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Initial stages of hydride formation: Hydrogen on Ce(001)

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The interaction of hydrogen with a Ce(001) single-crystal surface has been investigated with use of angle-resolved uv photoemission spectroscopy (ARUPS), electron-energy-loss spectroscopy (ELS), and low-energy electron diffraction (LEED). Hydrogen uptake from the gas phase results in a cerium-hydrogen solid-solution phase, which is evidenced by a 4.2-eV structure in UPS and a 3-eV H-derived interband transition in ELS. After larger H_2 exposures (>500 L) a low-energy plasmon feature at 1.6-eV loss energy signals the formation of a surface hydride phase of dihydridelike stoichiometry [1 langmuir (L)$\equiv 10^{-6}$ Torr sec]. The surface disorders as a result of hydride formation. It is suggested that hydrogen occupies tetrahedral sites in the solid solution and dihydridelike phases. Annealing of H_2-exposed Ce surfaces to 300—400 °C induces the population of octahedral sites by hydrogen in an activated process, and a corresponding UPS band is detected at 3.4 eV. A H-induced hexagonal reconstruction of the Ce(001) surface with a complex LEED pattern is observed after annealing to >400 °C, and the characteristic features of the UPS of this reconstructed surface suggest hydrogen in both tetrahedral and octahedral sites near the surface.

I. INTRODUCTION

The properties of metal-hydrogen systems are of both fundamental and technological interest.[1] On the one hand, the interaction of the H_2 molecule with a metal surface is the prototype of a molecule-solid reaction, and as such is of basic scientific relevance. The participation of hydrogen in surface reactions of the practical catalytic type, on the other hand, has provided further impetus to study the adsorption of hydrogen, and indeed, most chemisorption studies have been performed on surfaces of the important catalysts of the group-VIII metals. Different forms of chemisorbed hydrogen have been detected by various spectroscopic techniques,[2–5] and an overlayer model and an underlayer model—the latter involving hydrogen in subsurface positions—are presently under discussion.[3,5–8] Whereas the aforementioned studies have concentrated on characterizing the initial stages of the metal-hydrogen interaction, a great deal of scientific effort has also been devoted to establishing the physical and chemical properties of the end products of the metal-hydrogen reaction, namely, those properties of the metal hydrides. Again, basic scientific interest and potential technological applications (see, e.g., Refs. 1 and 9) have cooperated to stimulate increased activities in the field of metal hydride research. Thus, the electronic properties of metal hydrides have been studied extensively both by experimental and by theoretical methods,[10] and a fairly consistent picture of the electronic band structure and derived physical properties has emerged for monohydrides, dihydrides, and trihydrides by now. However, with few exceptions,[11] surprisingly little work has been directed towards investigating the low-x solid solution phases of MH_x compounds, in particular those phases of the technologically important electropositive early-transition metals.

The present work was aimed at contributing in closing this gap, and we report here the results of a spectroscopic study of the interaction of H_2 with a cerium (001) single-crystal surface. To our knowledge, this is the first study of hydrogen interaction on a well-defined single-crystal surface of a rare-earth metal, and this proved rewarding because of the structural information which may be obtained on such a periodic surface.

The hydrides of the light rare-earth metals, cerium in particular, provide a number of interesting properties, including phenomena such as core-hole screening effects associated with $4f$ localization in x-ray photoemission spectroscopy (XPS) experiments, a metal-to-semiconductor transition as a function of hydrogen concentration at $x \approx 2.75$, and the very recent observation of heavy-fermion-like behavior.[12] Cerium hydrides of various stoichiometries CeH_x ($2 \lesssim x \lesssim 3$) have been studied using photoemission and inverse photoemission by Schlapbach and co-workers,[13–15] by Fujimori *et al.*,[16–18] and by Peterman *et al.*[19] Fujimori *et al.* also reported augmented plane wave linear combination of atomic orbitals calculations to determine the band structure and densities of states.[17,18] In brief, hydrogen-induced states were observed at approximately 5 eV in photoemission, the density of states at E_F was reduced in the hydrides as compared to the metal and dependent on the composition x, and this is expected on theoretical grounds.[17,18,20] The $4f$ photoemission peak at 2-eV binding energy was found to be similar in the metal and in the hydrides,[13] thus signaling the chemical inertness of the $4f$ electron in this type of Ce compound.

In the present study we have used angle-resolved uv photoemission spectroscopy (ARUPS), electron-energy-loss spectroscopy (ELS), and low-energy electron diffraction (LEED) to characterize occupied electronic states, the electronic excitation spectra and structural parameters of the Ce(001) surface under the influence of hydrogen exposure. The results are interpreted in terms of initial hydrogen solution followed by hydride nucleation. The data suggest that tetrahedral interstitial sites are populated after dissociative chemisorption of H_2 from the gas phase, giving rise to an ultraviolet photoemission spectroscopy (UPS) feature at 4.2 eV. In addition, we conjecture that octahedral sites can be occupied in an activated process at elevated temperatures, and the corresponding UPS fingerprint appears at 3.4 eV. The nucleation of the hydride phase is particularly well evidenced in electron-energy-loss spectra. Finally, we report a hydrogen-induced hexagonal reconstruction of the (001) surface, and a possible model for the driving force of this reconstruction is discussed.

II. EXPERIMENTAL

Most experiments reported in this paper were performed in an angle-resolved Vacuum Generators Limited electron spectrometer VG ADES 400 with provisions for ARUPS, ELS, and LEED and the usual facilities for crystal preparation and cleaning. The angular resolution of the movable concentric hemispherical electron analyzer was ±1°, and the base pressure in this instrument $<5\times10^{-11}$ Torr. Energy resolution was typically set to 270 meV for UPS, and the total resolution in ELS as measured on the reflected primary beam (full width at half maximum) was 0.35 eV. Some experiments were car-

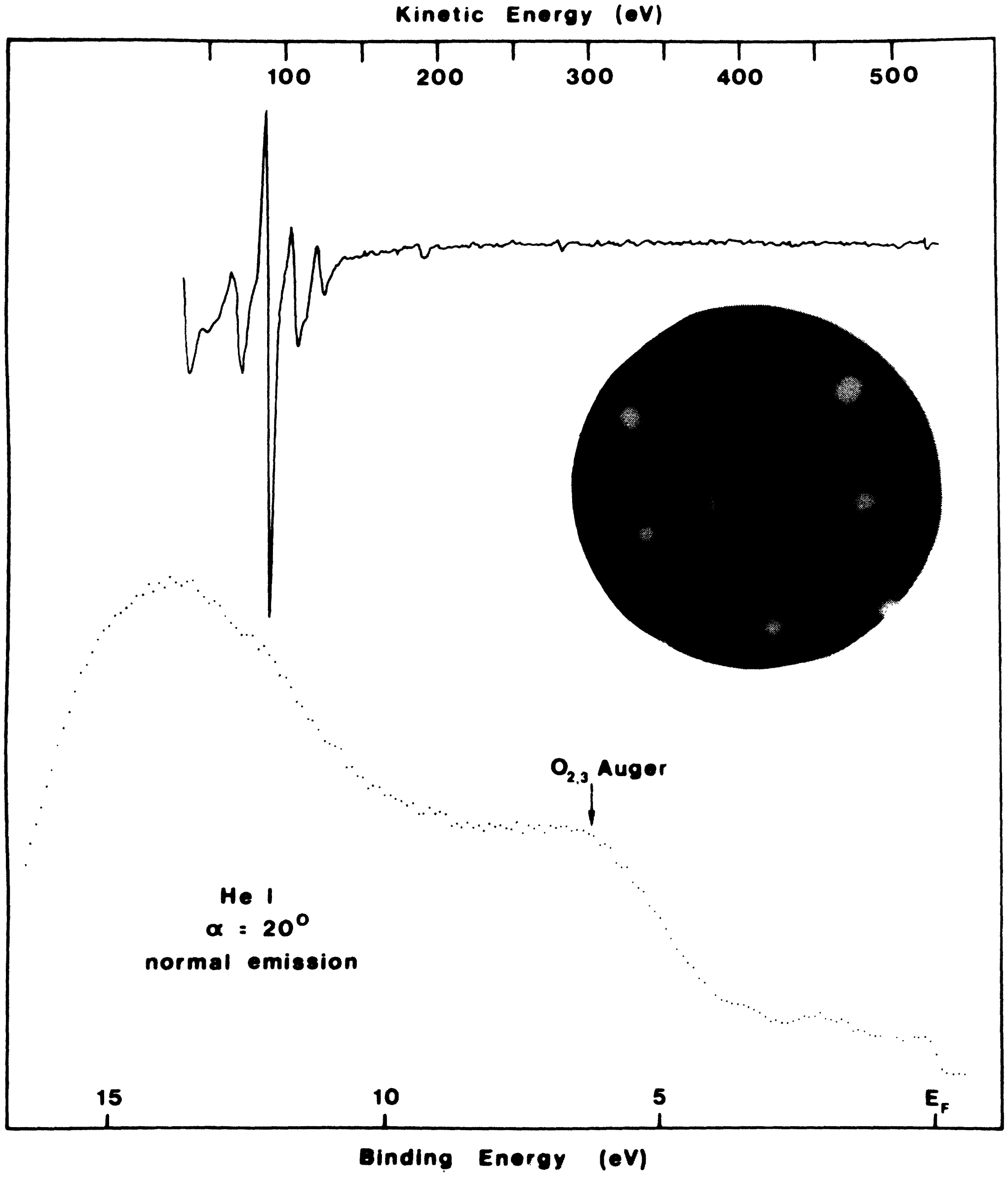

FIG. 1. Derivative Auger and He I UPS spectra of clean Ce(001) showing a (1×1) LEED structure. In the UPS spectrum (bottom curve) the photon angle of incidence $\alpha=20°$.

ried out in a second ultrahigh vacuum (UHV) system, where Auger and ELS were recorded with a large concentric hemispherical analyzer with an input lens system (Leybold-Heraeus EA10). The angular acceptance of this analyzer is of the order of 5°—10° and the total energy resolution in ELS was measured to be 0.5—0.6 eV under the conditions of the reported experiments. The base pressure in this spectrometer was $\lesssim 1\times10^{-10}$ Torr.

The γ-cerium crystal was polished and mounted as described previously.[21] *In situ* cleaning consisted of cycles of Ar sputtering followed by gentle heating in vacuum. After many sputtering and annealing cycles, 500-eV Ar ions, typically 8 μA for 20 min, with subsequent annealing to 280 °C resulted in a (1×1) LEED pattern, characteristic of a surface essentially free of contaminant signals in Auger and UPS spectra. This is shown in Fig. 1. In the He I ($h\nu=21.2$ eV) UPS spectrum (Fig. 1, bottom curve) a very broad feature is apparent between 4 and 10 eV below E_F. This feature is due to $\mathrm{Ce}O_{2,3}VV$ and $O_{2,3}N_{6,7}V$ Auger processes and not to residual surface contamination. The Auger structure changes intensity and shape under the influence of gas exposure, and this is responsible for the changing background in the UPS spectra of Figs. 2—4.

III. RESULTS

A. uv photoemission

He I ($h\nu=21.2$ eV) normal-emission spectra of clean Ce(001) and after various H_2 exposures are shown in Fig. 2. For low H_2 exposures (<100 L H_2) virtually no changes are observed in the UPS spectra of clean Ce, but for exposures >100 L H_2 a peak at 4.2 eV develops, and emission due to direct transitions near 1.8 eV and near E_F (Ref. 21) becomes quenched. The intensity remaining at 2.1 and 0.2 eV below E_F is due to $4f$ emission,[21] and is not influenced by hydrogen dosages up to 10^5 L H_2. This is consistent with the XPS results of Schlapbach and Osterwalder[13] on Ce hydrides, where emission near E_F is observable for $CeH_{2.1}$ but not for $CeH_{2.9}$, and indicates that a trihydridelike stoichiometry is not reached under present experimental conditions. The surface disorders at H_2 exposures 500—750 L as evidenced by the disappearance of the (1×1) LEED pattern, but this is not reflected directly in the photoemission spectra. No dispersion was found for the 4.2-eV hydrogen-induced peak.

Heating of H_2-exposed surfaces introduces remarkable changes in the UPS spectra. In curves *a* and *b* of Fig. 3, He I normal-emission spectra of Ce(001) recorded after exposure to 1800 L H_2 at room temperature and after heating the same surface to 350 °C for 5 min are displayed. A spectrum of Ce(001) + 10^5 L H_2, heated to 400 °C for 5 min is also included in Fig. 3 as curve *c*. We notice that the 4.2-eV peak decreases in intensity and shifts slightly in energy to 4.4 eV upon heating, and that a new feature at 3.4 eV has appeared. The shift of the 4.2-eV feature to 4.4 eV as a result of temperature treatment is most clearly apparent from curves *a* and *c*. Curves *d*—*f* of Fig. 3 show He II ($h\nu=40.8$ eV) spectra of clean Ce(001) (curve *d*), of Ce(001) exposed to 3000 L H_2 at room temperature

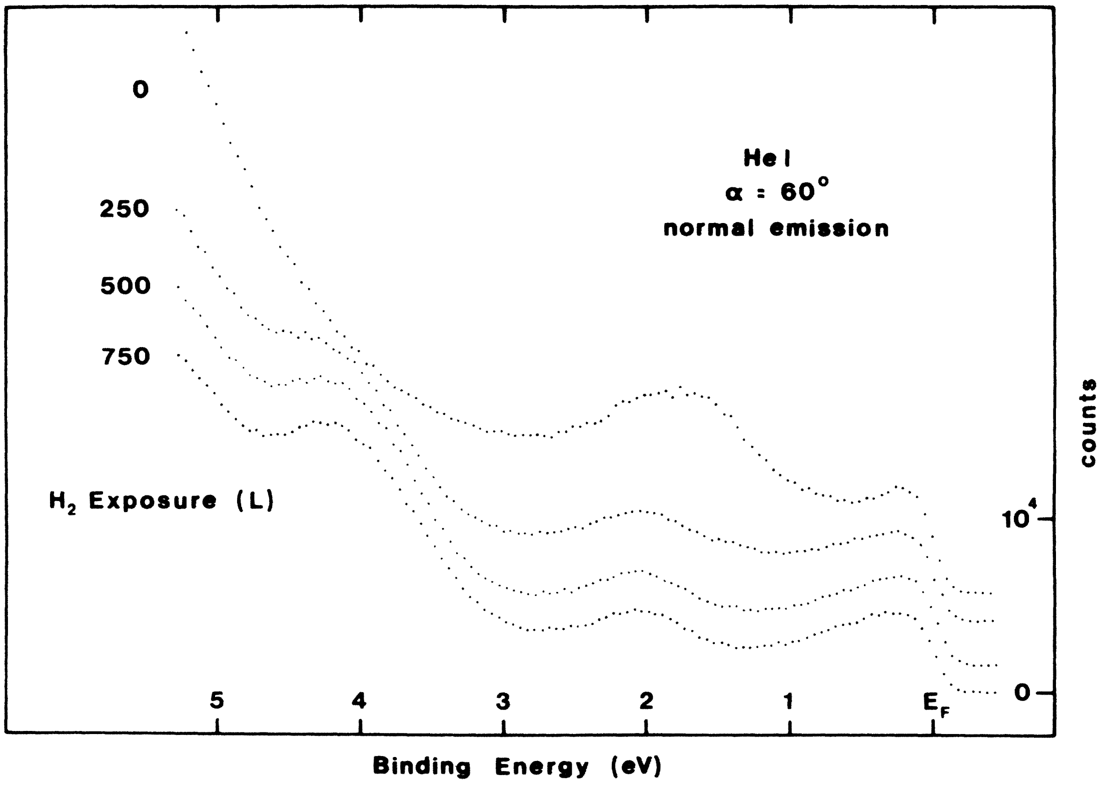

FIG. 2. Normal-emission UPS spectra (He I radiation $h\nu=21.2$ eV, photon angle of incidence $\alpha=60°$) of Ce(001) exposed to various amounts of hydrogen ($1\ \mathrm{L}\equiv10^{-6}$ Torr sec).

(curve *e*), and of Ce(001) exposed to 1800 L H_2, heated subsequently to 350 °C (curve *f*). The intensity of ARUPS with He II radiation is generally low in laboratory experiments, and long accumulation times have to be considered for acceptable signal-to-noise ratios. Surface contamination during spectra acquisition is therefore a problem, and this is reflected in the contamination signals at 5–6 eV (C,O) in spectra *d*–*f*. Nevertheless, the 4.2-eV H-induced feature is clearly evident in curve *e* of Fig. 3 as well as the 4*f*-derived emission at 2 and 0.3 eV below E_F. Note that the **k**-dependent valence-band features[21] have disappeared after the large H_2 dose (cf. curves *d* and *e* of Fig. 3). This is partly due to the mixing ("bonding away") of Ce *sd* states with H-derived *s* states,[10,20] and partly due to the loss of two-dimensional periodicity on the disordered surface. Gentle heating of the H_2 exposed surfaces again results in intensity reduction and energy shift of the 4.2-eV structure and in the appearance of the 3.4-eV peak (curve *f* of Fig. 3). It is important to mention that the (1×1) LEED pattern is restored after heating the H_2-exposed surfaces to 350 °C, and curve *f* of Fig. 3 shows the concomitant partial recovery of **k**-dependent emission in the region of 0–2 eV binding energy.

Extended heating of the Ce crystal to >400 °C leads to hydrogen segregation from the bulk to surface-near regions. The UPS spectra then show the structures at 4.4 and 3.4 eV. After reaching a certain critical H-concentration level near the surface, the (1×1) LEED pattern changes to a complex pattern, which may be indexed in matrix notation as

$$\begin{bmatrix} \frac{3}{5} & \pm\frac{1}{5} \\ \frac{1}{5} & \pm\frac{3}{5} \end{bmatrix}$$

(see Fig. 4). This structure can be interpreted in terms of a distorted hexagonal top layer sitting on the square second layer of the (001) substrate. Figure 4 compares normal emission He I spectra of the (1×1) and the reconstructed surface. Apart from the H-induced structures at 4.4 and 3.4 eV, extra emission is observed at 1.7 and 2.6 eV on the reconstructed surface. The features at 1.7 and 2.6 eV seem to be particularly characteristic of the surface reconstruction; compare for example spectra of the hydrogen-containing (1×1) surface (curve *c* of Fig. 3) and of the reconstructed surface (Fig. 4). It is therefore tempting to associate these spectral features with surface states on the reconstructed surface. Dispersion was examined in a limited range of **k** space, but no dispersion was found for the surface-state features; the 3.4-eV peak shows weak dispersive behavior and shifts by 0.15 eV to

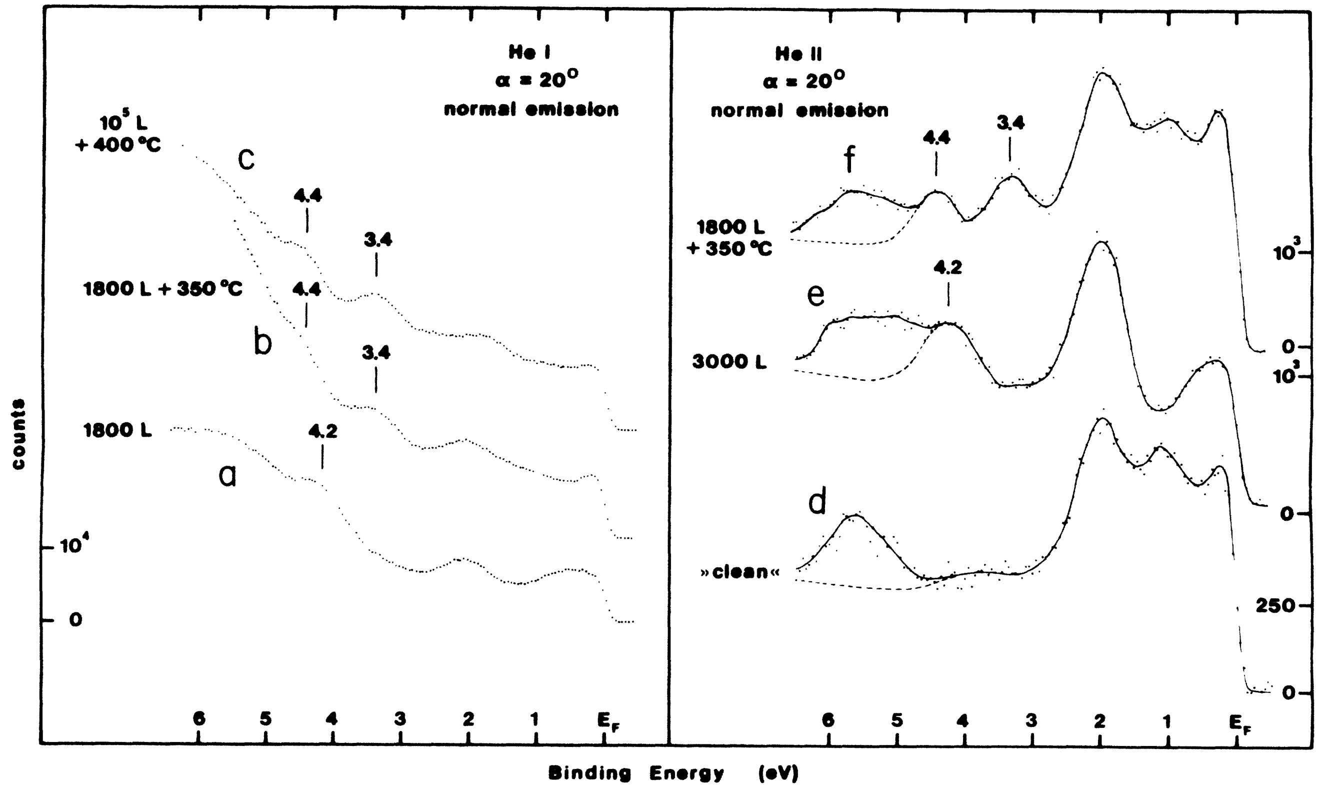

FIG. 3. Left panel: He I normal-emission spectra ($\alpha=20°$) taken after exposing Ce(001) to 1800 L H_2 at room temperature (curve *a*), after heating the same surface to 350 °C for 5 min (curve *b*), and of Ce(001) + 10^5 L H_2 followed by heating to 400 °C for 5 min. Right panel: He II ($h\nu=40.8$ eV) normal-emission spectra of Ce(001) (curve *d*), exposed to 3000 L H_2 at room temperature (curve *e*), and after heating a 1800 L H_2 dosed surface to 350 °C for 5 min.

lower binding energy when going from ΓX towards W. It has to be mentioned that we have not been able to obtain the reconstructed surface structure by hydrogen uptake from the gas phase alone followed by subsequent short annealing. As discussed later, it appears that some bulk H segregation is necessary under the present experimental conditions to induce this reconstruction.

B. Electron-energy-loss spectroscopy

Electron-energy-loss spectra of Ce(001) exposed to various amounts of H_2 are displayed in Fig. 5. Figure 5(a) shows spectra recorded with the wider-angle acceptance analyzer (Leybold-Heraeus) and Fig. 5(b) a set of spectra taken at high angular resolution (VG ADES 400). All spectra were recorded in or near specular reflection geometry. Comparison of the ELS spectra for the clean surface [bottom curves in Figs. 5(a) and 5(b)] reveals excellent agreement between the two sets. ELS of clean Ce(001) is characterized by a broad interband transition loss at ~ 3 eV, a surface-plasmon excitation at 7.5–8 eV, the bulk plasmon at 11.5–12 eV (at $E_p \simeq 100$ eV only visible as a shoulder) and by the onset of $5p$ excitations at 16.5 eV.[22,23] Hydrogen exposures up to 100 L introduce a new loss at ~ 3 eV and an intensity decrease of the surface-plasmon loss relative to the bulk plasmon [Fig. 5(a)]. The $5p$ excitations remain virtually unchanged, consistent with their atomiclike nature.[24]

After exposure of 300 L of H_2 a small feature at 1.6 eV is recognized in addition to the loss around 3 eV; this low-energy feature increases in intensity upon further exposure and becomes a very sharp, dominant feature at 900 L H_2 [Fig. 5(b)]. The surface plasmon at ~ 8 eV decreases concomitantly in intensity and is lost in the broad hump between 5–15 eV in the 900 L H_2 spectrum. In Fig. 5(b) the top curve represents an ELS spectrum recorded after 900 L H_2 exposure with a primary energy $E_p \simeq 1000$ eV; thus, the escape depth of backscattered electrons is markedly increased ($\sim$20–30 Å) as compared to the spectra with $E_p \simeq 100$ eV (~ 5 Å). However, the sharp 1.6-eV loss is still dominant in the high E_p spectrum, indicating that the spatial distribution of inelastic scattering

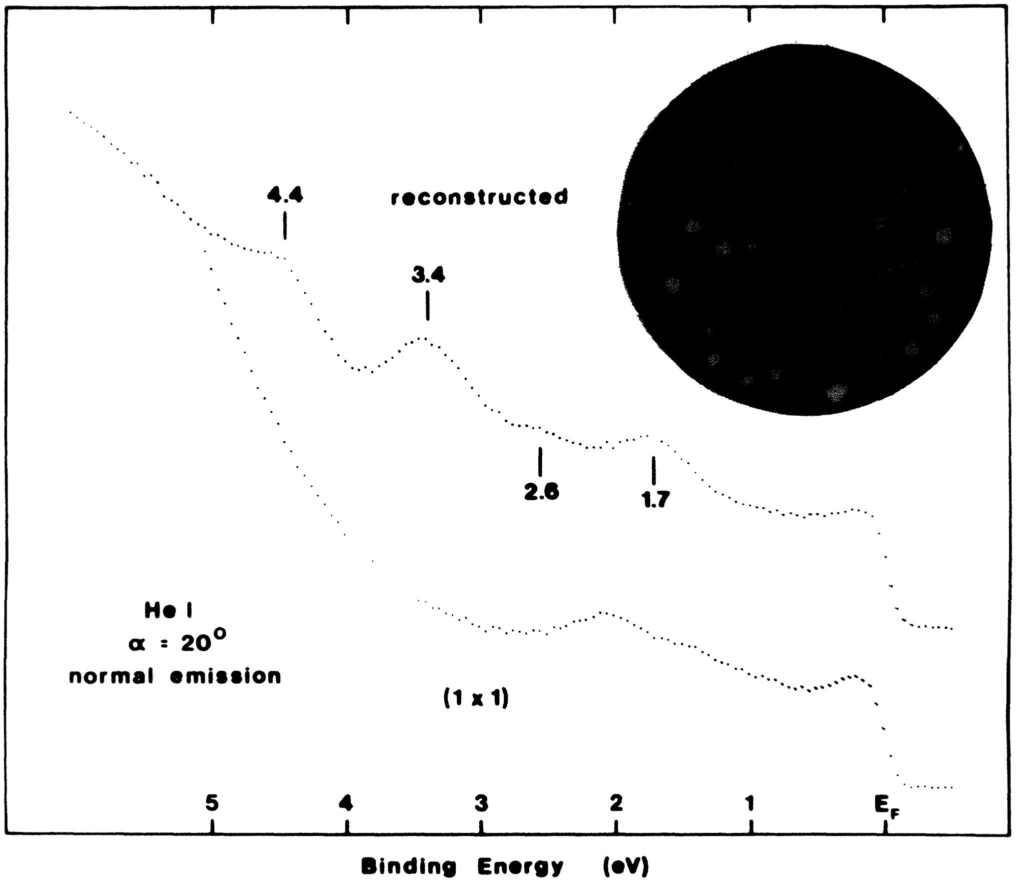

FIG. 4. He I normal-emission spectra ($\alpha = 20°$) of the (1×1) surface and the H-induced reconstructed

$$\begin{bmatrix} \frac{3}{5} & \pm\frac{1}{5} \\ \frac{1}{5} & \pm\frac{3}{5} \end{bmatrix}$$

surface of Ce(001). The reconstructed surface was obtained after 400 °C heat treatment of the sample.

events extends a number of layers into the crystal. Also, a bulk plasmon centered now at 13.5—14 eV, that is, ~1.5—2 eV shifted to higher energy with respect to the bulk plasmon on clean Ce(001), is apparent in this spectrum. Upon heating to 400 °C the sharp loss structures at 1—3 eV fade away and a broad feature of little prominence remains in the (2.5—4)-eV-loss energy region.

Before embarking on the general discussion it is appropriate to dwell somewhat on the interpretation of the presented loss results. The H-induced 3-eV loss is most likely classified as an interband transition from states of predominantly hydrogen-derived character to empty states above the Fermi level. The states seen at 4.2 eV in UPS are likely initial-state candidates, and excitonic effects may lower the transition energy as a result of the electron-hole interaction. The most interesting feature of this ELS investigation is the unusually sharp peak at 1.6-eV loss energy, which shows up at H_2 exposures of several hundred L. Comparison with the dielectric functions of rare-earth dihydrides, which have been derived from optical studies by Weaver and co-workers,[25,26] suggests interpretation in terms of a screened low-energy plasmon,[25] characteristic of a dihydridelike phase. Although we have no detailed information on the exact stoichiometry of the CeH_x phase, we take this low-energy plasmon loss as an indicator of the formation of a surface dihydride phase, presumably of substoichiometric character. The results obtained at high primary energy suggest that this hydride phase extends somewhat into the crystal, and is not just confined to the topmost layers. The shift of the Ce bulk plasmon from 12 to 14 eV is consistent with hydride formation.[27] In closing this section we note that the disappearance of the (1×1) LEED structure is roughly correlated with the development of the low-energy plasmon peak.

IV. DISCUSSION

The sticking probability of hydrogen on several rare-earth metals including Ce has been measured using a flow technique by Atkinson *et al.*[28]; a value of ~0.5 has been derived for cerium. In view of these results, the absence

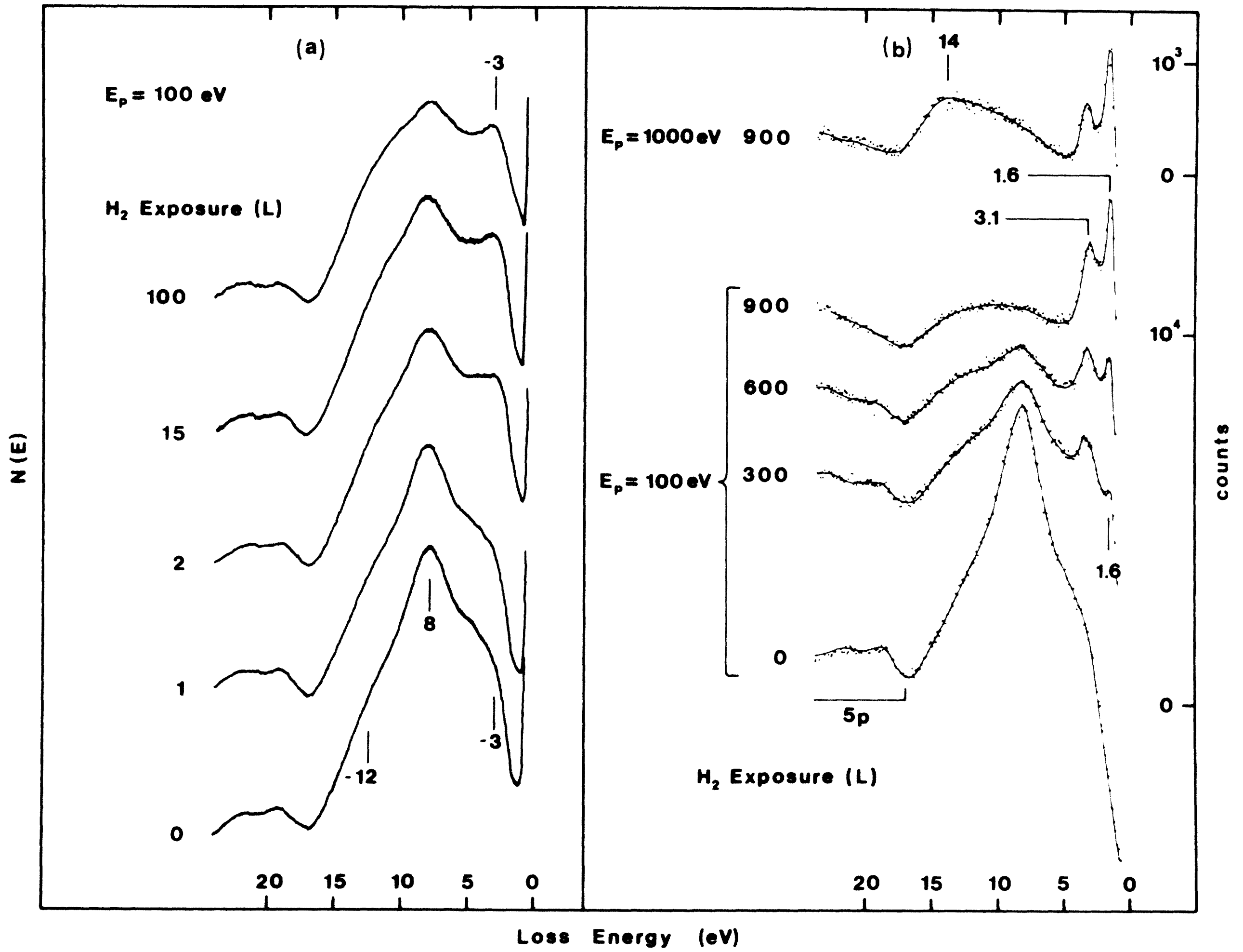

FIG. 5. Electron-energy-loss spectra of Ce(001) as a function of hydrogen dosage. The spectra in (a) and (b) were recorded with two different hemispherical analyzers (see text). The electron primary energy E_p was ~100 eV for all the spectra except for the top spectrum in (b), where $E_p \approx 1000$ eV.

of spectral changes in UPS at low H_2 doses (< 100 L) and the moderate effects in ELS together with minor work-function changes in this low-exposure regime[29] are rather surprising. The results of our investigations indicate therefore that the H concentration is low at and near the surface during the initial stages of hydrogen dosage. Rapid equilibration between surface and bulk at room temperature, however, is expected as suggested by Atkinson *et al.*[28] The dissociative chemisorption of H_2 on Ce is therefore followed by fast hydrogen dissolution into the bulk, but the chemisorption step itself could not be unambiguously isolated in the present studies. Cooling to lower temperatures might prove advantageous for the latter purpose, but this is not possible with a Ce single crystal because the $\gamma \rightarrow \alpha$ phase transition below 270 K (Ref. 30) would destroy the crystal.

In analogy to the light rare-earth dihydrides, where H occupies tetrahedral sites in a fluorite structure,[31] we suggest that dissolved H fills tetrahedral interstitial sites in the metal host lattice. Accordingly, the 4.2-eV UPS structure is associated with H in tetrahedral sites. Nucleation of a surface hydride phase starts at exposures > 500 L H_2. The appearance of the 1.6-eV plasmon in ELS is taken as an indicator of hydride formation, but no qualitative differences between the solid solutions and the hydride phase are detected in UPS: the 4.2-eV feature grows only in intensity as the H concentration is increased. This is consistent with the findings of Weaver *et al.*[11] for H on Sc films, which showed energetically similar photoemission structures for low-x solid-solution phases and a surface hydride phase. The disordering of the surface as evidenced by the disappearance of the (1×1) LEED pattern may also be cited in support of a hydride phase: the surface becomes scrambled as a result of the lattice expansion caused by the formation of surface hydride.

A number of experimental techniques have indicated that premature filling of octahedral sites is possible for MH_x compositions with $x<2$, that is before full tetrahedral-site occupancy,[25,32–34] and corresponding theoretical justification has been provided.[20,35,36] In order to interpret the results obtained here at elevated temperatures we advocate the occupation of octahedral sites as an activated process. According to this model population of octahedral sites may be induced by moderate heat treatment at 300–400 °C, and the 3.4-eV UPS feature is associated with H-induced states at octahedral positions. This suggestion is not completely without theoretical foundation. Several calculations have indicated that partial densities of states associated with H in octahedral sites have maxima at lower binding energy than corresponding ones of tetrahedral sites.[16,17,20,36] Following Fujimori and Tsuda,[16] octahedral hydrogen-induced states are expected at 1–4 eV below E_F for Ce hydrides, and this is in accord with our observations. The shift of the tetrahedral H UPS band from 4.2 to 4.4 eV upon filling octahedral sites may then be caused by the H potential at the octahedral sites. Apart from filling octahedral sites annealing of the H-exposed Ce crystal at 300–400 °C also destroys the surface hydride phase. This is seen in ELS, where the low-energy hydride plasmon disappears, and in LEED by the restoration of the (1×1) structure. Desorption of some hydrogen is possible, but more likely dilution of the H concentration near the surface is taking place by diffusion into the bulk.

A most interesting observation in this study is the hydrogen-induced reconstruction of the Ce(001) surface, which is seen when H is enriched near the surface assisted by H segregation from the bulk. The UPS fingerprint of the reconstructed surface (Fig. 4) suggests that both tetrahedral- and octahedral-site occupation is necessary. It is tempting, therefore, to speculate on the driving force for this reconstruction. A key element seems to be a certain *critical* concentration of H *in octahedral and in tetrahedral sites.* Between the first and the second layer of an fcc (001) surface, however, only tetrahedral hole sites are available, no octahedral sites are present in this interstitial layer. Sites of both symmetry, although distorted, may be generated if the top layer reconstructs into a hexagonal arrangement. We thus conjecture that the generation of octahedral-like sites and their subsequent population with hydrogen provides the driving force of this surface reconstruction. Of course, total energy calculations of the square and the reconstructed H containing Ce(001) surfaces are necessary to test these ideas, and we would like to urge appropriately those theoreticians whom it may concern. Hexagonal reconstruction of square fcc (001) surfaces is actually not unusual in the third transition series: on Ir, Pt, and Au (100) hexagonally reconstructed top layers have been found for the clean surfaces.[37]

A remaining question is why the reconstructed surface is not generated by H uptake from the gas phase alone? Though not completely understood, it appears that the critical concentration of H in both tetrahedral and octahedral sites cannot be established in this way under the present experimental conditions. Prolonged H_2 exposure disorders the surface as a result of hydride formation, but the necessary subsequent annealing reduces the H concentration near the surface again unless dissolved H in the bulk blocks the diffusing away of H or acts as a reservoir for segregation. In support of this we mention that longer annealing times had to be adopted to obtain the reconstructed surface after the crystal had become more and more depleted of dissolved hydrogen during the cleaning cycles of this study.

V. CONCLUSIONS

The results of this electron spectroscopic study of the interaction of hydrogen with Ce(001) may be summarized as follows. For low exposures of H_2 (< 100 L) dissociatively chemisorbed hydrogen dissolves rapidly into the bulk so that the H surface concentration remains low. For intermediate H_2 exposures (~ 100–500 L) a cerium hydrogen solid solution is formed and a H-induced band at 4.2 eV below E_F is detected in photoemission spectra. We suggest the population of tetrahedral sites in the metal host lattice. A dihydridelike phase is formed in the selvedge region (at least ten layers thick) after H_2 exposures > 500 L, and this is demonstrated by the advent of a low-energy hydride plasmon in electron-energy-loss spectra.

The surface layers disorder as a result of hydride formation.

Annealing of H_2-exposed Ce surfaces to 300—400 °C induces a new UPS structure at 3.4 eV, which we associate with H in octahedral sites populated in an activated process. A hydrogen-induced hexagonal reconstruction of the Ce(001) surface with a complex LEED pattern is observed after annealing to 400—500 °C, and the UPS fingerprint of this reconstructed surface suggests a critical concentration of H in both tetrahedral and octahedral sites. This critical concentration cannot be established by H_2 uptake from the gas phase alone, but it appears that H segregation from the bulk phase is necessary to assist this surface transformation.

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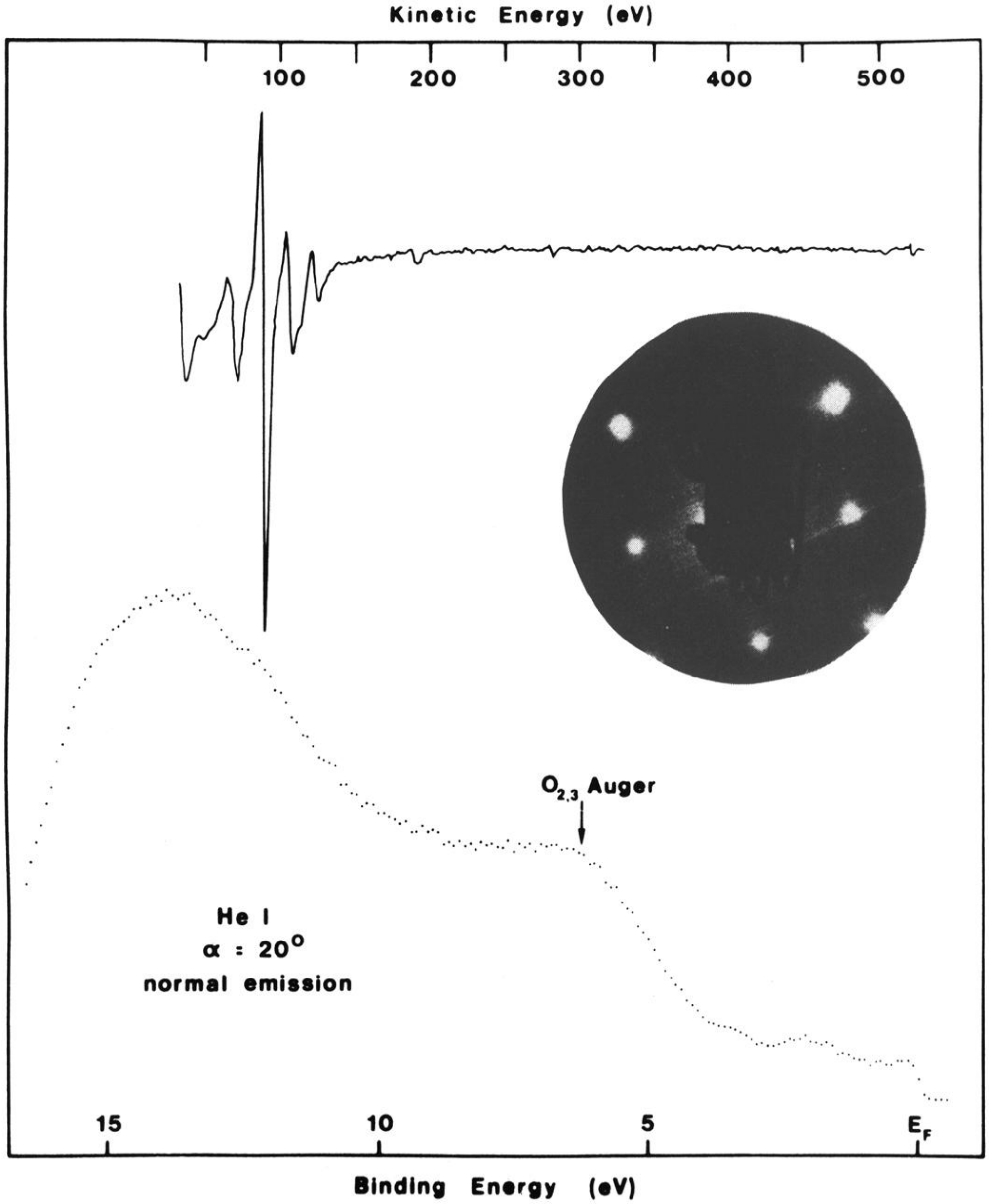

FIG. 1. Derivative Auger and He I UPS spectra of clean Ce(001) showing a (1×1) LEED structure. In the UPS spectrum (bottom curve) the photon angle of incidence $\alpha=20°$.

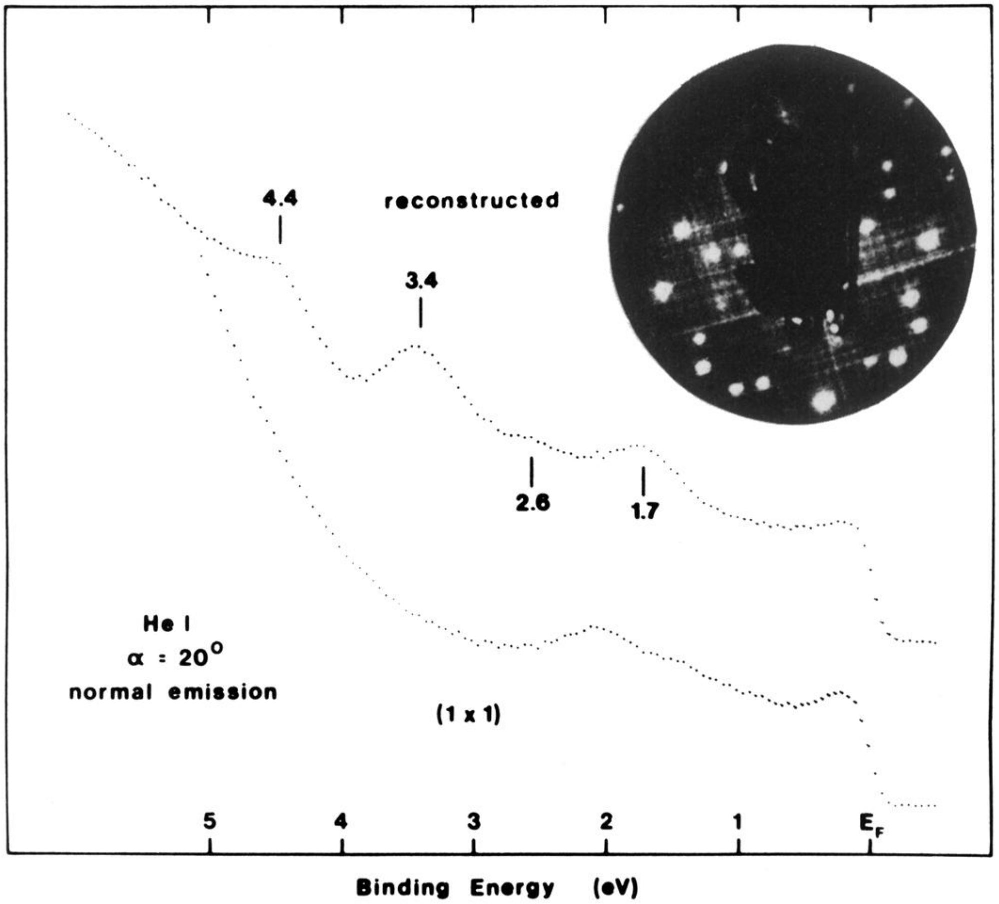

FIG. 4. He I normal-emission spectra ($\alpha=20°$) of the (1×1) surface and the H-induced reconstructed

$$\begin{pmatrix} \frac{3}{5} & \pm\frac{1}{5} \\ \frac{1}{5} & \pm\frac{3}{5} \end{pmatrix}$$

surface of Ce(001). The reconstructed surface was obtained after 400 °C heat treatment of the sample.