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High-resolution electron-energy-loss spectroscopy of hydrogen chemisorption at Nb(100) surfaces: Evidence for subsurface absorption sites

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The interaction of hydrogen with Nb(100) surfaces has been studied by use of high-resolution electron-energy-loss spectroscopy, low-energy electron diffraction, and work-function measurements. Experimental results indicate that hydrogen absorbs on Nb(100) at tetrahedral sites below the surface. Hydrogen in these subsurface sites exhibits reversible temperature-dependent effects compatible with the self-trapped subsurface sites proposed to account for the novel kinetics of hydrogen uptake by Nb.

The interaction of hydrogen with group-V*B* metals is a subject of considerable interest because of the technological importance and novel physical properties associated with these systems.[1-10] The extremely high mobility of hydrogen in the group-V*B* metals (V, Nb, and Ta), the unusual kinetics of hydrogen absorption exhibited by these metals, and the fact that group-V*B*-H systems serve as prototypes for understanding the behavior of interstitial atoms in metals represent some of the factors which have contributed to the interest in metal-hydrogen systems. In the present paper, attention is focused on a particular aspect of the interaction of hydrogen with group V*B* metals involving the role played by the surface. Several experimental and theoretical studies of the Nb-H system have concluded that Nb(110) exhibits a strongly bound subsurface state,[3,5-8,11] but the importance of this subsurface state in the hydrogen absorption kinetics of Nb is a matter of controversy.[7,9] An important aspect of kinetic models that includes the "subsurface bonding" is that these states act as a barrier (or valve) allowing reversible diffusion of hydrogen into the bulk above a system specific temperature.[8] Photoemission studies of hydrogen chemisorption on Nb(110) have revealed a reversible temperature dependence of a hydrogen induced bonding orbital.[11] These photoemission results are consistent with the existence of a subsurface state for Nb(110)/H[8,11] and support the surface "valve" hypothesis. Corresponding hydrogen-induced structures in photoemission spectra for Ni, Pd, and Pt exhibit an irreversible temperature-induced phase transformation,[12] and no surface valve effects have been noted from uptake experiments.

In this paper, we report the experimental observation of subsurface hydrogen on Nb(100) by high-resolution electron-energy-loss spectroscopy (EELS). The hydrogen subsurface sites are found to be similar in nature to the tetrahedral hydrogen sites of bulk niobium hydride. The EELS technique was selected for this study because of the well-established high sensitivity of EELS to vibrational modes of hydrogen at metal surfaces. The Nb(100) surface was selected from the high-symmetry Nb(crystal face)-H systems based on the simpler distribution of bulk hydrogen sites versus depth and the nonmixed nature of the vibrational modes perpendicular to the surface.

Figure 1 illustrates the crystal structure of the β phase of bulk NbH and several possible near-surface configurations involving hydrogen. Neutron and electron diffraction experiments[1] have established that hydrogen atoms occupy tetrahedral sites in the bcc Nb lattice. Ho, Tao, and Zhu[13] have performed first-principles total-energy calculations for the β phase of NbH and obtained lattice constants, bulk moduli, heats of formation, as well as vibrational frequencies of hydrogen and deuterium atoms in the Nb lattice. These studies verify the tetrahedral site as the preferred (lowest-energy) location. Figure 1 also illustrates three inequivalent tetrahedral locations for hydrogen atoms in the real-space unit cell at the surface of Nb(100). Normal modes of hydrogen atoms in the tetrahedral sites correspond to displacements along the [001] and [010] directions. Optical-mode phonon energies for these displacements have been calculated by Ho *et al.* and compared with experimental data.[14-16] Table I summarizes these results along with some surface vibrational data to be discussed. Examination of Fig. 1 shows that the "soft" [100] modes associated with the $(\frac{1}{2},-\frac{1}{4})$-type sites and the "hard" [100] modes associated with the $(\frac{1}{4},-\frac{1}{2})$-type sites yield dipole moments perpendicular to the surface that should be observable as dipole losses by EELS. The phonon energy for the $(\frac{1}{2},-\frac{1}{4})$ site may be slightly shifted from that of the $(\frac{1}{2},-\frac{3}{4})$ site due to lattice relaxation. The dipole moment of deeper sites may not be observable due to screening by conduction electrons.

Previous EELS studies of the initial stage of oxide formation at Al(111) surfaces[17,18] and of oxygen and nitrogen interactions with Ti(0001)[18] surfaces have shown that vibrations of subsurface chemisorbed atoms can be detected using this technique. The sensitivity of vibrational spectroscopy to hydrogen atoms and the ability of EELS to probe subsurface atoms suggests that EELS is a good technique to study the novel chemisorption behavior of hy-

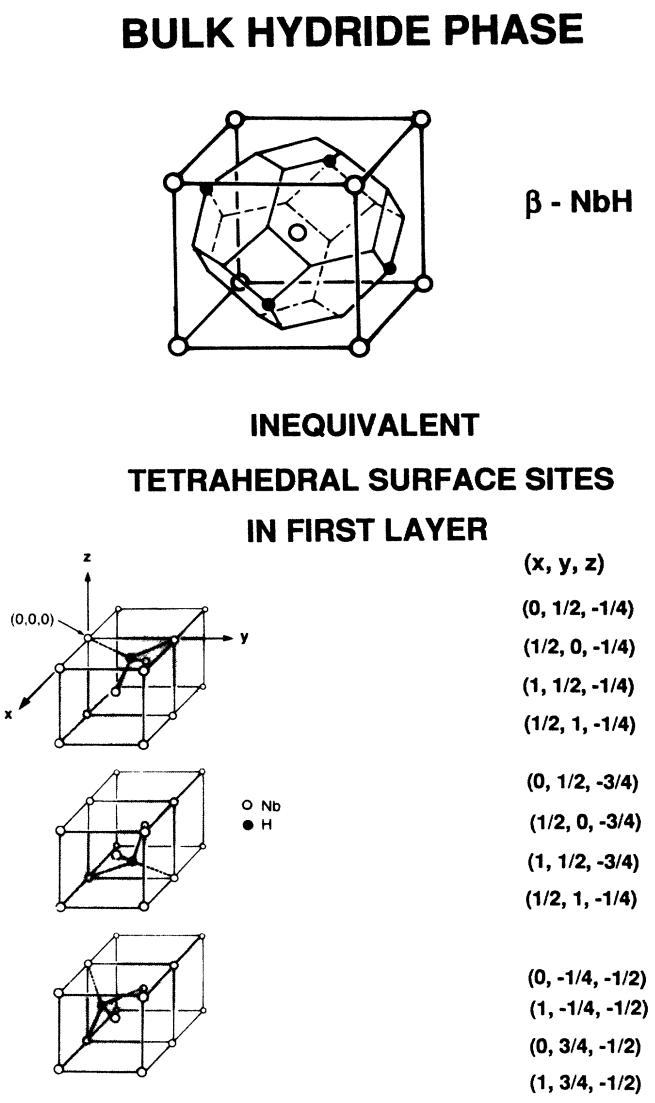

FIG. 1. Upper panel: real-space description of the bulk NbH. Hydrogen atoms are located at tetrahedral sites in the bcc Nb lattice. Lower panel: real-space description of the Nb(100) surface illustrating the three inequivalent tetrahedral locations where adsorbed hydrogen atoms reside.

TABLE I. Optical phonon energies.

		ω_{001}	ω_{010}	T (K)
Expt.[a]	α-$NbH_{0.05}$	106	163	300
	β-$NbH_{0.87}$	119	164	300
	γ-NbH	122	166	...
Calc.[b]	(anharmonic)	121	180	...
	(harmonic)	128	178	...
EELS[c]		117	168	300
		130		

[a]β-NbH, Eckert *et al.*, Phys. Rev. B **27**, 1980 (1983). α-NbH, Magerl *et al.*, Phys. Rev. B **27**, 927 (1983).
[b]Ho *et al.* (Ref. 13).
[c]This work.

drogen at group-V *B* metal surfaces.

Our experiments were carried out using 1-cm-diam 1-mm-thick single crystals of Nb(100) cut to within 1° and polished to a mirror finish. The crystals were cleaned by argon ion sputtering and annealed at high temperatures, and characterized by LEED and Auger electron spectroscopy prior to work function and EELS measurements. Work function measurements were taken using the field emission retarding potential method, and EELS measurements were carried out using a modified ELS-22 spectrometer which has been described previously.[19] The Nb surface was found to be particularly difficult to clean and maintain clean; all measurements were carried out under sub 10^{-10}-Torr vacuum conditions.

Figure 2 displays EELS spectra obtained from Nb(100) after exposure to 5 L hydrogen (1 L$=10^{-6}$ Torr sec). Higher hydrogen doses did not result in significant changes in the spectra; therefore, the spectra are representative of a "saturated" surface. The narrow peak at 62 meV is produced by trace amounts of surface oxygen. Calibration experiments involving oxygen doses and Auger and EELS analysis established that the surface concentration associated with the oxygen peak in the spectra of Fig. 2 is of the order of 1%.

The broad peak (which is actually several peaks superimposed) centered around 127 meV results from hydrogen. This assignment was verified by observing the isotope shift for equivalent doses of deuterium. Several striking features of the H-Nb(100) spectra are immediately apparent. First, the hydrogen loss peak is very broad compared to the elastic peak and the oxygen loss peak. Second, the scattering cross section (strength of loss signal) for hydrogen (and deuterium) is quite low compared to other similar systems, for example, H-W(100) which we have also investigated in some detail. Additional novel features associated with the H-Nb(100) system are the absence of work-function change on adsorption of hydrogen ($\Delta\phi \leq 0.1$ eV) and the reversible temperature dependence change in EELS loss features, illustrated in Fig. 3. Conditions under which this phenomenon occurred were carefully monitored (using a mass spectrometer) to make sure that a desorption effect was not being observed. Counting electronics were gated off during heating pulses (at 60 Hz) to avoid problems arising from stray fields. Also, the persistence of the annoying oxygen peak at 200 °C clearly shows that heating is not affecting the detection of loss signals.

These features, illustrated in Figs. 2 and 3, are consistent with the conclusion that exposure of Nb(100) to hydrogen results in hydrogen atoms located at tetrahedral sites *below* the surface. Small work-function changes and reduced scattering cross sections (in relation to those established for surface species) have been observed in the O-Al(111) system[17] which exhibits underlayer site occupation. The width of the hydrogen related loss peaks and their asymmetric shape, apparent in Figs. 2 and 3, suggests multiple modes associated with the various inequivalent tetrahedral sites shown in Fig. 1. We have studied the LEED intensity versus voltage properties of the (0,0) beam for clean Nb(100) and the hydrogen-saturated Nb(100) surface. These data (not shown) are

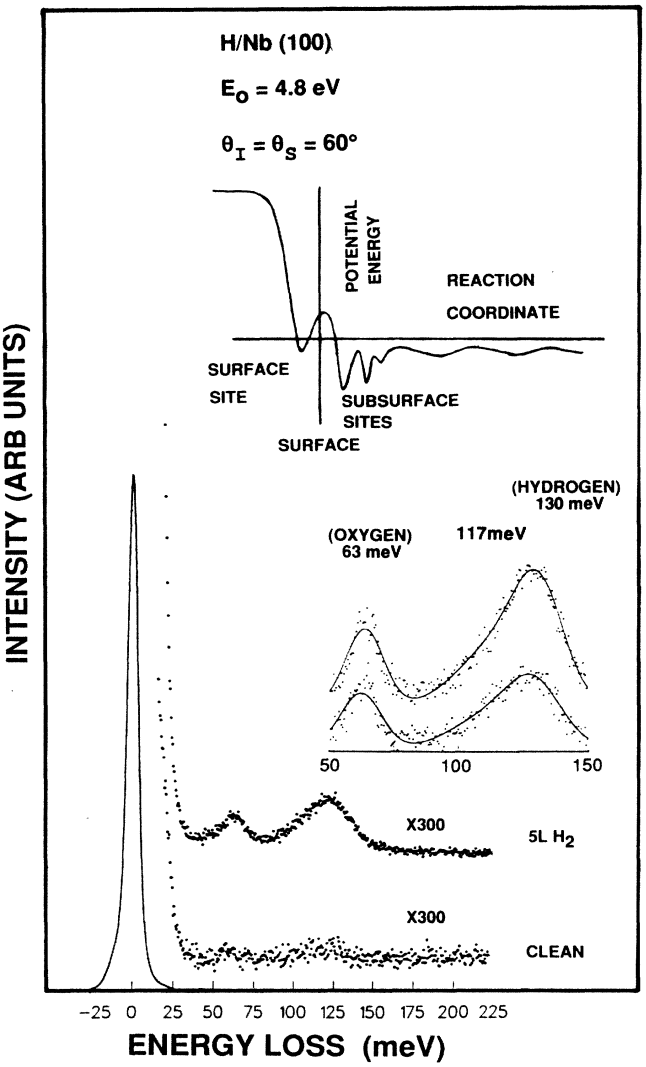

FIG. 2. EELS spectra for 5 L (1 L = 10^{-6} Torr sec) dose of hydrogen applied to Nb(100). Lower inset displays Gaussian-curve fit for the loss peaks. The 63-meV peak corresponds to ~0.1 monolayers of *surface* oxygen. The 117- and 130-meV loss peaks are produced by *subsurface* hydrogen located at inequivalent tetrahedral sites in the Nb lattice. Screening reduces the hydrogen-derived loss signals by roughly a factor of 5 compared with corresponding loss signals from *surface* hydrogen on W(100). Upper inset displays a reaction coordinate diagram for the subsurface sites.

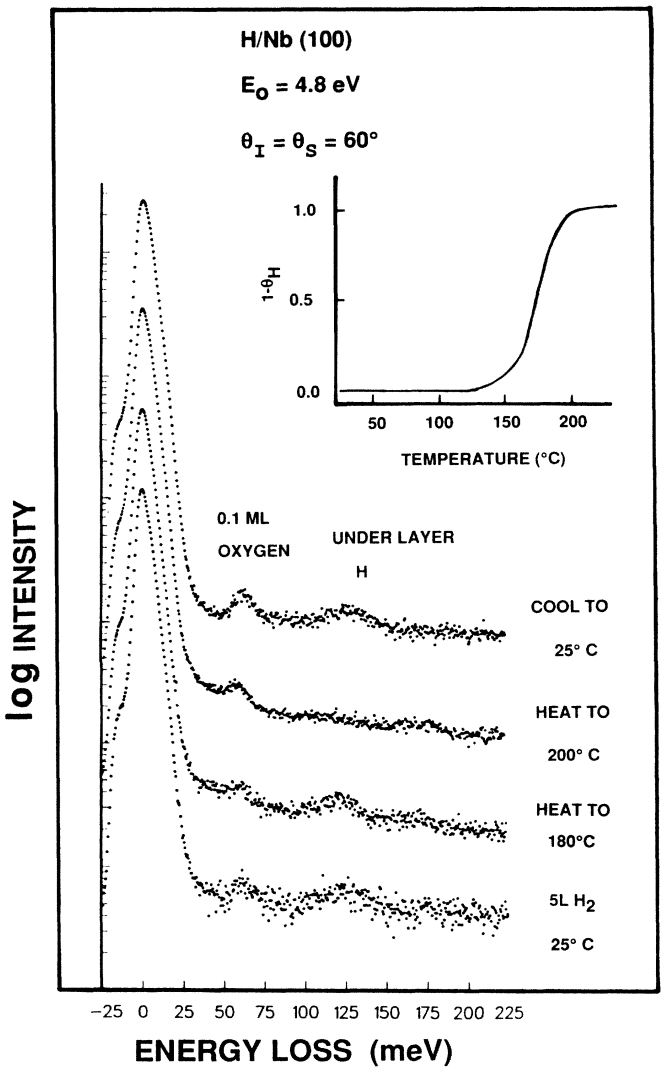

FIG. 3. Reversible temperature dependence for the subsurface hydrogen-loss features of H-Nb(100). The log intensity scale permits the absolute intensity of all peaks to be displayed. Elastic peak signal and oxygen loss peak signal do not change with temperature. Hydrogen-derived loss signals disappear above $T = 180\,^{\circ}C$. Inset illustrates temperature dependence of subsurface hydrogen concentration (as determined by EELS) vs temperature.

consistent with hydrogen atoms in ordered sites near the surface.[20] The quality of our EELS data permits decomposition of the asymmetric structure at 127 meV into two peaks at 118 and 130 meV by Gaussian fits, as shown in Fig. 2. The higher energy loss peaks at 168 meV (which is barely observable in Fig. 3) exhibit a similar width as would be expected. The energies of these hydrogen related surface vibrational modes are very close to the modes for γ NbH established by experiment[14–16] and obtained by Ho *et al.*[13] from their calculations. These vibrational energies are summarized in Table I.

The reversible phase transition observed to occur as temperature is varied around 200 °C lends support to the "surface valve" model which attempts to account for uptake behavior and other phenomena described in this paper. Previous observations of temperature-dependent effects associated with hydrogen on Pt surfaces based on photoemission have led to speculation that the hydrogen may still be near the surface but in a location in which the electronic excitation would not be observed by photoemission.[21] Our EELS results confirm that the hydrogen occupies sites near the Nb(100) surface which are depleted as temperature is increased, and that the process is reversible. It is unlikely that the subsurface hydrogen atoms simply migrate to other near-surface sites upon heating. If this were the case, one would expect a temperature-dependent

occupation of the sites which would be evident from the hydrogen loss peak strengths. Our data suggest the subsurface hydrogen atoms are driven into the bulk at $T > 200\,^{\circ}C$. A qualitative description of the hydrogen-Nb(100) surface potential which has emerged from our work, and the work of others, is illustrated in the inset in Fig. 3.

It has been suggested that the disappearance of the "subsurface bonding" state in certain bcc metal alloys would account for their rapid uptake of hydrogen at room temperature. We are preparing to study the anticipated disappearance of the subsurface bonding state for Nb metal alloys that show rapid hydrogen uptake kinetics at 25 °C. Further studies involving hydrogen adsorption on Nb(100) at low temperatures are in progress to search for a surface chemisorbed phase. Finally, corresponding studies of hydrogen absorption on the Nb(110) surface are in progress.

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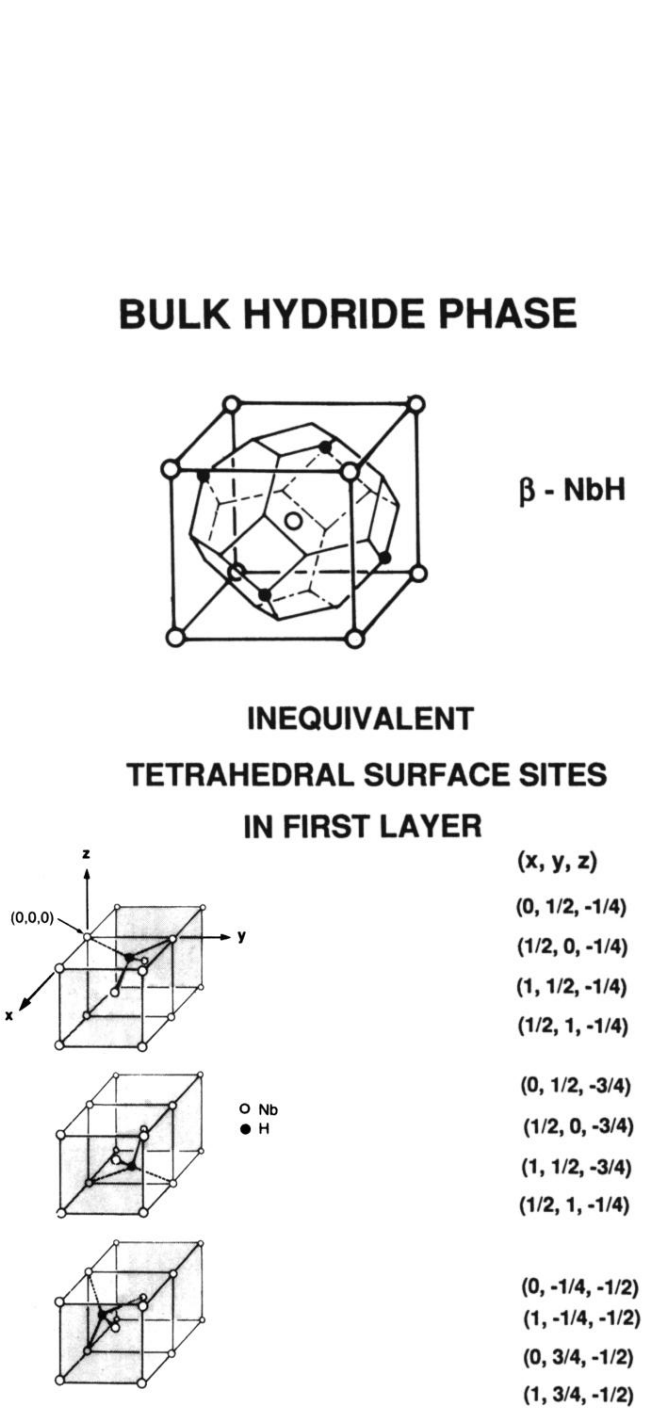

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