Neutron diffraction on single crystals under very high pressures in diamond and sapphire anvil cells

Igor Goncharenko

Laboratoire Léon Brillouin CEA-CNRS
**Single-crystal diffraction studies under extreme conditions:**

<table>
<thead>
<tr>
<th>pro</th>
<th>contra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precise information on crystal structures, especially low symmetry/distorted ones, or orientation of molecules molecular ordering</td>
<td>Difficult sample preparation: very small (10-100µ) pre-oriented crystals</td>
</tr>
<tr>
<td>Details on magnetic structures, for example choice between collinear and noncollinear orderings</td>
<td>Shattering of single crystals under pressure because of nonhydrostaticity or first-order phase transitions</td>
</tr>
<tr>
<td>Possibility to combine pressure with anisotropic conditions such as uniaxial stress or magnetic field</td>
<td>More expertise required for collecting data</td>
</tr>
</tbody>
</table>
Compact “LLB pressure cells” with sapphire/cBN/moissanite/diamond anvils


Max. load= 25 kN 30 kN 50 kN 250 kN
P = 7 GPa, V = 1 mm$^3$
Single-crystals in magnetic studies: provide key information on role of nonhydrostaticity (anisotropic pressure component) in high pressure studies.

**Morin transition in hematite $\alpha$-Fe$_2$O$_3$**

Orientational magnetic transition at $T=T_M \sim 260K$

(after Shull, Wollan, 1951)
High Pressure Powder Neutron Studies: Worlton et al., 1968 up to 4 GPa
Goncharenko et al. 1995 up to 10 GPa

At low pressures, $T_M$ seems to increase, but at higher pressures magnetic moments freeze in some intermediate direction.
2006: single crystal study in hydrostatic conditions. About 30 magnetic reflections measured at P=4 GPa.

Pressure cell at the 4-circles diffractometer at the LLB.

The magnetic moments along the rhombohedral axis within +/- 5°.
In non-hydrostatic conditions the Morin transition is controlled by uniaxial stress; hydrostatic pressure allows to complete the transition.

\[
F_{\text{magn}} = \sum J_{(R-R_i)} SS_i + \sum \delta J_{(R-R_i)} \delta R \cdot SS_i + \mu H
\]

- **Isotropic Heisenberg part;** allows to study microscopic origins of magnetic interactions
- **Anisotropic term induced by stress;** allows to study role of topology in magnetic interactions
- **Anisotropic term induced by field;** allows to estimate energy scale of ferro- or antiferro-interactions
**Tb$_2$Ti$_2$O$_7$: a quantum spin liquid down to T=0.1 K**

Degenerated regarding first-neighbor AF interactions

Corener-shared lattices: pyrochlore $A_2B_2X_7$, Laves phases $AB_2$


Gardner et al., *Nature 1998*
Measurements with a controlled component of uniaxial stress

Pressure cell mounted on a He\textsuperscript{3}-He\textsuperscript{4} dilution refrigerator

\[ T_{\text{min}} = 100\text{mK} \]
\[ H_{\text{max}} = 8\ T \]

Measurement of anisotropic stress by scanning the diffraction cone from NaCl
Measurements with a controlled component of uniaxial stress

Measurement of anisotropic stress by scanning the diffraction cone from NaCl

lifting counter single-crystal diffractometer 6T2
$\lambda=0.09-0.24$ nm
Pressure (2 GPa) and anisotropic stress (0.3 GPa): Crystallization of the spin liquid!
Long range magnetic order ($T_N = 0.8$ K)

$Tb_2Ti_2O_7$  $P=2.8$GPa

Mirebeau, Goncharenko, Revkolevski et al,  *PRL 2004*
Simple molecular solids $\text{H}_2$, $\text{D}_2$ under pressure. Complementary neutron and X-ray studies.

...of course, X-ray or neutron diffraction studies at a level sufficient to determine not only unit-cell parameters but also the contents of the unit cell would provide the ultimate test of the structure... (Edwards & Ashcroft, Nature 1997)

Ab-initio calculations for phqs II:
Kitamura et al., Nature 2000
Kohanof et al., PRL 1997
Different predictions, no experimental proof!
Combined X-ray/neutron study on the same sample in the same thermodynamical conditions: the most powerful method to study crystal structures in extreme conditions?
Neutron and X-ray studies on the *same sample* in the *same P-T conditions*

New LLB “hybrid” cell: membrane and screw drive; axial and radial scattering geometries; compatible with neutron and X-ray instrumentations

Neutron cell at the ID27 and ID9 at the ESRF
Neutron and X-ray diffraction study of the broken symmetry phase transition in solid deuterium

Neutron and X-ray diffraction study of the broken symmetry phase transition in solid deuterium

Neutron and X-ray diffraction study of the broken symmetry phase transition in solid deuterium

A “quadrupole” order, similar to what was found in metastable f.c.c. ortho-para mixtures at P=0?

The variations in intensities through the transition are much weaker than those predicted by ab initio calculations.
A “quadrupole” order, similar to what was found in metastable f.c.c. ortho-para mixtures at P=0?

The variations in intensities through the transition are much weaker than those predicted by ab initio calculations.

Topological frustration of the Pa3 type order in the h.c.p. lattice leads to an incommensurate modulation in the a-b plane?
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Intensity</th>
<th>$\Delta I/I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>1600</td>
<td>-5%</td>
</tr>
<tr>
<td>42</td>
<td>2800</td>
<td>-5%</td>
</tr>
</tbody>
</table>

(0-10) reflection shows an intensity change of $\Delta I/I = -5\%$.

(100) reflection shows an intensity change of $\Delta I/I = -2\%$.

(-110) reflection shows an intensity change of $\Delta I/I = -5\%$.

(100), (0-10), (-110): equivalent reflections in the P3 cell.
(-120), (2-10), (-1-10) : weaker intensities, but stronger sensitivity to the BSP transition
(-120), (2-10), (-1-10) : weaker intensities, but stronger sensitivity to the BSP transition
New « open geometry » pressure cells compatible with X-rays and neutrons

High Press. Research, 2007

Thanks to:
A. Gukasov,
P. Loubeyre,
I. Mirebeau
J.-M. Mignot
M. Mezouar
M. Hanfland