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Interstitial site occupation in α-$LaNi_5$-H studied by deep inelastic neutron scattering

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Abstract

Deep inelastic neutron scattering (DINS) from hydrogen is a new technique made possible by the advent of accelerator-based neutron sources such as ISIS at the Rutherford Appleton Laboratory. DINS measures both the concentration and the mean kinetic energy of hydrogen in the sample. H concentrations of less than 1% relative to the metal can be measured, since the hydrogen signal is well separated from the metal signal. In situ measurements on un-cycled α-$LaNi_5$-H revealed that the sample contained trapped hydrogen after desorption. The changes in H concentration measured with DINS were in good agreement with manometric measurements. The H kinetic energy did not change significantly with concentration, suggesting that the trapped and untrapped H atoms occupy essentially the same interstices.

Keywords: Inelastic; Interstitial; Metal hydride; Neutron scattering

1. Introduction

Accurate knowledge of atomic positions and vibration modes is an essential prerequisite to theoretical modelling of hydrogen in metals. Whilst in pure metals these are relatively well known, recent progress in applying statistical mechanics to $LaNi_5$-H is hard to evaluate because of the continuing uncertainty about site occupation by the interstitial H.

Crystallographic studies of deuterated metals by neutron powder diffraction have been the mainstay in this area. However, diffraction detects only changes in the phase of the scattered wave, and so is insensitive to small shifts in atomic positions. Where such shifts are merely away from the ideal site prescribed by the symmetry of the lattice, the effects may be insignificant. In the case of the dilute solid-solution (α) phase of $LaNi_5$-H, however, confusion between say the 3f quasi-octahedral and closely surrounding 12n quasi-tetrahedral sites (of which 3f sites form a subset) of the P6/mmm lattice may be highly significant because of the different vibration energies generally expected. In this circumstance, inelastic neutron scattering, taking advantage of the high incoherent cross section of H, has proved valuable. Nevertheless, uncertainty about even the much-studied α-$LaNi_5$-H persists.

Deep inelastic scattering (DINS) in the range of energy transfers 1–100 eV occurs on such a short timescale that the momentum distribution of H, unaffected by correlations, is observed. DINS has been applied to some simple (i.e., non alloy) metal hydrides with considerable success [1]. We expected that this technique would prove valuable in determining whether H simultaneously occupies more than one site with different vibrational energies. DINS spectra were recorded using the electron-Volt Spectrometer (eVS) at the pulsed neutron source ISIS. eVS was used in this case as a light-atom mass spectrometer, able to uniquely identify vibrating H atoms by their mass, and measure their concentration and average kinetic energy. Taken together with existing diffraction data [2–4] our results provide new information on interstitial occupancy in this phase.

2. Summary of previous results

Previous studies have suggested the occupation of several interstitial sites. Based on powder diffraction these are: Fischer et al. [2], 3f; Soubeyroux et al. [3], 12n, perhaps, with the same site(s) being occupied in both hydrogen-cycled and un-cycled samples; Kisi et al. [4], 3f or 12n, with the best refinement obtained using a site which is a mixture of these. Using INS, i.e., inelastic

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neutron scattering in the range of energy transfers 10^{-2}–10^{0} eV, Hemplemann et al. [5] concluded that 3f and 6m sites are occupied. The recent work by Schönfeld et al. [6] on H dynamics in α-$LaNi_5$-H is founded on the latter occupancy model, despite the lack of support for any significant static occupation of 6m from the diffraction studies, which agree that H occupies a site in or near the basal plane. Moreover, test refinements of the data reported in [4] with sites out of the basal plane gave D/M ratios in serious disagreement with those measured manometrically during the experiment. In [6] it was concluded that the broadened INS spectrum observed in cycled material was due to H trapped in regions of the lattice strained by the activation process. This was also found by Fairclough et al. [7]. Based on a thermodynamic study, Dantzer et al. [8] suggested that, at the lowest H concentrations, H occupies 3f and trap sites, migrating to 12n at higher concentration.

3. Experimental details

The measurement of atomic momentum distributions in condensed matter systems by high energy neutron scattering is analogous to the measurement of electron momentum distributions by Compton scattering and measurement of nucleon momenta by Deep Inelastic Scattering [9]. The principle is the same in each case; the momentum distribution of target particles (electrons, components of nuclei or atoms respectively) is measured by inelastic scattering of high energy incident particles (photons, electrons or neutrons). For accurate DINS measurements energy transfers ~100 times greater than the mean atomic kinetic are required and only pulsed neutron sources can supply a sufficiently high intensity of neutrons at the energies required to satisfy this condition, which is formalised in the Impulse Approximation (IA) [10,11]. The electron volt spectrometer (eVS) at ISIS [12] is dedicated to the development of the DINS technique.

The IA states that, if the momentum lost by the incident neutron is sufficiently large, scattering occurs from a single atom with conservation of kinetic energy and momentum. Consider a scattering event in which a neutron loses momentum q and energy ω scattering from an atom of mass. If the momentum of the atom is $\boldsymbol{p}$ before the collision, then from conservation of momentum it is $\boldsymbol{p}+\boldsymbol{q}$ after the collision and to conserve kinetic energy the equation

$$\omega = \frac{(\boldsymbol{p}+\boldsymbol{q})^2}{2M} - \frac{p^2}{2M} \tag{1}$$

must be satisfied. Rearrangement of Eq. (1) gives

$$y = \boldsymbol{p}\cdot\hat{\boldsymbol{q}} = \frac{M}{q}\left(\omega - \frac{q^2}{2M}\right) \tag{2}$$

where $\hat{\boldsymbol{q}}$ is the unit vector along the direction of $\boldsymbol{q}$ and y is the component of atomic momentum along the direction of $\boldsymbol{q}$. In other words, from a measurement of the neutron $\boldsymbol{q}$ and ω we can determine y. In an experiment we measure a large number of neutron-atom collisions and build up a distribution of atomic momenta, *J(y)*. The kinetic energy of the target atoms in an isotropic sample is found from the one-dimensional by calculating the three-dimensional average of $p^2/2M$ for the atoms:

$$K = \frac{3}{2M}\int_{-\infty}^{\infty} y^2 J(y)\,\mathrm{d}y \tag{3}$$

An important feature of the DINS technique is that the energy lost by the neutron when it collides with an atom depends upon the atomic mass. The signal from hydrogen is usually well separated from that produced by other atoms and its position in neutron time-of-flight spectra can be accurately calculated. Thus the kinetic energy of the proton can be unambiguously determined and, from a measurement of the peak area, one can also determine the concentration of hydrogen in the sample. Details of the actual energy analysis technique used on eVS are given in [13,14].

The sample in this study was polycrystalline α-$LaNi_5$-H. The coarsely-powdered metal was first annealed in flowing hydrogen at 1000 °C to minimise the dislocation density. While several absorption–desorption cycles were subsequently conducted within the pure α phase, extreme care was taken to avoid the nucleation of the β phase and its attendant massive mechanical damage. Measurements were made near room temperature because, at such high energy transfers, the phonon background which degrades INS data at lower energy transfers is unimportant.

4. Results

INS measurements (to be published) immediately prior to the present work suggested that some H was trapped in the sample after desorption by pumping. Therefore, the sample was heated under a vacuum of 10^{-5} mbar for 3 h at 70 °C before beginning the DINS study. Fig. 1a and Fig. 1b show TOF spectra of the supposedly desorbed sample at two different scattering angles. The tall peak arises from the metal atoms. Because the mass resolution decreases rapidly for heavier atoms, Ni and La are not practically distinguishable. Whereas, using INS, a spectrum feature at a plausible H vibration energy might also arise in the background due to the other components of the sample, in this case the small but obvious DINS peak on the low-TOF side of the metal peak is unequivocally due to H remaining in the sample after the desorption treatment. We will refer to the equivalent H-to-Metal ratio as H_{trapped}/M. Further DINS spectra were recorded after adding H equivalent to $H_{\mathrm{trapped}}/M\ +0.023$ and $H_{\mathrm{trapped}}/M\ +0.045$. Spectra at $H_{\mathrm{trapped}}/M\ +0.045$ are shown in Fig. 1c and Fig. 1d. The

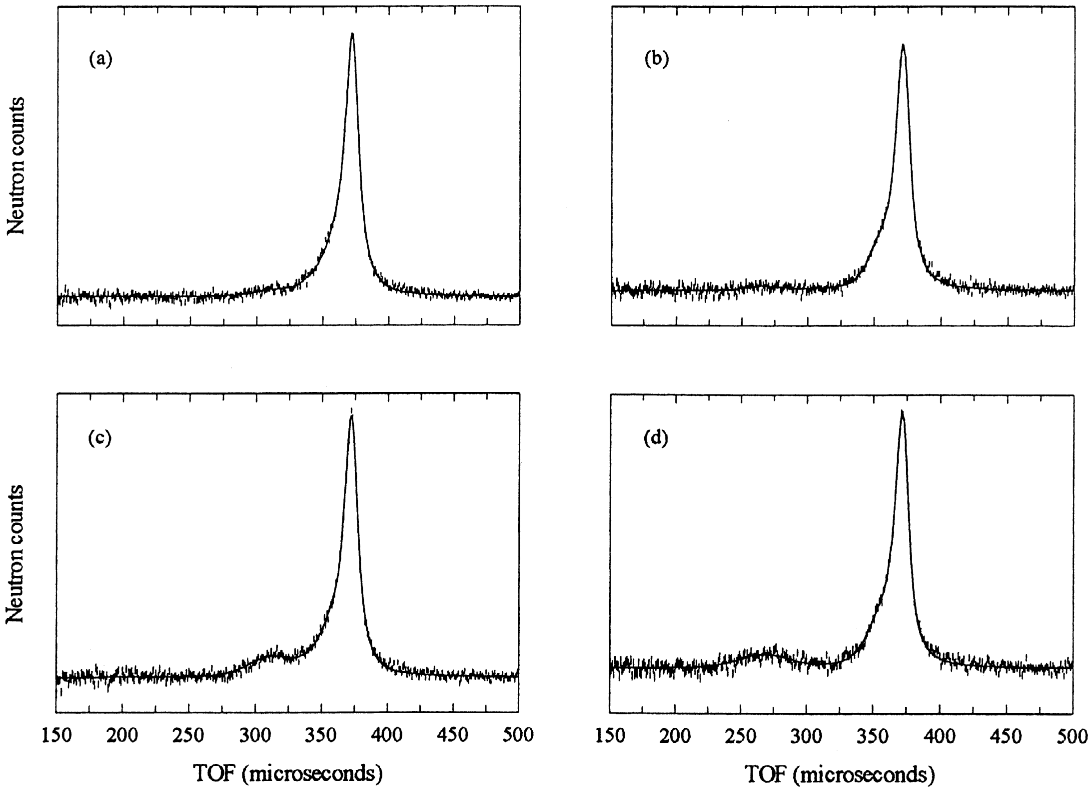

Fig. 1. Examples of time-of-flight spectra measured on eVS at different scattering angles θ and H/M ratios. (a) $H/M=0$, $\theta=34°$; (b) $H/M=0$, $\theta=55°$; (c) $H/M=0.045$, $\theta=34°$; (d) $H/M=0.045$, $\theta=55°$. Note that the separation of the H peak from the La/Ni peak increases with scattering angle. The points are data and the solid lines are fits to the data using the procedure outlined in the text.

increase in the area of the H peak relative to the desorbed state is readily discernible.

5. Analysis and discussion

We note that these data on an annealed powder can be validly compared to those taken with a single crystal [6], as no β-phase had been formed in our sample. Conversely, it appears that even a single crystal will contain a significant density of dislocations and some trapped H after cycling through the α-phase.

The data analysis is in principle very simple. Each time-of-flight (TOF) spectrum contains a peak from each atomic mass. The area of each peak is determined by the concentration and scattering cross-section of each mass and the width is determined by the atomic kinetic energy and the instrument resolution. For strongly scattering samples, however, multiple scattering must be taken into account. In Fig. 1, the peak on the low-TOF wing of the metal peak is multiple scattering, mainly from Ni. The multiple scattering was modelled statistically to check that it was correctly identified. It was represented analytically in the fit to the TOF spectra by three phantom masses of 5, 10 and 20 amu. This allowed for the different angular dependence of the multiple scattering and primary inelastic signals. The multiple scattering was found to contribute 50% of the area of the metal peak in the TOF spectrum. Hence true H/M values were found by first comparing the areas under the H and metal peaks, then doubling the answer. Each TOF spectrum was therefore fitted by sum of five gaussians (H, 3 for multiple scattering, 1 for metal), convolved with the instrument resolution function. The positions of the peaks are not included as fitting parameters, since those due to primary inelastic scattering can be accurately calculated from the atomic mass. Fig. 1 shows the fits to the data as solid lines. The fitted parameters and errors are summarized in Table 1 as means and standard deviations of the values obtained from 16 detectors. Vibration energies are expressed as harmonic oscillator equivalent for easiest comparison with INS studies. It is worth noting that, although the separation of the H peak from the La/Ni peak varies considerably with scattering angle, good consistency of both peak areas and atomic

Table 1
Results of fitting to 16 time of flight spectra with scattering angles between 34° and 55°

Nominal H/M ratio	Fitted H/M ratio	Mean ω (meV)
0.0	0.017 ± 0.002	116 ± 19
0.023	0.052 ± 0.003	102 ± 12
0.045	0.073 ± 0.008	116 ± 7

kinetic energies was obtained over the whole range of scattering angles. This suggests that the data analysis is free from any systematic errors and should give reliable values of concentrations and kinetic energies.

The values of H/M derived from the ratios of measured peak areas are in good agreement with the nominal values, provided that H_{trapped}/M ~0.02. Although the discrepancy between the changes in H/M derived from manometry and DINS lies outside the estimated error, the result is a good one in view of (i) the small absolute concentration of H and (ii) the unfavourable circumstance of the high multiple scattering.

Within the resolution of the DINS measurements, there was no change in the average H vibration energy with H/M, so, at least in this un-cycled sample, there is no obvious change of site occupation with increasing H/M. Moreover, the H trap sites are not discernibly different from the reversible H sites. The actual equivalent harmonic oscillator energy of around 110 meV is consistent with the modes identified in a single crystal [6], although not readily associated with any particular interstitial site, as several of the proposed o- (fundamental plus first overtone) and t-site energies were in this range. In the study of trapped H at much higher concentrations by Fairclough et al. [7] fundamental vibrations were observed at considerably higher energies, in the 140–170 meV range. Hence the nature of traps in cycled material does appear to be quite different to those in un-cycled material.

Basal-plane strain is evident even in the diffraction pattern of un-cycled α-LaNi$_5$-H [3], and dislocations have been observed in an uncycled sample [15]. In the detailed TEM study of desorbed samples by Kim et al. [16], the Burgers vector was found to lie parallel to the basal plane, propagating tensile and compressive basal-plane strain into neighbouring cells. It is likely that the traps are associated with dislocations, but it remains to be shown how a trap is created, thereby greatly increasing the activation energy for diffusion, without drastically changing the vibration energy of an H atom occupying it.

6. Conclusions

Even our desorbed sample, which had never formed the (phase, contained a significant concentration of H in traps, equivalent to H/M ~0.02. We conclude that previous studies of α-LaNi$_5$-H by diffraction and INS necessarily included trapped H. We found that H had the same average kinetic energy in a range of H/M values between 0.02 and 0.07. The location of the trap sites remains to be found by diffraction experiments on samples containing more than a few percent trapped H.

DINS has proved to be a sensitive probe for trapped hydrogen in materials. One can determine both the concentration and mean kinetic energy of H at concentrations around 1%, even in the presence of strong multiple scattering, as in our relatively unfavourable sample. The technique is still at an early stage of development and will certainly improve in accuracy and sensitivity to low H concentrations. However, the measurements reported here demonstrate that the technique already has considerable potential for providing information on site occupancy in metal hydrides.

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