PHYSICAL REVIEW B, VOLUME 65, 113404

Anomalous layer expansion in thin niobium films during hydrogen absorption

Ch. Rehm,[1,2] H. Maletta,[1,*] M. Fieber-Erdmann,[1] E. Holub-Krappe,[1] and F. Klose[2,†]
[1]*Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany*
[2]*Argonne National Laboratory, Spallation Neutron Source Project, Argonne, Illinois 60439*

(Received 13 November 2001; published 15 February 2002)

Hydrogen absorption in Nb layers of Fe/Nb and W/Nb films was explored *in situ* by small-angle neutron/x-ray reflectometry, high-angle x-ray diffraction, and EXAFS spectroscopy. In addition to the hydrogen-induced Nb lattice expansion, the experiments reveal an anomalously large thickness expansion of the Nb layers. This expansion is interpreted to be caused by the rearrangement of Nb atoms, and the creation of additional lattice planes in response to the hydrogen-induced lateral lattice strain. This effect is likely the origin of the extraordinarily large hydrogen concentrations found in these films.

DOI: 10.1103/PhysRevB.65.113404 PACS number(s): 68.55.Ln, 61.10.−i, 61.12.Ha, 68.60.−p

Over the last few decades, hydrogen in bulk metals, intermetallic compounds, and semiconductors has attracted considerable research interest. Much of this research in recent years has focused on the behavior of hydrogen in thin films. As in the case of bulk materials showing the ability to absorb large quantities of hydrogen (for example, Nb, V, Pd, and the rare earth metals), the interaction of hydrogen with the host films can lead to significant modification of electronic, magnetic, and structural properties.[1] Exciting results have been achieved recently for thin metal films. Among these are Y and La thin films which reversibly switch their optical properties upon hydrogen absorption,[2] and Fe/Nb,[3] or Fe/V (Ref. 4) multilayers which reversibly switch their magnetic coupling and magnetoresistivity during hydrogen charging and decharging. In some systems such as Fe/V (Ref. 5) and Nb/Pd,[6] giant lattice expansions caused by hydrogen absorption have been reported.

For a theoretical understanding of the remarkable changes of film properties due to hydrogen charging, it is important to know how hydrogen is incorporated into the films, whether structural phase diagrams of bulk materials are applicable, and how hydrogen absorption depends on external parameters such as temperature and hydrogen pressure. Our work is motivated by the fact that current literature is not yet consistent in relating hydrogen concentration and associated structural effects. Most existing studies have relied solely on x-ray diffraction and have rarely used direct *in situ* methods for determination of hydrogen concentrations.

In this contribution, we present insights on the interrelation between hydrogen uptake and structural changes in thin Nb layers. Our results clearly indicate that the commonly accepted model of the hydrogen absorption process in thin films requires a revision. In particular, we studied the absorption process at *high* hydrogen concentrations and its reversibility. We present results obtained from *in situ* experiments on epitaxial W/Nb(001) and polycrystalline Fe/Nb(110) multilayers. The nominal compositions of the films were [26 Å W or Fe/X Å Nb], where X = variable thickness, repeated n times to optimize intensity for scattering experiments. In both systems, the Nb layers can easily be charged with hydrogen from the gas phase. Due to a large negative enthalpy of mixing, only the Nb layers of the multilayer absorb hydrogen. After each charging step, the hydrogen concentration was found to be equal in all Nb layers of the stack. We never found detectable amounts of hydrogen in the W or Fe layers (for further details, see Refs. 7 and 8).

Due to the strong interaction of neutrons with hydrogen atoms, neutron reflectivity is a direct and precise method to determine the hydrogen concentration in thin films with a depth resolution in the nanometer range (see Ref. 8 for an extensive discussion). Figure 1 shows the results of *in situ* measurements on Fe/Nb multilayers performed at the V6 (Hahn-Meitner-Institut Berlin) and the POSY2 (IPNS, Argonne National Laboratory) neutron reflectometers. Reflectivity curves have been measured on uncharged samples and at hydrogen pressures ranging from 10^{-3} to 900 mbar in increasing sequence. Figure 1 compares the uncharged and the final states at 900 mbar. Note that during these and all the following experiments, the temperature was kept constant at $T = 185\,°\mathrm{C}$. This temperature allows for reasonably fast hydrogen uptake dynamics (see Ref. 8) and is high enough to avoid a possible phase separation process, which is well

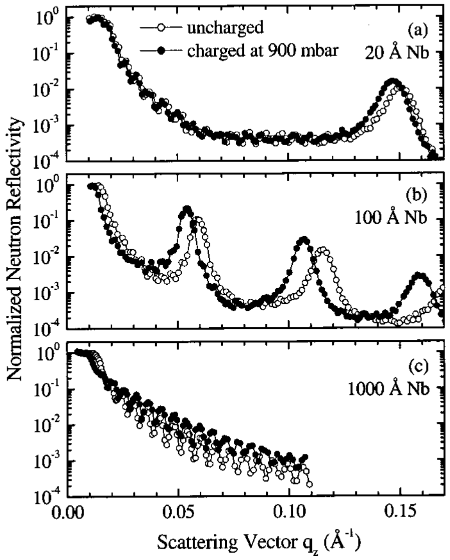

FIG. 1. Neutron reflectivity curves of Fe/Nb multilayers with various Nb layer thicknesses, measured after sample preparation (open symbols) and at a hydrogen pressure of 900 mbar (filled symbols).

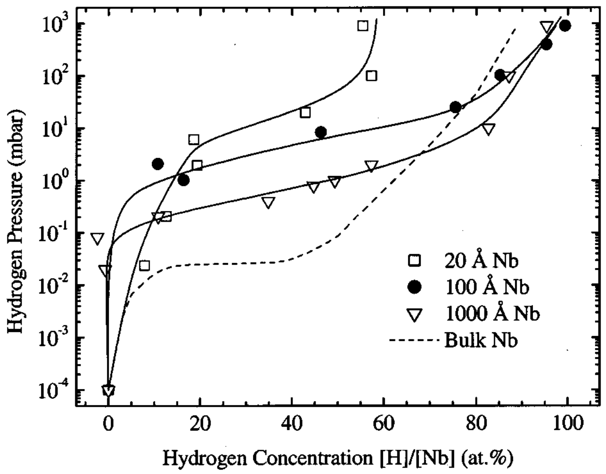

FIG. 2. Hydrogen solubility curves of Fe/Nb multilayers with various Nb layer thicknesses at $T = 185\,°\mathrm{C}$. The dashed line for bulk Nb is extrapolated from literature.

known for the bulk hydrogen/niobium system (for bulk Nb the critical temperature T_c is 171 °C). In addition to this, a saturating magnetic field was applied in order to avoid possible hydrogen-induced changes of the magnetic scattering of the samples, which could complicate the hydrogen concentration determination.[3] As can be seen in Fig. 1, the effect of hydrogen absorption on the reflectivity spectra is quite dramatic. The charged samples show strongly enhanced chemical Bragg peaks due to the increase in scattering contrast between Nb+H and Fe, and pronounced shifts in the Bragg positions indicating the expansion of the Nb film thickness. For samples with higher overall Nb content, one also observes a decrease of the critical q value for total reflection due to the lowering of the scattering length density in Nb upon hydrogen absorption.

The average hydrogen concentration values in the Nb layers were determined from the scattering contrast and Nb layer thickness changes in the reflectivity curves of Fig. 1 (see Ref. 8 for details). The results are displayed in Fig. 2. Very similar results were obtained on W/Nb multilayers.[7] Obviously, the hydrogen solubility in the Nb films strongly differs from that in bulk Nb and is dependent on the film thickness. The plateaulike pressure region of the curves, at which most of the hydrogen is absorbed, is more than an order of magnitude higher compared to the bulk values. The hydrogen concentration saturates for layers with large Nb thickness at one hydrogen atom per niobium atom, close to the corresponding value for bulk material. This is surprisingly high in view of the restricted possibility for the in-plane expansion of the Nb lattice. Films with thinner Nb layers ($d_{\mathrm{Nb}} < 50$ Å) show greatly reduced hydrogen concentrations. It has been emphasized that short-range electron spill over may suppress hydrogen solubility in the vicinity of the interfaces.[9] Our measurements, however, indicate that long-range mechanical interactions between the hydrogen absorbing Nb layers and adjacent nonabsorbing Fe layers are also quite important for the hydrogen uptake process. Only long-range mechanical effects can be responsible for the vastly different plateau pressure positions of the 100 and 1000 Å Nb films.

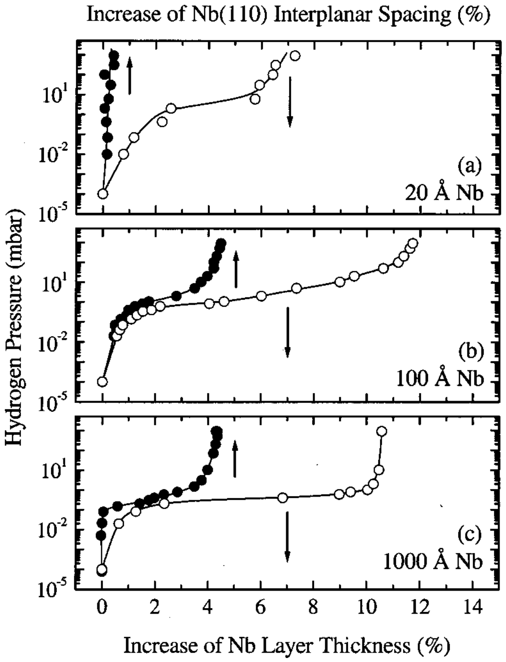

FIG. 3. Comparison between hydrogen-induced relative increase of the out-of-plane Nb(110) interplanar spacing (filled symbols), and increase of Nb layer thickness (open symbols) in Fe/Nb multilayers for various hydrogen pressures.

Up to now it has always been assumed that hydrogen absorption in thin films is comparable to the absorption process in bulk metals where by far the dominant mechanism is hydrogen occupation of interstitial lattice sites in the host metal. The main difference between thin films and bulk materials with respect to hydrogen-induced structural changes was thought to be the predominantly one-dimensional lattice expansion out of the plane of the films, caused by the adhesion of the film to the substrate, in contrast to the three-dimensional lattice expansion of bulk materials (see Ref. 10).

Our studies of the Nb films reveal a second, unexpected effect of equal importance to the interstitial lattice expansion. Analyzing scattering data of the *in situ* hydrogen loaded multilayers, we found a remarkable result as displayed in Fig. 3: There is a huge difference between the hydrogen-induced out-of-plane lattice expansion (determined by diffraction in the high-angle regime) and the expansion of the Nb layer thickness (determined by reflectivity measurements). The relative increase at the macroscopic level of the Nb layer thickness is much larger than the relative increase at the microscopic level of the interplanar spacing. Experiments on W/Nb multilayers[7] exhibit similar features. The details, however, depend on the actual thickness of the Nb layers (which will be discussed in a forthcoming paper). Hence, hydrogen absorption at interstitial sites and the related lattice expansion (widely assumed to be proportional to the concentration) are only partly responsible for the observed structural effects in the Nb films.

Recently, we have performed extended x-ray absorption

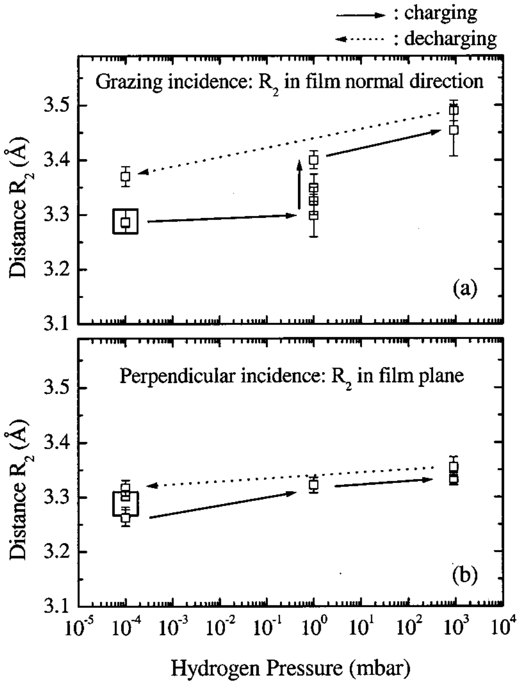

FIG. 4. Determination of second nearest-neighbor distance changes R_2 in W/Nb multilayers by EXAFS spectroscopy for various external hydrogen pressures: (a) in the direction of the film normal; (b) in the film plane (the large symbols at 10^{-4} mbar represent measurements on a reference foil). All data points represent equilibrium values, except the measurements at 1 mbar in (a). In this case it took 6 h before the R_2 value finally stabilized. These data points mirror the time dependence of the out-of-plane lattice expansion which is associated with a slow transformation of the initially well ordered epitaxial Nb films into much smaller domains (the data points were taken in increments of 1.5 h).

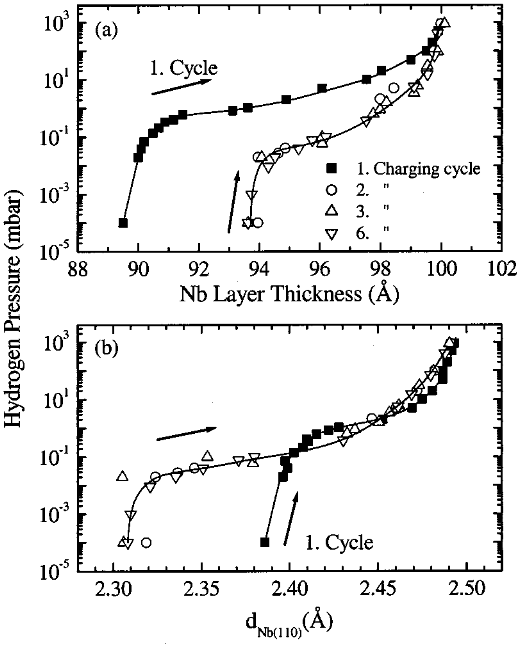

FIG. 5. (a) Expansion of Nb layer thickness upon repeated hydrogen charging and decharging, and (b) corresponding expansion of Nb(110) lattice planes in Fe/Nb multilayers.

fine structure (EXAFS) measurements on *in situ* hydrogen loaded Fe/Nb and W/Nb multilayers,[7] which enable us to suggest an interpretation of the anomalous results displayed in Fig. 3. The experiments were carried out at the RÖMO II station at HASYLAB, Hamburg, at photon energies near the *K*-absorption edge of Nb (18.985 keV) using the fluorescence detection mode. From such data one obtains selective information about structural changes occurring perpendicular to the layer and within the layer, by measuring at grazing and normal incidence geometries, respectively. For the (001) orientated epitaxial [26 Å W/100 Å Nb]×60 multilayer, EXAFS allows one to determine the out-of-plane distance R_2 between next-nearest Nb neighbors [results shown in Fig. 4(a)], as well as the corresponding in-plane values [see Fig. 4(b)]. The experiments confirm the out-of-plane expansion of 6.2% at 900 mbar obtained by x-ray diffraction. However, more importantly, they also reveal a small 2.5% in-plane expansion of the Nb lattice under hydrogen absorption.

The in-plane expansion of 2.5% and the corresponding out-of-plane lattice expansion of 6.2% result in a total increase in volume of 11.5%. This amount coincides with the relative increase of the Nb layer thickness expansion of 11.1% as determined from reflectivity experiments. Hence, one only has to take into account the boundary condition of *a fixed in-plane area* (i.e., a one-dimensional degree of freedom to expand macroscopically in the out-of-plane direction) in order to explain quantitatively the results in Fig. 3.

This model implies a three-dimensional rearrangement of Nb atoms caused by the massive mechanical lateral strain and its relaxation with increasing hydrogen charging within the Nb layers, especially near the interfaces to the substrate and the unloaded Fe or W layers. As a result, individual Nb atoms are squeezed out of existing lattice planes and start to form additional planes, which finally causes the anomalous large expansion of the layer thickness. Note that the newly created partial lattice planes imply a large amount of additional dislocations. The latter are evidenced by the fact that the out-of-plane diffraction peaks broaden significantly upon hydrogen absorption. For [26 Å W/100 Å Nb]×60, for example, we find a decrease in coherence length in growth direction from 90 Å after preparation, to 55 Å after hydrogen absorption at 900 mbar. Further evidence comes from the EXAFS measurements on this sample, which also indicate an increase in disorder upon initial hydrogen loading. The distance fluctuations between next-nearest Nb neighbors in out-of-plane direction, more precisely the mean square deviation value σ^2, increased from 0.0126 Å^2 in the noncharged state, to 0.0285 Å^2 at 900 mbar. Since lattice imperfections effectively trap hydrogen atoms, the new effect likely also explains the extraordinarily high hydrogen concentrations found in our Nb films (see, for example, Fig. 2) and the partial nonreversibility of the hydrogen absorption process itself, which we emphasized in Ref. 8.

The reversibility of the geometrical rearrangement of Nb atoms during repeated hydrogen loading cycles has been studied by conventional x-ray scattering for the case of the

[26 Å Fe/100 Å Nb]×10 multilayer (the layer thicknesses are *nominal* values). Figure 5 shows a comparison of the hydrogen-induced *macroscopic* Nb layer expansion (measured by reflectivity) and the *microscopic* expansion of the Nb(110) lattice planes (measured by high-angle diffraction). The displayed data sets represent changes in the out-of-plane direction, measured during the first three and the sixth charging cycles. Data are presented only for the increasing branches of the cycles. The decharging branch has been monitored too and was assumed to be completed when constant values for the Nb layer thickness and Nb lattice spacing were approached (typically after 12 h). In the as-prepared state, the Nb layer thickness was determined to be 89.5 Å and increased finally to 100 Å when a H_2 pressure of 900 mbar was applied. This corresponds to an enormous relative increase of 11.7% during the first charging. The removal of the hydrogen gas in the loading chamber resulted in a layer thickness of 93.8 Å. The subsequent charging cycles are reversible and show relative thickness increases of only 6.7%. Note that in all cycles the same maximum thickness of 100 Å is reached. The Nb lattice spacing shows just the reverse behavior. In this case the expansion during the first hydrogen loading was small. The lattice spacing increased only 4.4%, from 2.385 to 2.485 Å. Decharging the film resulted in $d_{\mathrm{Nb}(110)}=2.320$ Å. Note that this value is now considerably closer to the Nb(110) bulk value of 2.333 Å, which demonstrates the effect of *hydrogen-induced annealing*. The subsequent loadings are again reversible with relative increases of around 7%. The vast difference between macroscopic and microscopic expansion of Nb during the initial hydrogen loading indicates that a relaxation process takes place, which may easily be explained according to our model and involves formation of additional Nb planes. The rearrangement itself must be a one-time process since in the second and subsequent loading cycles, the relative layer and lattice expansions are almost equal. The first hydrogen loading of the corresponding W/Nb superlattice shows, compared to the polycrystalline sample, an even more dramatic behavior, since the initially well-ordered epitaxial Nb layers break down into much smaller domains.

In summary, we have investigated repeated hydrogen charging of Nb-containing multilayers in a combined study by x-ray, neutron, and synchrotron methods. We have found an anomalously large macroscopic expansion of the Nb layers during the initial loading of the films. In spite of their different structures (polycrystalline in the case of Fe/Nb and epitaxial in the case of W/Nb), the two multilayer systems essentially show the same behavior. This process is explained as a mechanical response of the Nb lattice to the enormous stress that acts on the films during hydrogen loading. Our results emphasize the importance of geometrical constraints and give new important insights into the hydrogen absorption process in thin films. These findings need to be taken into account in the experimental determination of hydrogen concentration in thin films.

The authors kindly acknowledge experimental assistance from R. Goyette/ANL, H. Fritzsche/HMI, and L. Tröger/HASYLAB, and useful discussions with W. Press and J.F. Ankner.

---

*Email address: Maletta@hmi.de

†Email address: FKlose@anl.gov

[1] H. Zabel, in *Encyclopedia of Materials Science and Technology* (Pergamon, New York, 2001).

[2] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London) **380**, 231 (1996).

[3] F. Klose, Ch. Rehm, D. Nagengast, H. Maletta, and A. Weidinger, Phys. Rev. Lett. **78**, 1150 (1997).

[4] B. Hjörvarsson, J. A. Dura, P. Isberg, T. Watanabe, T. J. Udovic, G. Andersson, and C. F. Majkrzak, Phys. Rev. Lett. **79**, 901 (1997).

[5] G. Andersson, B. Hjörvarsson, and H. Zabel, Phys. Rev. B **55**, 15 905 (1997).

[6] Q. M. Yang, G. Schmitz, S. Fähler, H. U. Krebs, and R. Kirchheim, Phys. Rev. B **54**, 9131 (1996).

[7] F. Klose, Ch. Rehm, M. Fieber-Erdmann, E. Holub-Krappe, H. J. Bleif, H. Sowers, R. Goyette, L. Tröger, and H. Maletta, Physica B **283**, 184 (2000).

[8] Ch. Rehm, H. Fritzsche, H. Maletta, and F. Klose, Phys. Rev. B **59**, 3142 (1999).

[9] B. Hjörvarsson, J. Rydén, E. Karlsson, J. Birch, and J.-E. Sundgren, Phys. Rev. B **43**, 6440 (1991).

[10] G. Song, M. Geitz, A. Abromeit, and H. Zabel, Phys. Rev. B **54**, 14 093 (1996).