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Hydrogen detection in metals by neutron interferometry^{a)}

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The neutron interferometer is used to determine the H and D concentration in V and Nb samples. The hydrogen content changes the average coherent scattering length and, therefore, the phase shift of the coherent beams which can be measured precisely. The results are compared with the weighing and the epithermal neutron scattering method. Characteristic values for the sensitivity obtained with the interferometer method are 0.02–0.06 at.% or 6–12 ppm by weight. As soon as precipitation occurs in the sample, a loss of contrast indicates additional small-angle scattering.

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I. INTRODUCTION

The behavior of hydrogen in metals is of scientific and economic interest because hydrogen represents the simplest possible impurity in metals, and, in some cases, an efficient hydrogen storage can be achieved.¹⁻⁵ In this case, an effective detection method is important. Besides the standard method of sample weighing, various other methods are treated in the literature.^{4,6-10} Much effort is made to get the spatial distribution, especially during diffusion.

The systems V-H(D) and Nb-H are well known according to their structure, phase diagram, and morphology.¹¹⁻¹⁴ At present, low hydrogen concentrations are of interest, and, therefore, the samples are within the α or β phases only.

The development of neutron interferometry¹⁵ allows a rather simple and accurate method for the determination of coherent scattering lengths.^{16,17} The coherent scattering length \bar{b} for a statistically mixed system is given by the average about the atomic abun-

TABLE I. Summary of data.

Sample	Thickness (mm)	Weighing, Ref. 19 (at.%)	H(D) concentration determined by		
			Epithermal neutron scatt. Ref. 23 (at.%)	Neutron interferometry (at.%) (ppm weight)	
V	9.17 ± 0.01	0	0	0	0
VH _{0.004}	9.79 ± 0.01	0.40 ± 0.04		0.43 ± 0.06	84 ± 12
VH _{0.0085}	9.18 ± 0.01	0.85 ± 0.04	0.86 ± 0.12	0.82 ± 0.07	163 ± 14
VH _{0.035}	9.21 ± 0.01	3.51 ± 0.04		3.37 ± 0.03	667 ± 7
VH _{0.062}	9.20 ± 0.01	6.20 ± 0.04	
VD _{0.011}	9.21 ± 0.01	1.15 ± 0.02		1.21 ± 0.02	477 ± 10
VD _{0.021}	9.21 ± 0.01	2.13 ± 0.02		2.11 ± 0.02	832 ± 10
VD _{0.057}	9.21 ± 0.01	5.71 ± 0.02		5.64 ± 0.04	2230 ± 16
VD _{0.11}	9.27 ± 0.03	10.71 ± 0.02	
Nb	10.495 ± 0.015	0	0	0	0
NbH _{0.0042}	10.51 ± 0.015	0.42 ± 0.04		0.31 ± 0.08	34 ± 9
NbH _{0.015}	10.46 ± 0.015	1.48 ± 0.04		1.41 ± 0.06	153 ± 6
NbH _{0.029}	10.52 ± 0.015	2.89 ± 0.04	1.31 ± 0.15 (1.69 ± 0.15)	2.75 ± 0.08	300 ± 8
NbH _{0.06}	10.43 ± 0.015	5.99 ± 0.04		6.11 ± 0.07	662 ± 7
NbH _{0.09}	9.26 ± 0.04	9.15 ± 0.04	9.68 ± 0.25
NbH _{0.2}	10.63 ± 0.03	19.46 ± 0.05	

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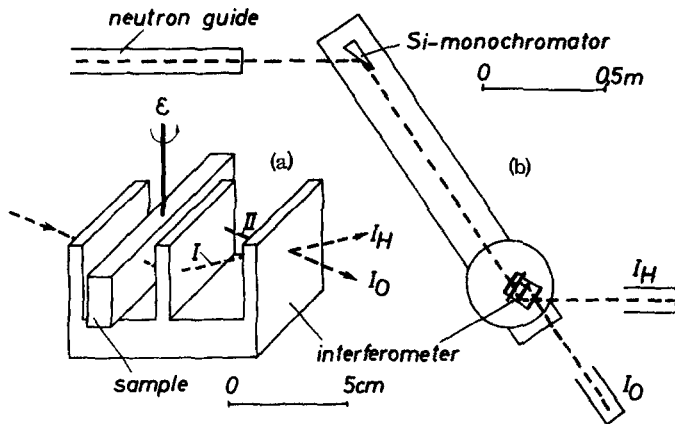


FIG. 1. Sketch of the interferometer setup (b) and of the interferometer crystal (a).

dances N_i as $\bar{b} = \sum_i N_i b_i / \sum_i N_i$. Since the scattering lengths b_i are known in distinct cases, the atomic abundances can be determined with a high sensitivity. The advantage for the investigation of the metal-hydrogen system is the rather large scattering length of H and D; $b_H = -3.741 \pm 0.001$ fm, $b_D = 6.674 \pm 0.006$ fm, $b_V = -0.408 \pm 0.002$ fm, $b_{Nb} = 7.11 \pm 0.04$ fm.¹⁸ As soon as precipitates of hydrides exist within the sample, these act as neutron optical inhomogeneities destroying the coherence accordingly and causing small-angle scattering.

II. SAMPLE PREPARATION

Polycrystalline V and Nb samples with dimensions of about $60 \times 30 \times 10$ mm are used. After etching, the samples were hydrogen degased for 1 h at 1000°C within a

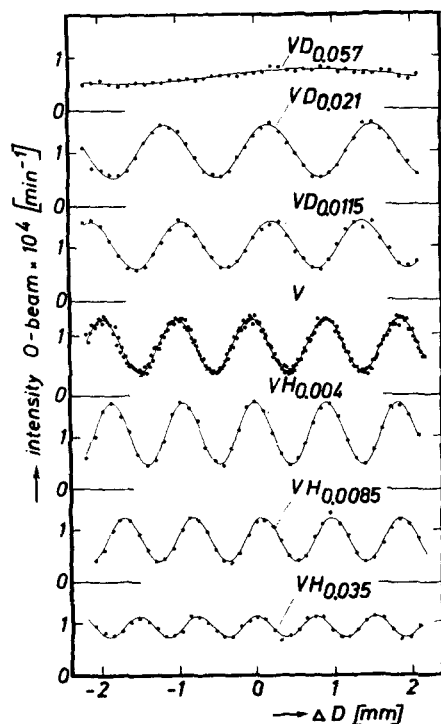


FIG. 2. Measured intensity oscillations for V-H and V-D samples.

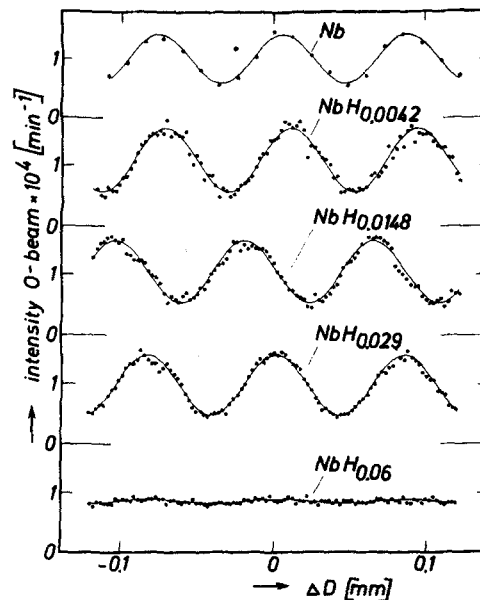


FIG. 3. Measured intensity oscillation for Nb-H samples.

vacuum of 10^{-6} Torr. Afterwards, the samples are loaded with H(D) at 600°C with H pressures ranging from 2.5 up to 850 Torr. The concentrations are determined by the difference of weight before and after the loading. The accuracy of weighing was ± 0.5 mg. The integral concentration values are given in Table I.¹⁹ Most of the samples are within the α phase because the β phase begins at 20°C for V-H at 2.2 at. % (we use N_H/N_V , etc. as percentage), for V-D at 4.05 at. %, and for Nb-H at 3.5 at. %.¹³

III. INTERFEROMETER MEASUREMENTS

The perfect crystal neutron interferometer¹⁵⁻¹⁷ was used at the high-flux reactor at Grenoble. A sketch of the experimental arrangement is shown in Fig. 1. The sample with a thickness D is rotated within the two coherent neutron beams I and II of the interferometer,

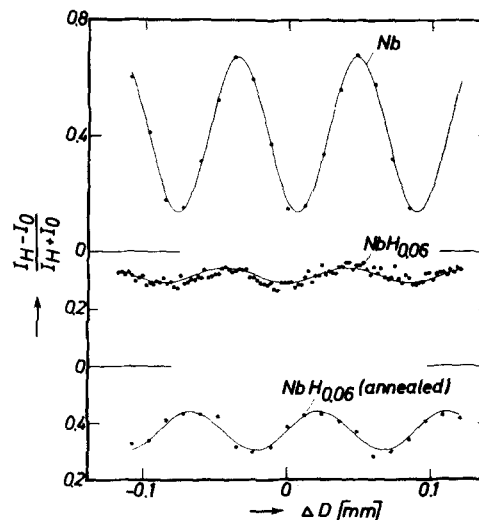


FIG. 4. Normalized intensity modulation for the Nb reference sample (upper) and for the nonannealed and annealed NbH_{0.06} sample which is partially in the β phase.

which causes a path difference ΔD of the beams, within the sample, of

$$\Delta D = D \left(\frac{1}{\cos(\theta_B + \epsilon)} - \frac{1}{\cos(\theta_B - \epsilon)} \right),$$

where θ_B is the Bragg angle of the interferometer reflection and ϵ is the angle of sample rotation.

According to the index of refraction n of the sample, a phase shift between the coherent beams is produced which yields an intensity oscillation of the beams behind the interferometer:

$$n = 1 - \lambda^2 \left(\sum_i N_i b_i \right) / 2\pi,$$

$$I_0 = A + B \cos(2\pi \Delta D / D_\lambda + C),$$

$$I_H = E - I_0,$$

where D_λ is the λ thickness, $D_\lambda = 2\pi / (\lambda \sum_i N_i b_i)$, λ is the neutron wavelength, A, B, C , and E are characteristic parameters of the interferometer, and I_0 and I_H are intensities of the beams behind the interferometer. For the metal (M)-gas(H) system the quantity $\sum_i N_i b_i$ can be divided into $\sum_i N_i b_i = N_M b_M + N_H b_H$, where $N_M b_M$ is determined by the measurement with a nonloaded sample and can include contributions from other impurities in the sample. The intensity modulation behind the interferometer can be measured, and a least-squares fit to the results gives values for the λ thickness D_λ . This quantity determines $\sum_i N_i b_i$, and, therefore, the concentration N_H / N_M can be obtained.

Typical results for selected runs for the V-H(D) system are shown in Fig. 2 and for the Nb-H system in Fig. 3. The variation of the periodicity as a function of the H and D concentration is visible. In addition, the results show a decrease of the contrast for higher loaded samples which are partially in the β phase where precipitates exist. Such hydride precipitates cause a spatial variation of the index of refraction Δn averaged along the neutron path. This results in a loss of coherence. To demonstrate this relationship between the sample homogeneity and the interference contrast

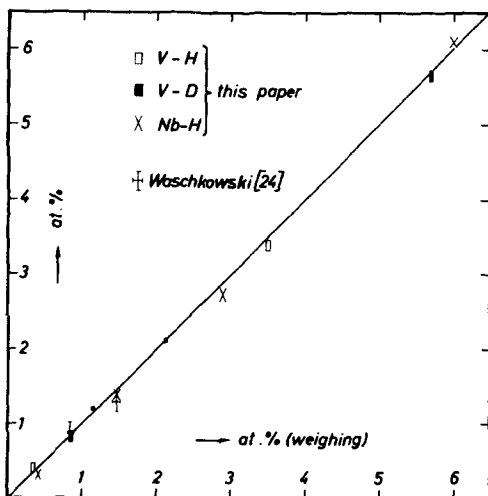


FIG. 5. Comparison of the results. The size of the symbols indicate the error bars.

the, $\text{NbH}_{0.06}$ sample was annealed at 175 °C for about 1 h in a nitrogen atmosphere. Figure 4 shows that the beam modulation can be increased by this procedure which indicates a higher amount of dissolved hydrogen within the samples. Some further samples with even higher H concentration (up to 20 at. %) show no beam modulation at all and could not be measured by the interferometer method.

The interferometer setup is used in the nondispersive position of two perfect crystals (Fig. 1) where the rocking curve is rather small, and, therefore, it is suited for small-angle experiments.^{20,21} For all samples shown in Figs. 2 and 3, the widths of the rocking curves were 2.6 ± 0.2 sec of arc, and no broadening could be observed. For the other samples, a broadening could be measured; e.g., for the $\text{NbH}_{0.2}$ sample, the width of the rocking curve is increased to 16.8 ± 0.4 sec of arc. The contrast of the O beam for the reference Nb sample was 50%, while for the $\text{NbH}_{0.06}$ sample, the contrast is reduced to 4% for the nonannealed and to 10% for the annealed sample. These results indicate that the degree of modulation is more sensitive to precipitates than the small-angle scattering.

IV. DISCUSSION

The least-squares fit to the measured oscillations determines the λ thickness and, therefore, $\sum_i N_i b_i$ of the sample. According to the statistics of the experiment, the accuracy of this quantity is $\Delta D_\lambda / D_\lambda \sim (3-5) \times 10^{-3}$ for the V samples and $(3-4) \times 10^{-4}$ for the Nb samples. The standard errors are calculated using Gaussian error distributions. The results for the H(D) concentrations in the samples are summarized in Table I.

To obtain more information about the precision of the measurement, the hydrogen concentrations were independently determined by the epithermal neutron scattering method at the Reaktorstation Garching.^{8,22} The remeasurement of the weight, density, and thickness agreed rather well with the previous results. The neutron measurement done at 5.2 and 1.26 eV gives the values shown in Table I.²³ A comparison with rather complete degased high-purity V and Nb samples showed, for our V and Nb reference samples, an "effective hydrogen content" of 0.25 ± 0.07 and 0.41 ± 0.11 at. %, respectively. Presumably, this amount corresponds to other gases which were not degased, such as O and N and metallic impurities. Therefore, the effective gas content of the reference samples is subtracted for the values in Table I.

A comparison of the results is shown in Fig. 5. The rather high accuracy of the interferometer method is demonstrated. It is 0.03–0.06 at. % which corresponds to 6–12 ppm by weight. An increase in sensitivity by a factor of 2–3 can be achieved if longer measuring periods are used. As the neutron interferometer measures an integral coherent interaction power $\sum_i N_i b_i$, the kind of gas to be determined has to be known for the analysis of the data. On the other hand, in comparing the different methods, it should be noted that in contrast to the sample-weighing method the neutron interfero-

meter and the scattering method allows one to scan the sample to obtain the spatial hydrogen distribution.

The loss of contrast for samples with precipitations could be used to obtain information about the size and the amount of such hydrides. A theoretical interpretation of this effect which is caused by a partial loss of coherence is necessary to use this effect for further solid-state-physics applications.

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