Hydrogen absorption in epitaxial W/Nb(001) and polycrystalline Fe/Nb(110) multilayers studied in-situ by X-ray/neutron scattering techniques and X-ray absorption spectroscopy

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Abstract

Hydrogen can be absorbed in large quantities by 100 Å thin Nb layers embedded in epitaxial W/Nb and polycrystalline Fe/Nb multilayers. The solubility and the hydrogen-induced structural changes of the host lattice are explored in-situ by small-angle neutron/X-ray reflectometry and high-angle diffraction. These measurements reveal for both systems that the relative out-of-plane expansion of the Nb layers is considerably larger than the relative increase of the Nb interplanar spacing indicating two distinctly different mechanisms of hydrogen absorption. In Fe/Nb multilayers, hydrogen expands the Nb interplanar spacing in a continuous way as function of the external pressure. In contrast, the Nb lattice expansion is discontinuous in epitaxial W/Nb multilayers: A jump in the Nb(002) Bragg reflection position occurs at a critical hydrogen pressure of 1 mbar. In-situ EXAFS spectroscopy also exhibits an irreversible expansion of the Nb lattice in the film plane for $p_{H2} > 1$ mbar. This can be regarded as a structural phase transition from an exclusively out-of-plane to a three-dimensionally expanded state at low and high hydrogen pressures, respectively.

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1. Introduction

Hydrogen in metals has been studied thoroughly since the early 50's, initially in view of metal-hydride applications in reactor technology. For hydrogen absorbing bulk materials it was generally found that hydrogen changes structural or magnetic properties, in certain cases quite drastically [1].

In recent years improvements of experimental techniques have allowed to study hydrogen absorption also in thin film structures. Fascinating hydrogen-induced property changes have been found, for example rare-earth films which reversibly switch their optical properties from metallic reflecting to transparent [2] or exchange coupled Fe/Nb [3] and Fe/V [4] multilayers which change their magnetic coupling and magnetoresistivity effect from antiferromagnetic to ferromagnetic and vice versa. In some systems like Mo/V [5], Fe/V [6] and Nb/Pd [7], giant lattice expansions caused by hydrogen absorption have been reported.

In the present paper we will focus on hydrogen induced structural changes. We will compare results obtained on epitaxial W/Nb (001) and polycrystalline Fe/Nb (110) multilayers with 100 Å Nb layer thickness. One should note here, that due to thermodynamic reasons only the Nb layers absorb hydrogen. We have never found evidence that Fe or W layers absorb noticeable amounts of hydrogen under the conditions applied during our experiments.

2. Sample preparation and structural characterization prior to hydrogen loading

The Fe/Nb multilayer was prepared by ion beam sputtering under UHV conditions onto a Si substrate at RT. The nominal composition of the film was [26 Å Fe / 100 Å Nb] with 10 double layers. X-ray characterization showed that the structure of the film

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is polycrystalline, but highly (110)-textured in the growth direction. The preparation procedure and the X-ray results are very similar to the ones presented in Ref. 8. The W/Nb film was prepared by magnetron sputtering onto an etched MgO(001) crystal at a substrate temperature of 200 °C. The nominal composition of the sample was [26 Å W / 100 Å Nb] with 60 double layers. Epitaxial growth could be achieved by depositing a 50 Å W buffer layer at 800°C prior to the growth of the W/Nb multilayer. Both samples have a 50 Å Pd capping layer to prevent oxidation and to facilitate hydrogen absorption.

Fig. 1a shows the results of X-ray scans with the scattering vector along the surface normal of the W/Nb multilayer. In the small-angle region, distinct Bragg reflections from the double layer period can be observed. At high scattering angles one recognizes solely the (002) Bragg reflections from the W and Nb layers besides the (002) and (004) reflection from the MgO substrate. Note that in the growth direction the Nb/Nb distances are slightly expanded compared to the bulk value due to the epitaxial stress. The epitaxial growth of the Nb and W layers and their orientation relative to the MgO substrate can be derived from Fig. 1b. It shows φ-scans from different (hkl) reflections where the scattering vector has large in-plane components (φ is the turning angle around the film's surface normal). All materials show four reflections in the -180° < φ < +180° region in agreement with the fourfold symmetry of these cubic crystals. Nb(103) and W(103) have peaks at the same φ as MgO(113) which indicates that the Nb and W (001) crystal planes grow under a turning angle of 45° onto the MgO(001) substrate planes.

3. Structural changes induced by hydrogen loading and concentration measurements

The samples, which were never before exposed to hydrogen, were charged from the gas phase at hydrogen pressures ranging from 10^{-4} to 900 mbar. Neutron/X-ray reflectivity and X-ray diffraction measurements were carried out in-situ at a temperature of T = 185°C. The reasoning for this temperature is twofold. First, at this elevated temperature the hydrogen absorption is relatively fast. In most cases it takes only minutes until equilibrium is reached. Second, the Nb/H bulk phase diagram shows a separation into a hydrogen rich and a hydrogen depleted Nb phase below a critical temperature of 171°C. This feature would severely complicate the interpretation of our experimental data.

One goal of the present study was to identify the amount of hydrogen-induced expansion of the Nb lattice as a function of the external hydrogen pressure. This expansion takes place mainly in the out-of-plane direction because the clamping of the film to the substrate largely hinders in-plane expansion. For the Fe/Nb multilayer, we found that a relative out-of-plane lattice expansion of 4.2 % can be achieved at a hydrogen pressure of 900 mbar (see also discussion of Fig.3). As expected, we observe that the Nb lattice stays in a single phase upon loading (the same holds for various other Nb thicknesses ranging from 20 Å to 1000 Å, see also Ref. 8).

In contrast, the epitaxial W/Nb multilayer shows a remarkably different behavior. As can be seen in Fig. 2a, the Nb (002) reflection moves to a smaller scattering angle for a low hydrogen loading pressure of 0.6 mbar. Raising the pressure to 1 mbar results in broadening of the reflection after a few hours. Note especially the shoulder that forms after 4 h on the left side of the Nb (002) reflection in Fig. 2b. After 11 h the intensity of the initial reflection has strongly diminished, while the shoulder has

developed into the main peak. No further changes could be observed later on. Our interpretation of this transformation is that above a critical hydrogen pressure the Nb lattice cannot keep its structural coherence to the W and the substrate lattice. It seems that the initially only slightly expanded Nb (marked as phase I) undergoes a non-coherent transition to a largely expanded phase at hydrogen pressures above 1 mbar (the latter is marked as phase II in Fig. 2b). We note that only a very small fraction of the Nb is still in phase I at 900 mbar, but the sum of the integrated intensities of the phase I and phase II peaks stays constant for all hydrogen pressures which reveals the non-destruction of the Nb epitaxy at the transition from phase I (low out-of-plane expansion) to phase II (high out-of-plane expansion).

Fig. 3 compares the hydrogen-induced relative increase of the out-of-plane Nb interplanar spacing (obtained by high-angle X-ray diffraction) for the Fe/Nb and W/Nb multilayers (see upper x axis). Compared to Fe/Nb, the lattice expansion of phase II in the W/Nb system is slightly higher.

Also shown in Fig. 3 is the relative increase of the Nb layer thickness of both systems obtained from analysis of small-angle X-ray and neutron reflectivity data. Remarkably, there is a huge difference in the expansion of the Nb layers at the microscopic level of interplanar spacing and at the macroscopic level of the film thickness independent of the epitaxial or polycrystalline nature of the samples. For 100 Å Nb film thickness the macroscopic expansion is roughly two times larger than the change in the atomic distances.

X-ray absorption spectroscopy (EXAFS) has been measured on the epitaxial W/Nb multilayer in order to determine the amount of in-plane lattice expansion associated with the structural phase transition discussed in Fig. 2. For a (001) oriented sample, EXAFS allows to distinguish between in-plane and out-of-plane expansion in a

unique way since the contribution of the neighboring atoms to the absorption spectrum is weighted by $\cos^2\alpha$. Here α is the angle between the X-ray polarization vector and the vector from the absorber atom to the backscattering atom in the first or second neighboring shell. In orienting the sample such that the electric field vector of the linearly polarized synchrotron beam is parallel to the Nb(001) direction (grazing incidence geometry) one is sensitive to Nb/Nb distances in the out-of-plane direction if the second nearest neighbor distance R_2 is analyzed. Using perpendicular incidence geometry highlights exclusively R_2 within the film plane. Note that R_2 in the in- and out-of plane direction is identical with the Nb lattice parameter in these directions. As expected, the nearest neighbor distance R_1 measured in both detection geometries is observed to be identical within the experimental error.

Fig. 4 shows the experimental results. "Out-of-plane" EXAFS spectra have been measured in the uncharged state (10^{-4} mbar), after 2.75 h, 4.25 h, 5.75 h and 14.5 h of hydrogen charging at 1 mbar, and at 900 mbar (Fig. 4a). The in-plane value for R_2 at 1 mbar was measured after 10 h of loading. The R_2 values for the uncharged state are close to the bulk value measured on a Nb reference foil. The out-of-plane values for R_2 closely resemble the X-ray diffraction results. At 900 mbar a maximum lattice expansion of 6.2 % has been analyzed from EXAFS while the corresponding X-ray value was 6.3 %. The in-plane lattice expansion at 1 mbar was determined to 1.84 %. Note that this value was taken after 10 h of hydrogen loading where, according to the X-ray results of Fig. 2b, the phase transition was already passed. At 900 mbar a maximum in-plane expansion of 2.5% was observed, which clearly shows that also after the phase transition the in-plane expansion is still much smaller than the out-of-plane expansion.

Fig. 5 shows the hydrogen concentration in the Nb layers in the H_2 pressure range up to 900 mbar. The data were determined by scattering contrast changes in neutron reflectivity measurements (see Ref. 8 for an extensive discussion). This method measures the *average* hydrogen concentration in the Nb layers. The concentration can have contributions from hydrogen absorbed at interstitials and hydrogen trapped in lattice imperfections. For 100 Å Nb thickness we observe a total amount of 80 or 100 [H]/[Nb] at.% for the W/Nb and Fe/Nb multilayer, respectively.

Another remarkable aspect of the data presented in Fig. 5 is that the plateau-like pressure region, at which most of the hydrogen is absorbed, is found more than an order of magnitude higher compared to bulk values. This again emphasizes the importance of the mechanical interactions between the substrate and the hydrogen absorbing layers for the solubility curves.

4. Discussion

Up to now it has generally been assumed that hydrogen absorption in thin films is comparable to the absorption process in bulk metals where by far the most dominating mechanism is that hydrogen occupies interstitial lattice sites in the host metal. This implies that there should not be a difference between relative layer expansion and lattice expansion. It was thought that the main difference between hydrogen absorption in bulk materials and thin films is only a geometrical effect, since the clamping of the film to the substrate restricts its expansion largely to the out-of-plane direction in contrast to the three-dimensional lattice expansion of bulk Nb (see Ref. 9 for an in depth discussion of this effect).

As can be seen in Fig.3, hydrogen absorption at interstitial sites is only partly responsible for the total amount of hydrogen incorporated in the films independent of

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whether the multilayers are polycrystalline or epitaxially ordered. To explain the data in Fig. 3, we certainly need to consider other absorption mechanisms resulting in layer expansion without necessarily inducing lattice expansion. Most likely is a trapping mechanism of hydrogen in lattice imperfections like grain boundaries, dislocations, voids etc. Such mechanism is well established for bulk materials but is a minor effect compared to the dominating absorption at interstitial sites (see references in [8]). However, the situation is much different for thin films, according to our observations. There are two likely locations where hydrogen could be easily trapped in lattice imperfections: at the interface regions and in cracks that might develop within the Nb layers during the lateral expansion process, i.e. the transition from phase I to phase II. This issue will be addressed in forthcoming experiments.

While there is only a minor difference in the maximum amount of hydrogen atoms absorbed in polycrystalline Fe/Nb and epitaxial W/Nb, there is a clear difference in the mechanical response of the crystal lattice. In contrast to Fe/Nb, where only a continuous lattice expansion could be observed upon hydrogen charging, we observed at a hydrogen pressure of 1 mbar a sudden jump in the out-of-plane lattice parameter for the case of W/Nb. Furthermore a significant (non-reversible) in-plane expansion is revealed at this condition by EXAFS spectroscopy. Our interpretation of the experimental results is that at 1 mbar hydrogen pressure a phase transition takes place from an exclusively one-dimensional out-of-plane lattice expansion at low hydrogen pressures to a three-dimensional expansion at high pressures.

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Figure Captions

Fig. 1. X-ray diffraction on W/Nb(001) multilayers (Cu K_α radiation)

(a) small-angle and high-angle regions in the out-of-plane direction

(b) φ scans (see text)

The dashed lines indicate the positions for the Nb(200) and W(200) bulk reflections.

Fig. 2. X-ray diffraction on W/Nb(001) multilayers

(a) as function of external hydrogen pressure

(b) time resolved measurements at 1 mbar (see text)

The dashed lines indicate the positions for the Nb(200) and W(200) bulk reflections.

Fig. 3. Comparison between the hydrogen-induced increase of the out-of-plane Nb interplanar spacing (filled symbols, see uppermost x-scale), and the increase of the Nb layer thickness (open symbols, see bottommost x-scale) for various hydrogen pressures

(a) for Fe/Nb(110) multilayers

(b) for W/Nb(001) multilayers (I and II indicate the expansions of phase I and

  phase II)

Fig. 4. Determination of second nearest neighbor distance changes R_2 in W/Nb multilayers by EXAFS spectroscopy for various external hydrogen pressures

(a) in the direction of the film normal

(b) in the film plane

(the large symbols at 10^{-4} mbar represent measurements on a reference foil)

Fig. 5. Hydrogen solubility curves of Fe/Nb (filled circle) and W/Nb (open circle) multilayers with 100 Å Nb layer thicknesses. The dashed line for bulk Nb is extrapolated from the literature.
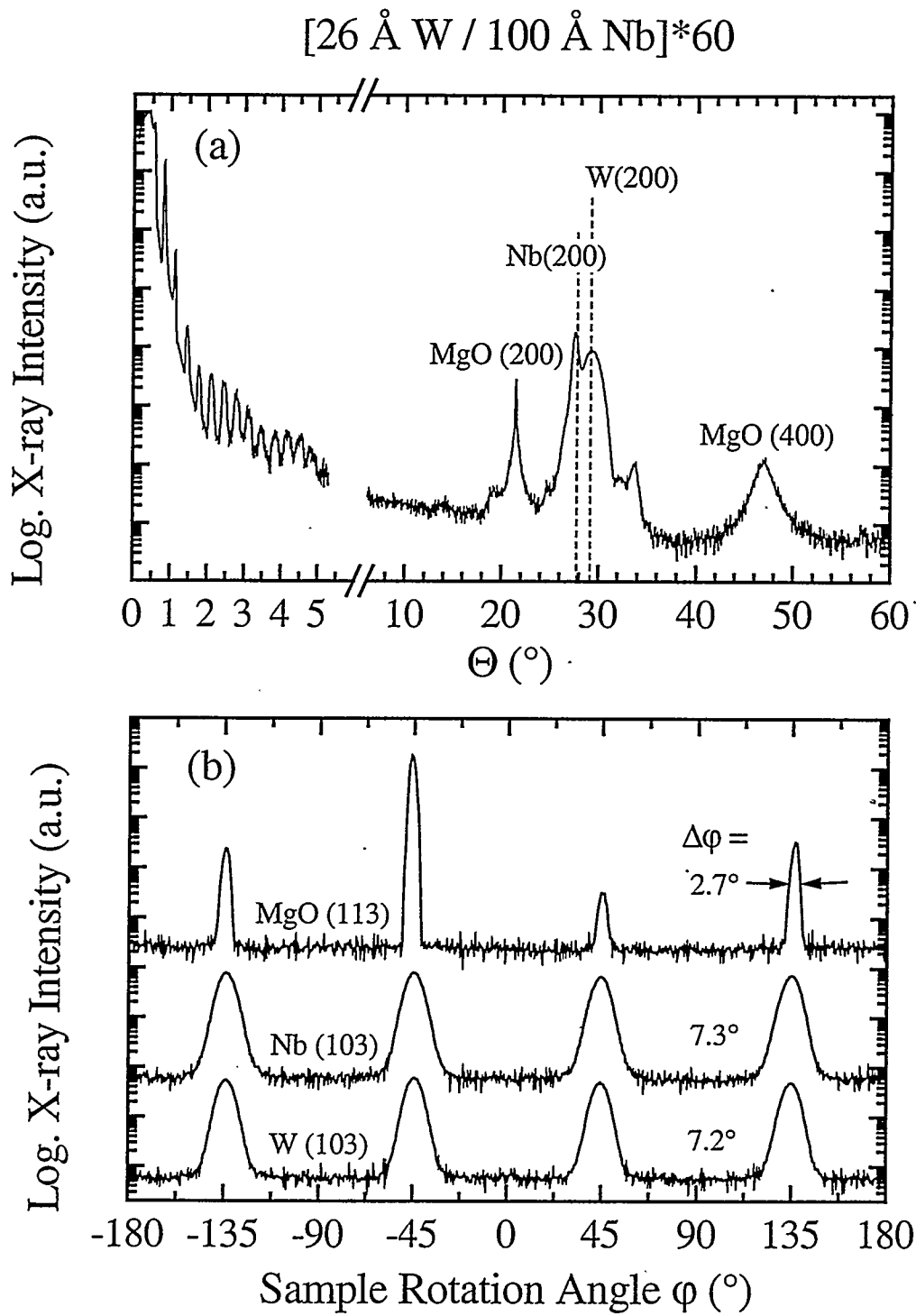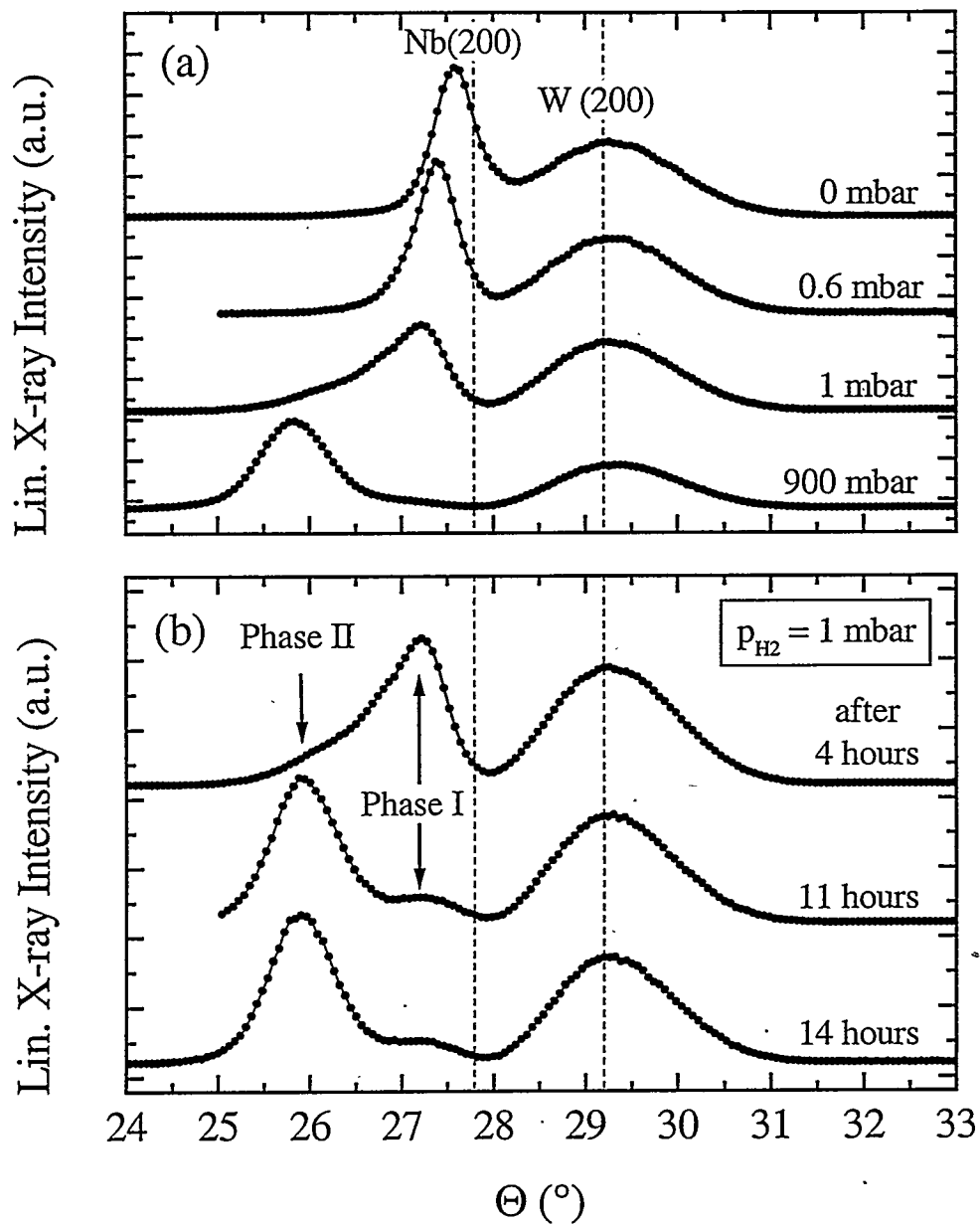
[26 Å W / 100 Å Nb]*60

Fig. 1, F. Klose et al.

[26 Å W / 100 Å Nb]*60

Fig. 2, F. Klose et al.

Increase of Nb interplanar spacing (%)

(a)

p_{H2} (mbar)

[26 Å Fe / 100 Å Nb]*10

(b)

I   II

p_{H2} (mbar)

[26 Å W / 100 Å Nb]*60
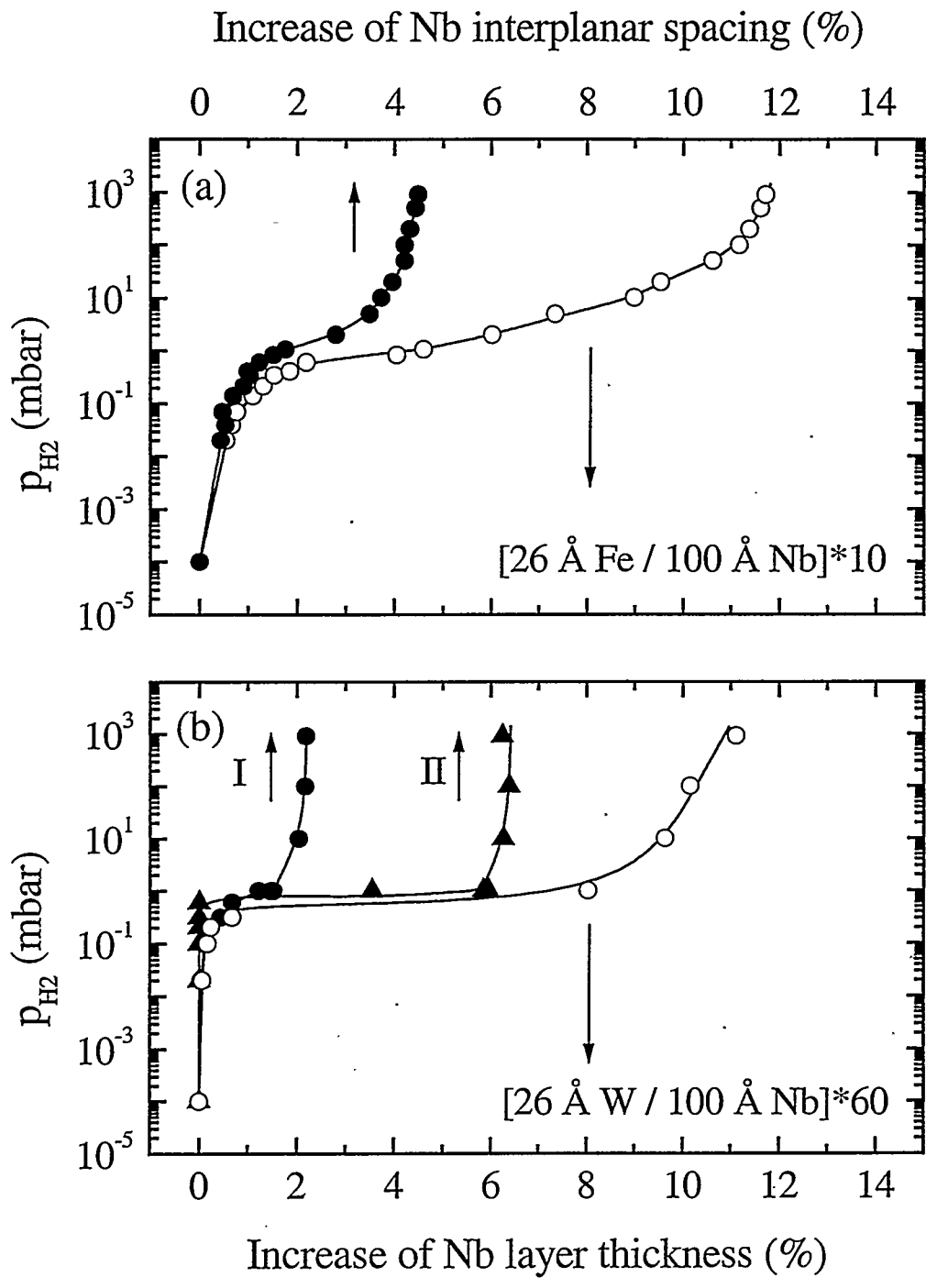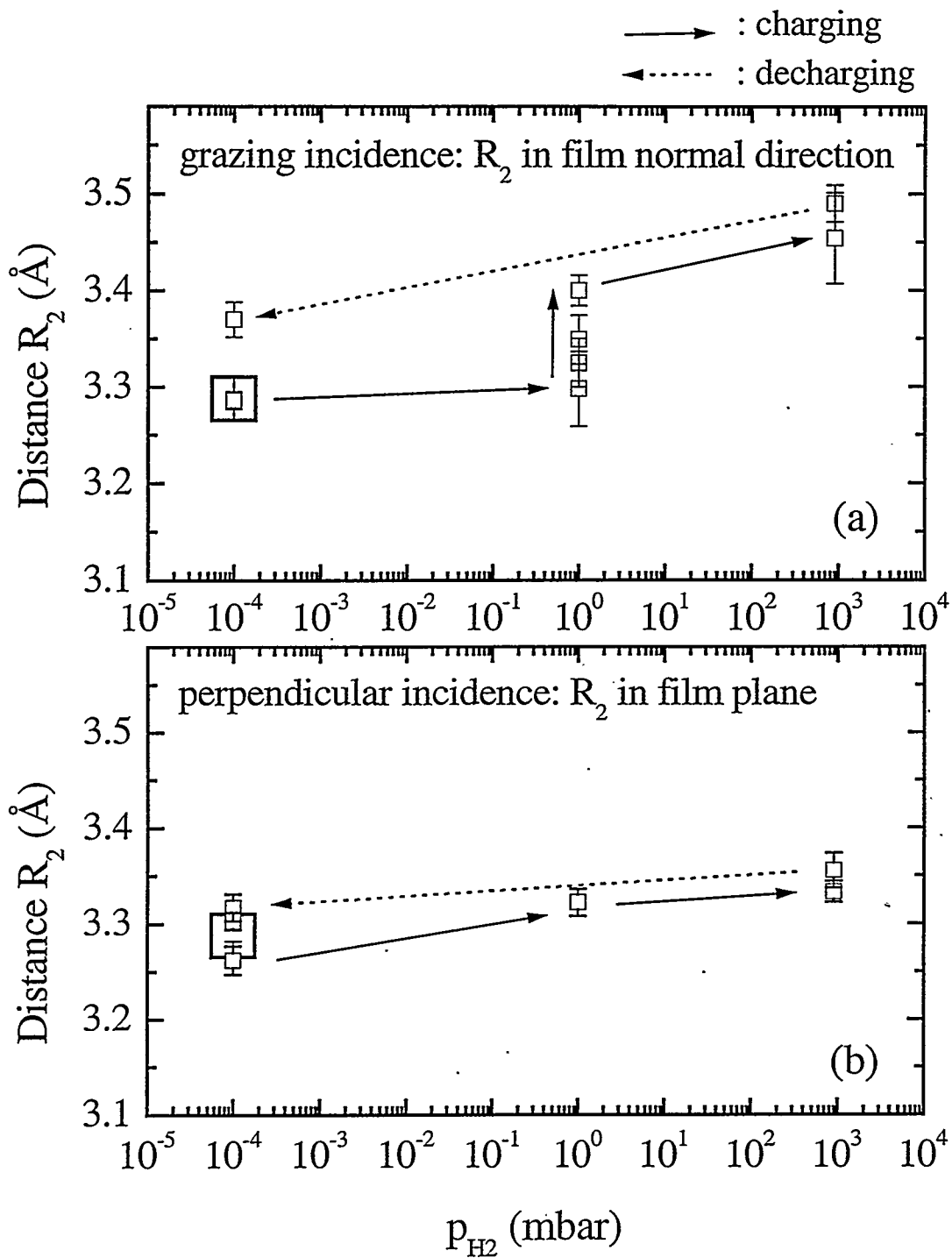
Increase of Nb layer thickness (%)

Fig. 3, F. Klose et al.

Fig. 4, F. Klose et al.
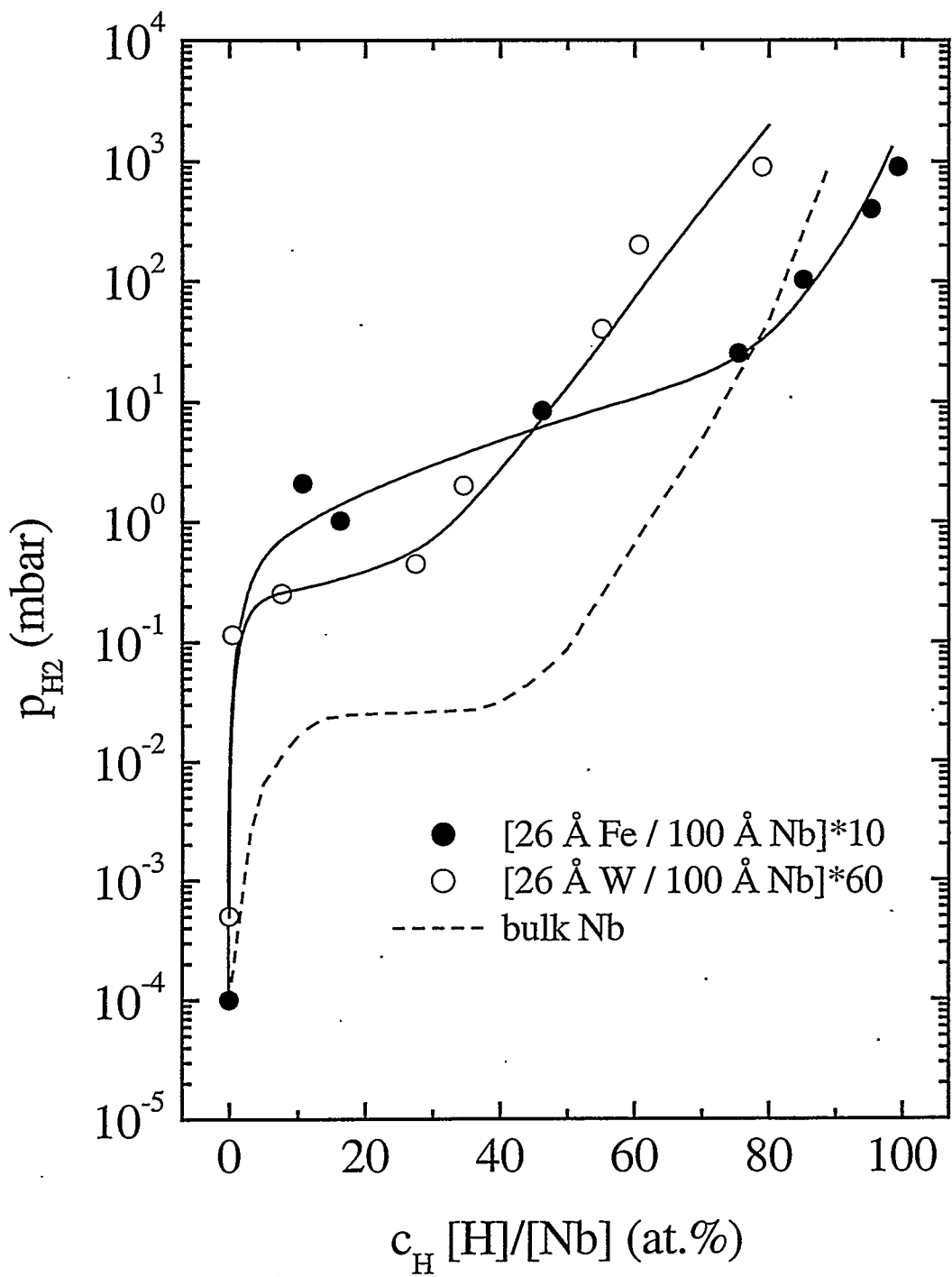
Fig. 5, F. Klose et al.