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Neutron holography of metal–hydrogen systems

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Abstract

Neutron holography constitutes a novel technique to obtain structural information on an atomic scale. It is based on the recording of the interference pattern of neutron waves coherently scattered by atomic nuclei located on a crystal lattice with an appropriate reference wave. The technique is particularly well suited to obtain holograms of metal–hydrogen systems. In one approach, a point-like source of spherical neutron waves is realized inside a single-crystalline sample by making use of the large incoherent neutron scattering cross section of hydrogen nuclei, i.e. protons. Alternatively, strongly neutron-absorbing nuclei can be used as point-like detectors within a sample. Various features of the method are explained referring to a recent holographic reconstruction of the positions of the metal atoms around hydrogen on octahedral interstitial sites in a palladium–hydrogen single crystal. Further, the potential of the method for the investigation of metal–hydrogen systems, in general, is discussed.

Keywords: Hydrogen storage materials; Metals; Crystal structure; Neutron scattering

1. Introduction

Holography was invented by Gábor [1] with the aim to construct an electron microscope attaining atomic resolution without image distortions due to electromagnetic lenses. Despite the widespread use of holographic techniques in the wavelength range of visible light, which followed the development of highly coherent laser beams, the original idea to record images on an atomic scale could be realized only about 40 years later. During the last decade, holographic methods based on electrons (i.e.matter waves) were successfully extended to electromagnetic waves (X-rays and γ-rays) readily available from synchrotron radiation. A major part of this work has been reviewed, e.g. in [2].

Limitations in applying the above techniques arise in the case of electrons from their extremely strong interaction with condensed matter restricting them essentially to the investigation of surfaces. X-rays, on the other hand, while being able to penetrate more deeply into matter, exhibit variations of sensitivity covering several orders of magnitude over the periodic table impeding their use for many systems involving particular combinations of elements. Neutrons, in principle, are not subject to these drawbacks. However, for various reasons, partly related to the limited intensity of presently available neutron beams, their application was not considered feasible. Only recently [3] experimental setups were put forward permitting to transfer certain conceptions developed in the context of X-ray holography to the case of neutrons.

Holographic imaging techniques are based on the recording of the interference pattern of two coherent waves originating from the same source. The first wave, that reaches the detector directly, serves as the reference wave; the second one is scattered by the object of interest and subsequently interferes with the reference wave. In the context of holography with atomic resolution basically two techniques are in use which are called the inside-source and the inside-detector setup, respectively.

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2. Neutron holography

In the case of neutrons [3–5], the inside-source concept requires a point-like source of spherical neutron waves within the sample. Hydrogen nuclei (i.e. protons) are extremely well suited to serve this purpose due to their large incoherent elastic scattering cross section (∼80 barns) for thermal neutrons. Metal–hydrogen systems, therefore, are a natural choice in studying various features of this novel technique. The feasibility of Neutron Inside Source Holography (NISH) was demonstrated in an experiment on a mineral containing hydrogen by a Canadian group at Chalk River [6] and in another experiment, performed by the present authors, on the metal–hydrogen system PdH (see below) [7]. The second method, Neutron Inside Detector Holography (NIDH), requires the application of strongly neutron-absorbing isotopes which act as point-like detectors within the sample. It was successfully applied in an experiment at the ILL in Grenoble recording the holographic image of a lead single crystal containing a small fraction of neutron-absorbing cadmium [8].

In assessing the feasibility of a holography experiment, the first consideration is directed towards the size of the holographic modulation relative to the background due to the reference wave. An estimate of this quantity, based on taking into account only the shell of next neighbours around the probe nucleus (source or detector), can be obtained by regarding the ratio between the coherent neutron scattering length b_c and the interatomic distance between the probe nucleus and its nearest neighbours [3–5]. With few exceptions, b_c lies in the range 3–10 fm, while nearest neighbour distances are typically around 0.3 nm. Summing over nearest neighbours (e.g. 8 in bcc or 12 in close-packed structures), therefore, yields typically 1×10^{-4} to 1×10^{-3} for the amplitude of the interference term due to the first neighbouring shell. Note, however, that there is a small number of natural elements (essentially H, Li, Ti, Mn) and a larger number of pure isotopes exhibiting negative scattering lengths so that the interference term may become very small or even vanish if the neighbourhood of the probe nuclei is made up of different scatterers characterized by scattering lengths of opposite sign.

3. Holography of PdH

In the first investigation, demonstrating the applicability of neutron holography to metal–hydrogen systems a holographic image of palladium nuclei in a $PdH_{0.78}$ single crystal was recorded [7]. The sample was a slightly irregular-shaped slab with the dimensions ∼ 2.8 mm × 15 mm × 8 mm. It was covered with a thin copper film whose thickness (∼30 μm) was sufficient to avoid hydrogen loss. Hydrogen is well known to occupy octahedral interstitial sites in the fcc palladium lattice. The palladium nuclei play the role of the object while the hydrogen nuclei (i.e. protons) serve as point-like neutron sources inside the sample.

The experiment was done with the goal to overcome certain technical problems in order to open the way towards a wider range of applications. A particular challenge of the experiment consisted in the extraordinarily strong variations of the scattering intensity due to the size and irregular shape of the sample exceeding the weak holographic modulation ($\sim 10^{-3}$) by several orders of magnitude. This problem, however, could be solved by the application of suitable filtering and image processing techniques. In addition, it was shown that the problem of Bragg peak contaminations encountered in the first inside-source measurements [6] can be completely avoided by choosing an experimental setup, where the sample is rotated about two perpendicular axes while the detector is kept fixed at a scattering angle where the momentum transfer does not fulfil the Bragg condition [5]. In the same way, contributions of Debye–Scherrer rings due to the copper coating could be circumvented and, more generally, this technique applies to any sample environment.

The experiment was carried out at the 6T2 four-circle diffractometer at the Orphée research reactor (Laboratoire Léon Brillouin), Saclay. The sample was mounted on the cradle of the diffractometer and rotated about the angle χ through a range of 45 °C and about the angle ϕ through a range of 350 °C. The angular step-width was 5 °C for both rotations leading to a mesh of $10 \times 71 = 710$ pixels forming the hologram, the neutron wavelength was ∼0.9 Å. A mathematical reconstruction of the positions of the Pd atoms occupying crystal lattice sites around hydrogen probe nuclei is shown in Fig. 1.

4. General aspects of neutron holography in metal–hydrogen systems

In discussing applications of neutron holography one has to take into account the relative magnitude of the coherent, incoherent and absorption cross sections σ_{coh}, σ_{inc} and σ_{abs} of the sample and the probe nuclei. Each of these scattering cross sections defines an absorption length (or penetration depth) and it is the largest of these cross sections which limits the sample size. Of course, this consideration has to be applied in using the effective cross sections $\sigma_{eff} = c\sigma_{in}$, i.e. the interaction cross section of the nuclide multiplied with its concentration according to the sample composition. For a stoichiometric metal–hydrogen sample, therefore, the volume effectively contributing to the holographic signal will be typically on the order of several mm in diameter.

Regarding the few experiments done so far one observes that in the case of the mineral simpsonite [6] roughly 5% of the atoms are hydrogen so that the effective incoherent scattering cross section is about 4 barn/atom for the entire sample. In the case of Pb, the concentration of Cd atoms was 0.26% [8]. At wavelengths around 1 Å ($E \sim 100$ meV), being best suited for neutron holography, this gives an effective absorption cross section close to 3 barn/atom. At present, therefore, an effective cross section for absorption (NIDH case) or in-

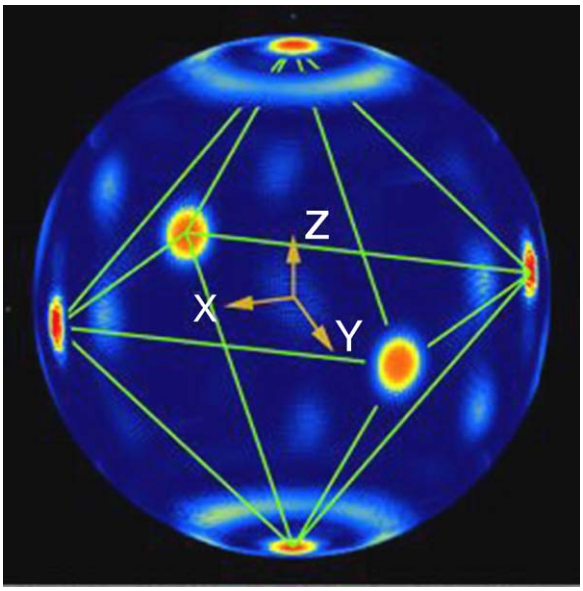

Fig. 1. The reconstructed positions of six Pd atoms forming the first neighbouring shell around a hydrogen nucleus on an octahedral interstitial lattice site [7]. The Pd atoms are arranged on a fcc lattice. Both the orientation of the sample and the interatomic distances are in very good agreement with the crystallographic data determined in a conventional diffraction experiment. The faded patterns visible in the figure are mostly artifacts due to the mathematical reconstruction algorithm and the highly unfavourable shape of the sample.

coherent scattering (NISH case) on the order ∼5 barn/atom can be considered sufficient for a successful holography experiment.

In looking for other elements suitable for inside-source experiments one finds about a dozen candidates including Cl, Sc, V, Co, Ni and several rare earths. The incoherent scattering cross sections in these cases are, however, mostly in the range 5–10 barn from which follows that in an inside-source experiment the source atoms always have to represent a substantial fraction of the sample composition. Even in the case of hydrogen (80 barn) at least several percent of hydrogen will be required though this offers already access to a large variety of substances. One can ask the question whether also deuterated samples may be useful in studying metal–hydrogen systems in view of the fact that deuterium exhibits only a moderate incoherent scattering cross section (∼2 barn). This is probably too small to be of use except for systems whose hydrogen content is very high but deuteration may be applied in combination with other incoherently scattering isotopes. For example, in an experiment on deuterated vanadium hydride the dominating part of the holographic modulation will show the lattice sites of deuterium which are recorded by means of the spherical waves generated by incoherent scattering from the vanadium nuclei ($\sigma_{inc} \sim 5$ barn). The contribution of incoherent scattering from deuterium, however, will not be negligible in many cases.

On the other hand, there are many elements available exhibiting reasonably high absorption cross sections warranting their use in inside-detector experiments. In fact, all the elements with $Z \geq 45$ (except for Sn, Ba, Ce and Pb) have absorption cross sections close to 5 barn or higher. For $Z < 45$ about 15 elements fulfil this condition and for several more there exist suitable isotopes (e.g. $^{40}_{19}$K, $^{53}_{24}$Cr). Furthermore, in several cases absorption cross sections are so high that these elements can (and must) be used in dilute form, i.e. their atomic fraction in the sample has to be on the order of 1% or even less. A potential advantage of the inside-detector technique consists in the possibility to record holograms detected by different isotopes emitting, correspondingly, γ-rays with different energies which can be separated by γ-detectors with good energy resolution (e.g. Ge detectors). This would provide a way to record holographic images of the local environment of nuclei located on different sublattices.

For lack of space, we restrict the further discussion to one single example which has been chosen because it is particulary suitable to demonstrate several important features of potential holography experiments on metal–hydrogen systems: ScH (scandium hydride) is well known for its peculiar linear ordering of hydrogen pairs [9] previously observed also in the rare earths lutetium [10] and yttrium [11]. It would offer the intriguing possibility to perform NISH and NIDH on the same sample and even during the same experiment. Scandium ($Z = 21$, $A = 45$) has a sufficiently large incoherent scattering cross section (4.5 barn) as well as a considerable absorption cross section (27.5 barn at a neutron energy of 25 meV) so that it can serve both as a source (NISH) and a detector nucleus (NIDH). The coherent scattering cross section (19.0 barn) is also large so that Sc will create a strong holographic modulation if, alternatively, hydrogen is used as the source in a ScH crystal. In general, a NISH experiment on ScH will lead to the recording of a superposition of holograms generated due to Sc or H acting as a source, respectively.

In addition to obtaining structural information about ScH (which, of course, has been derived earlier from diffuse neutron scattering experiments [9]), another aspect of neutron holography could be studied which has not been investigated so far: due to their zero-point vibrations hydrogen nuclei actually are not point-like sources of spherical waves but rather extended while the positions of the much heavier Sc atoms are strongly confined so that broadening due to vibrations should be negligible. The effect of the hydrogen vibrations on the resolution which can be achieved in recording holograms is not entirely clear at present and various experiments are conceivable in this context (to simplify matters we neglect incoherent scattering from deuterium in what follows), for instance: (a) a NISH experiment on ScH using hydrogen as the source would permit to observe the possible broadening of the reconstructed positions of scandium atoms due to the hydrogen source vibrations. (b) If scandium is used either as the source (NISH) or the detector (NIDH) in an experiment on deuterated ScD the positions of the deuterium atoms should be broadended due to the deuterium vibrations. On the other hand, the positions of Sc atoms should be sharply defined within the resolution of the experimental setup. (c) A NISH experiment on a mixed ScHD crystal employing hydrogen as

a source would reveal possible differences between the effects caused by the delocalization of only the source (which is reflected in the positions obtained for Sc atoms) and the combined delocalization of both source and object (reflected in the positions obtained for D atoms).

Several fields of investigation are immediately suggested in metal–hydrogen systems including the direct determination of interstitial sites occupied by hydrogen, direct determination of atomic displacements induced by hydrogen as well as effects due to hydrogen vibrations. A brief qualitative discussion of these topics can be found in [4].

Presently, a major technical drawback for wider applications of neutron holography is the long measuring time (∼1 week) required to record a hologram. However, up to now neutron holography experiments have been done using only single detectors. The use of multidetectors instead would improve the situation significantly. Since the size and resolution of multidetector arrays are continuously improving, gains of several orders of magnitude over the single detector setup can be envisaged in the near future.

Another important issue in discussing potential applications of neutron holography is the applicability of various sample environments like furnaces, cryostats or pressure cells. The prospects of such experiments are good since both neutrons (NISH) and energetic γ-rays (NIDH) penetrate relatively easily through matter. Complications may arise in the inside-source case from intense Debye–Scherrer lines due to the sample environment which can, however, be avoided by choosing a fixed detector position at an angle where no such lines are observed (see above). In inside-detector experiments, the sample environment can contribute massively to the background. For this reason an approach based on the use of Ge detectors in a Compton suppression arrangement appears most promising.

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