature at the pressure of 38 GPa. Another interesting feature is the presence of incommensurate satellites (1-x, 0 0) in neutron and X-ray diffraction patterns.

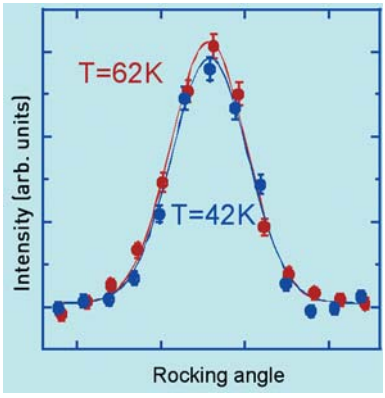

Figure 4. Rocking curves of the (0-10) reflection measured at different temperatures.

Based on our observations, and a proposition of local ordering from a MD simulation by Cui et al [7], we suggest another type of orientational ordering with is similar to that in metastable ortho-para mixtures having cubic f.c.c. structure (so called Pa3 structure). This structure minimises the electric quadrupole-quadrupole energy. It has P-3 symmetry. If developing in a h.c.p. structure, it exhibits a topological frustration (Fig. 5): the molecules have to choose 3 orientations from 6 possible directions along the body diagonals in a bi-pyramid. Stacking faults between different possible orientations might result in a short-range ordered structure or a long-range incommensurate modulation, similar to that observed experimentally. The obtained results should stimulate further theoretical works on orientational ordering and quantum phenomena in dense hydrogen.

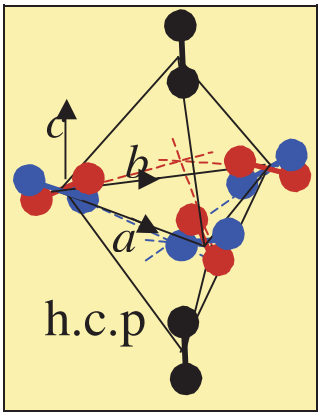

Figure 5. Two possible "frustrated" types of orientational ordering in the BSP phase. The orientations shown in red and blue colours have the same quadrupole-quadrupole energy.

Finally, by a combination of state-of-art synchrotron and neutron techniques, we carried out the first direct diffraction study of the quantum BSP phase in solid D_2, which was a mystery for about 25 years. Forthcoming neutron experiments in an extended **q** range and also similar measurements in solid H_2 at the pressure of 70 GPa should help to improve the understanding of the crystal structure of the BSP phase and to study the isotopic effect on the structure.

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