

	<b>Experiment title:</b> High-resolution XRD and EXAFS/XANES structural study of yttrium and lanthanum hydrides	<b>Experiment number:</b> HC-3618
<b>Beamline:</b> BM23	<b>Date of experiment:</b> From: 04-07-2018 to 11-07-2018	<b>Date of Report:</b> 27.01.2020
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## Report:

### 1. Introduction

The discovery of superconductivity in  $\text{LaH}_{10}$  at 250–260 K under an ultrahigh pressure of 170–200 GPa [1,2], together with numerous theoretical calculations predicting a critical temperature above room temperature, sharpened the question of the accurate identification of the hydride structure in the high-pressure phase. The X-ray diffraction (XRD) methods at synchrotron radiation provide extremely important information on the type of crystal structure, but are essentially integral and, due to the extremely small factor of scattering of X-rays by light hydrogen atoms, cannot fundamentally establish positions of hydrogen atoms in the lattice.

At the same time, an alternative to XRD structural method is the X-ray absorption spectroscopy (XAFS). XAFS is a fine oscillating structure arising in the X-ray absorption spectrum above the absorption edge of deep ( $K$ ,  $L$ ) levels due to interference of the initial and reflected from the nearest surroundings atom-absorber of photoelectron waves generated by an X-ray quantum when an electron is excited into the free state band above Fermi level. XAFS spectra divide on X-ray absorption near edge fine structure - XANES, arising from multiple scattering of photoelectron on the nearest environments of absorbing atom and extended X-ray absorption fine structure - EXAFS, arising mainly from single scattering processes. The XANES region provides information on the local electronic structure, the valence state of ions, and the symmetry of the local environment of the absorber atom.

In addition to the XRD integral structural data, EXAFS provides unique information about the crystal structure of a substance at a local level, i.e. on the local environment of a selectively

isolated element in a complex compound, including radii, coordination numbers, and Debye-Waller factors of the nearest coordination shells of the environment. The temperature dependences of the Debye-Waller factors, which in EXAFS are the standard deviation from the average interatomic distance between the absorbing atom and the scattering atom, provide information on the mutual vibrations of atoms, including the amplitude of zero vibrations.

The photoelectron wave scattering observed in XAFS techniques has the scattering amplitude on hydrogen atoms many times higher than for X-ray radiation in XRD, and, despite the fact that it is small in comparison with scattering amplitudes on any other atoms, the contribution of hydrogen to XANES and EXAFS spectra are not negligible.

The experimental technique for studying the XAFS spectra at high pressures in diamond anvils is quite well developed. To achieve extreme accuracy in determining the local structure of hydrogen-containing compounds we used the traditional method of XAFS spectra measurements. However, the study of EXAFS spectra by the traditional method at ultrahigh pressures imposes very stringent requirements on both the equipment used and the choice of compound for research. First of all, this is due to the inability to use conventional diamond anvils with single crystal diamonds. When measuring the EXAFS spectrum, numerous Bragg peaks from the crystallographic planes of diamond appear in the measured signal. The only way to overcome this obstacle is to use nanodiamonds synthesized by a unique technique in Japan. The strength of nanodiamonds is inferior to single-crystal diamonds; therefore, to achieve the same values of ultrahigh pressures, large thicknesses are required that reduce transmission in the X-ray region of synchrotron radiation.

Yttrium hydride  $\text{YH}_3$  turned out to be the optimal material from the point of view of achieving maximum transmission of diamond anvils, since the  $K$ -Y energy of the absorption edge of 17038 eV lies in the window of minimum absorption of diamond, which is much less than the absorption at the  $L_3$  absorption edge of lanthanum (5483 eV). The use of the  $K$ -La absorption edge with an energy of 38925 eV is inferior to the  $K$ -Y edge in the accuracy of extracting local structure parameters from EXAFS spectra, due to the significantly larger energy broadening of the edge. The foregoing determined our choice of material in favor of  $\text{YH}_3$ , especially since we had high-quality stable  $\text{YH}_3$  single crystals synthesized in Poland.

*The goal* of project was to use the combined X-Ray diffraction and EXAFS/XANES for providing unique information about phases and processes appearing and undergoing in  $\text{YH}_3$  under ultrahigh pressure.

## 2. Experiment

X-ray absorption spectra above  $K$ -Y (17038 eV) absorption edge were collected at micro-focus BM-23 beamline of European Synchrotron Radiation Facility (ESRF, Grenoble, France) in transmission mode. The double-crystal Si (311) monochromator (detuned to reject 50% of the incident signal in order to minimize harmonic contamination) were used for measurements above  $K$ -Y edge, which allowed us to record EXAFS-spectra with the very high signal-to-noise ratio up to  $16 \text{ \AA}^{-1}$  in momentum space. Energy resolution was  $\sim 0.5 \text{ eV}$  for XANES and  $\sim 2 \text{ eV}$  for EXAFS measurements. For low-temperature XAFS studies the diamond anvil cell camera was mounted in a liquid helium continuous flow cryostat with a temperature control of  $\pm 1 \text{ K}$ . To achieve maximum intensity, synchrotron radiation was focused using a system of mirrors into a spot with a radius of  $30 \text{ \mu m}$ , which was less than the size of the sample.

## 3. Results

Using XANES measurements we firstly obtained the confirmation of the phase transition Hexagonal (hcp) – (fcc) Face-centered cubic (see Fig. 1)

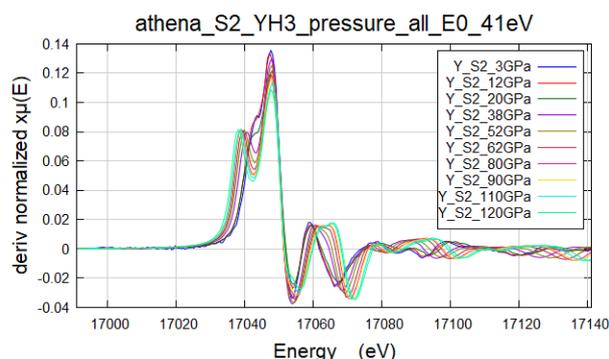


Fig.1. XANES spectra derivative of YH<sub>3</sub> at different pressure.

EXAFS measurements showed that the most stable crystalline fcc phase of YH<sub>3</sub>, with minima value of static disorder and maximum of Y-Y bond stiffness appears at pressure about 80 GPa. EXAFS spectra analysis using the new reverse Monte-Carlo (RMC) technique allowed us to observe the abnormal Debye-Waller factor (MSRD) temperature dependence for Y-Y bonds of the first three coordination shells for this phase (see fig.2). This fact points to the existence of the abnormal anharmonic potential of atom vibrations.

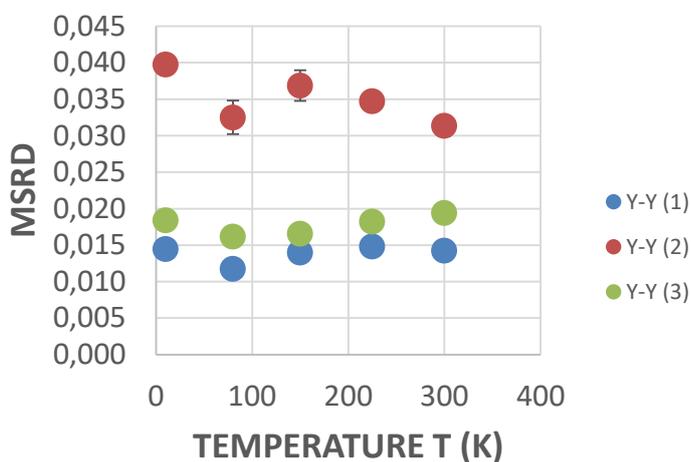


Fig. 2. Debye-Waller factor (MSRD) temperature dependence for Y-Y bonds

It is worth to notice, that the practical similar behaviour was observed for DW factor (MSRD) dependence from the pressure (see Fig. 3)

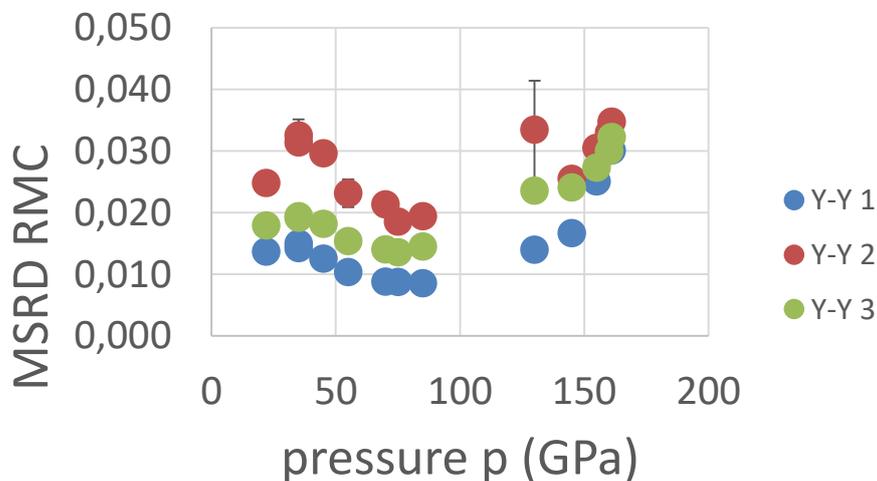


Fig. 3. Debye-Waller factor (MSRD) dependence from pressure for Y-Y bonds

Besides we performed two different types of EXAFS spectra fitting and founded that including of hydrogen sublattice to the model improves the quality of the fitting results. It allowed us to modelling the pair distribution function, which includes two different position of hydrogen atoms in  $\text{YH}_3$  structure (see Fig. 4).

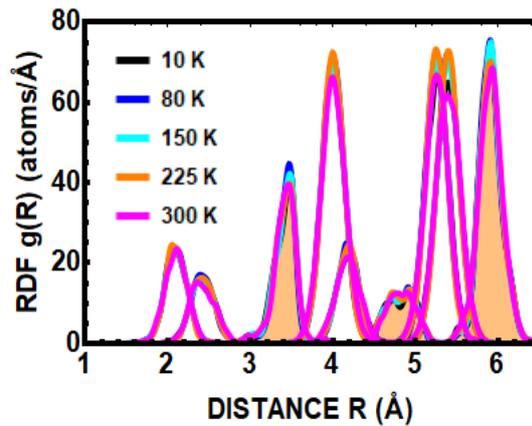


Fig. 4. Pair distribution function PDF, obtained from EXAFS spectra simulation including of hydrogen sublattice ( $\text{H}_1$  and  $\text{H}_2$  at about 2.2 and 2.5 Å, respectively).

### Conclusion

XANES and EXAFS analysis of local electronic and crystal structure of  $\text{YH}_3$  at ultrahigh pressure up to 180 GPa allowed us to observe abnormal behavior of DW factors of Y-Y bonds depending as from temperature, so from pressure. It points to the existence of abnormal anharmonic vibrations of both Y and H atoms at ultrahigh pressure. The obtained results are in good agreement with the anharmonic model of superconductivity in  $\text{LaH}_{10}$  [3] and can be connected with the existence other than BCS mechanism of superconductivity in the metal hydrides in according with some theoretical predictions [4].

### References

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