Electronic interactions in metal-hydrogen solid solutions: ScH_x, YH_x, and $V_{0.75}Nb_{0.25}H_x$

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The electronic interactions of hydrogen in a host metal lattice have been studied with synchrotron-radiation photoemission for low-x solid solution phases of ScH_x, YH_x, and $V_{0.75}Nb_{0.25}H_x$ for $0.15 \leq x \leq 0.25$. For each system, a single well-defined hydrogen-induced feature is observed 5 eV below the Fermi level due to the local interaction of H with bonding metal-derived states, in agreement with linear combination of atomic orbitals supercell calculations for low-concentration hydrides. However, for the low-concentration hydrides the hydrogen-derived feature is shifted to lower binding energies than for the high-x hydrides, a trend which is in contrast to the calculations. We attribute this shift to smaller interatomic Coulomb interaction due to less positive metal atoms in the low-x phases. This suggests more ionic contribution to the cohesive energies of the high-x hydrides than the low-x solid solutions, consistent with x-dependent thermodynamic properties of metal-hydrogen systems. Results obtained by H dosing of Sc films showed initial chemisorption states which are energetically similar to those of the solid solution. However, a surface reaction occurs by 100 langmuirs exposure (1 langmuir $\equiv 10^{-6}$ Torr sec) and the resulting surface region is indistinguishable from ScH_2. In contrast, the surface of the α-phase hydride is found to be much less sensitive to hydrogen exposure. Finally, we have no evidence for hydride formation induced by cleaving the α-phase hydride samples.

I. INTRODUCTION

The interactions of hydrogen in solids have been and continue to be of great scientific and technological interest.[1,2] A large body of research has shown that the effects of hydrogen in a lattice can be large and that hydrogen incorporation can have a significant impact on the properties of the solid. Hydrogen concentrations in solids range from the ultradilute limit in solid solutions to the monohydrides, dihydrides, and trihydrides. The hydride of thorium Th_4H_{15} holds the record for the greatest concentration[3] with a hydrogen density much greater than that of liquid hydrogen at 20 K. Although early studies treated hydrogen as either an anion or a cation, recent work has shown the limitations of such a model and have demonstrated metal-hydrogen charge hybridization. Indeed, as shown by a number of recent calculations,[4–13] the modeling of the electronic properties of hydrides now appears to be solidly grounded. In contrast, the understanding of the electronic properties for the low-x or solid solution systems is far less advanced, despite extensive concern about the role of hydrogen in phenomena related to embrittlement and its presence in most environments.[14]

In this paper, we present synchrotron-radiation photoemission studies of the energy states of hydrogen in solution for the host metals Sc, Y, and $V_{75}Nb_{25}$. As we will show, the hydrogen-induced states appear split off from the d states of the metal, falling 5 eV below E_F. At the same time, hydrogen modifies the electronic states of the metal, as can be seen by changes in the d-band distribution of states. We interpret the experimental results on the basis of local or defect-like perturbations to the host states since no long-range order exists for the solid solution. Comparison of these low-x results to those for V and Nb monohydrides[15] and Sc and Y dihydrides[16] shows the effect of increasing the hydrogen content and compound formation. Supercell calculations[10] based on assumed order show modifications to the electronic states which are consistent with experiment. However, the experimental results show a shift of the H-induced states to greater binding energy with increasing hydrogen concentration, in contrast to the non-self-consistent supercell calculations. We interpret these differences in terms of charge redistribution effects upon hydride formation. Experiments involving the exposure of thin Sc films to H in the gas phase show that reaction to ScH_2 can occur, even for low exposures at room temperatures.

II. EXPERIMENTAL PROCEDURE

The photoemission experiments were performed at the Wisconsin Synchrotron Radiation Center using radiation emitted from Tantalus I and dispersed by either the toroidal grating monochromator or the grasshopper Mark

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II monochromator. The experimental chamber has been described in previous detailed discussion of our work with metal hydrides.[15–18] Samples were mounted on copper blocks which could be interchanged *in situ* at operating pressures of 5×10^{-11} Torr. These samples were fractured with a tungsten carbide cleaving tool and a stainless-steel anvil. No hydrogen loss was observed upon fracturing since there was neither a pressure burst nor an increase in the hydrogen peak of the quadrupole mass spectrometer. Upon cleaving, the sample was positioned at the mutual focus of the electron energy analyzer (a double-pass cylindrical mirror analyzer) and the photon beam. All measurements were done at room temperature. In this way, the samples could be cleaved and the first spectrum acquired within 5 min.

The results presented here show that extreme care must be exercised to avoid oxygen contamination of the surface coming from either the residual vacuum or from the environment of the sample at the time of cleavage (movement of sample against cleaver). For the α-phase results and for the evaporated Sc films, it was never possible to be completely free of oxygen contamination, and the spectra we show represent our best case results. Poor cleaves showed much stronger emission 6–7 eV below E_F and $3p$-core line shapes indicative of oxidation. These cleaves were discarded. Detailed studies involving ultralow exposures of the samples to oxygen showed what effect a 0.01 L dose would have (1 L$=10^{-6}$ Torr sec) and, as a result, we show with dashed lines in the figures the probable effect of a fraction of a monolayer of oxygen present on the surfaces. At this ultralow coverage, it is unlikely that the presence of oxygen would alter the conclusion of this paper—but the high partial photoionization cross section of oxygen relative to hydrogen at these energies made it imperative that the oxygen contribution to the energy distribution curves (EDC's) be made as small as possible.

The samples used in this study were prepared in bulk form from high-purity Ames Laboratory V, Nb, Sc, and Y. The metals typically contained less than 500 at. ppm total metallic impurities and less than 200, 100, and 200 at. ppm of O, N, and C, respectively. They were charged with hydrogen by gas-phase charging at 600 °C.[16] Comparison of results for single and polycrystalline α-phase samples showed no meaningful differences. Metallographic analysis of the charged alloys showed no hydride phase in any case. Thick films of Sc and V were prepared *in situ* by deposition onto inert substrates from resistively heated sources. All depositions were done in vacua of better than 2×10^{-10} Torr, as described in greater detail in previous papers dealing with metal overlayers on semiconductors.[19]

III. ELECTRONIC STRUCTURE OF α-PHASE HYDRIDES

On the left-hand side of Fig. 1 we show photoemission energy distribution curves taken at $h\nu=40$ eV for an evaporated film of Sc, for α-phase $ScH_{0.2}$, and for ScH_2. We show analogous results on the right-hand side for the α phase and dihydride phase of Y. Together, these spectra show the energy location of the hydrogen-induced states

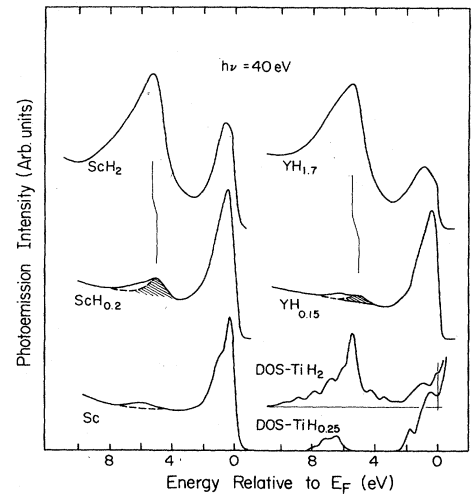

FIG. 1. Energy distribution curves (EDC's) comparing α-$ScH_{0.2}$ with Sc metal and ScH_2 (left-hand side) and α-$YH_{0.15}$ with $YH_{1.7}$ (right-hand side). For the α-phase hydrides, the effect of hydrogen is indicated by the cross-hatched region. The dashed lines indicate the effect of oxygen present on the surface at $<1\%$ levels. In the lower right-hand side we show calculated densities of states for $TiH_{0.25}$ and TiH_2 corrected for the one fewer electron in Y relative to Ti (from Ref. 11).

of the low-x samples, i.e., the development of emission centered 4.8–5 eV below E_F. Likewise, they demonstrate the concentration-dependent effects of H on the metal-d—derived bands of Sc and Y.

In Fig. 2 we show photoemission results for hydrogen in the α-phase bcc solid solution $V_{75}Nb_{25}$. This system has very high terminal solid solubility of hydrogen in the alloy compared to either V or Nb. For comparison to the α-phase spectra, we also show results obtained with a thin film of elemental vanadium (left panel) and a bulk sample

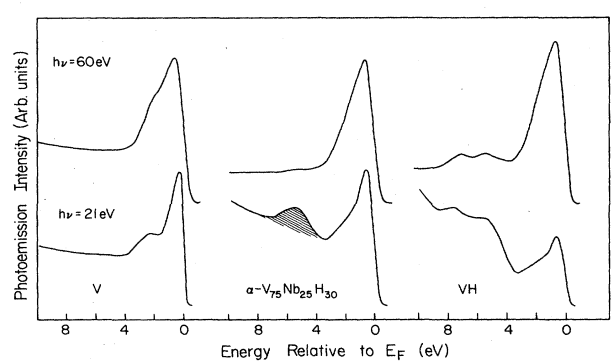

FIG. 2. EDC's comparing $-V_{75}Nb_{25}H_{30}$ with V metal (left-hand side) and VH (right-hand side). Hydrogen absorption induces a well-defined band of states centered 5 eV below E_F. With increasing H content, these broaden and their centroid shifts to greater binding energy, analogously to the results of Fig. 1 for Sc-H and Y-H.

of VH (right panel). The effect of hydrogen is again quite clear, as can be seen from the development of structure centered 5.5 eV below E_F for $V_{75}Nb_{25}H_{30}$. Unlike VH or NbH, however, the α-phase hydride does not show the double-peak structure in the hydrogen-induced band, which, according to the recent calculations by Ho *et al.*,[20] is due to the nearest-neighbor hydrogen-hydrogen interaction in the α phase. The EDC's of Fig. 2 also demonstrate that the partial photoionization cross section of these hydrogen-induced states is large at lower photon energies but decreases with increasing $h\nu$ (compare EDC's at $h\nu=21$ and 60 eV in Fig. 2).

The $h\nu$ dependence of this emission is consistent with the dominant hydrogen 1*s* character of the states involved. At the same time, the effect of hydrogen is to broaden the valence-band emission near E_F, producing relatively featureless valence bands. As the hydrogen content increases and the hydride forms, the hydrogen-induced states grow in relative intensity, broaden asymmetrically about the energy of the low-x hydrogen states, and shift to higher binding energies by 0.5—1.5 eV.

In previous papers,[15–18] we have discussed the changes in the electronic structure of the metal due to hydride formation. Guided by band calculations,[4–13] we have shown that these hydrogen-induced states for the hydrides are of mixed angular-momentum character, representing hybrid states of H-1*s* and metal *s* and *d* character. The interpretation of the present low-x experimental results can likewise be guided by the results of calculations.

Fujimori and Tsuda[10] recently reported calculations of the density of states for the Ti-H system for $x=0$, 0.25, 0.50, . . ., 2. In their linear combination of atomic orbitals (LCAO) calculations, the assumed model involved a supercell based on an fcc Ti lattice to provide the symmetry necessary to make the calculations possible. In Fig. 1 we reproduce the predicted density of states for $TiH_{0.25}$ with account taken of the extra electron in Ti relative to Sc. As can be seen, the predicted behavior is qualitatively consistent with our experimental results: upon introduction of hydrogen into the lattice, a split-off, hydrogen-derived band of states appears well below the metal *d* bands and even below the bottom of the metal *s* band. These split-off states have been calculated to have predominant hydrogen 1*s* atomic orbital character with small metal *s* and *d* components, consistent with the observed $h\nu$ dependence of the 5-eV emission. These supercell calculations for TiH_x further predicted that the hydrogen states would grow as x increases, ultimately producing the now well-known signature of the dihydrides shown in Fig. 1. Experimentally, the hydrogen-induced states also broaden in an asymmetric fashion with the appearance of additional states at greater binding energy relative to the low-x or precursor hydrogen-induced states.

The supercell calculations have predicted an energy shift of the hydrogen-induced states to lower binding energies as x increases—but the present experiment shows the opposite shift between the α phase and the dihydrides. We consider the following points in reconciling the disagreement between theory and experiment.

(1) In the LCAO calculations, the center of the H-induced band has been calculated to lie a few eV below the "bare" H 1*s* atomic orbital energy due to bonding-antibonding shifts resulting from hybridization between H 1*s* and metal *sd* orbitals, since the H-induced states can be regarded as bonding states formed by the hydrogen and metal orbitals.[10] Thus, when the hydrogen concentration becomes sufficiently large compared to metal atoms, the shift of the H-induced states to greater binding energy may not be as effective as for low H concentration, as a sufficient number of metal *sd* orbitals may not be available. In particular, above $x=1$ the number of metal *s* orbitals becomes smaller than that of H 1*s* orbitals.

(2) In addition to these hybridization energy shifts, we can also expect that electronic charge redistributions associated with charge transfer from metal to hydrogen can perturb the hydrogen potential and lead to energy shifts of the H states. This charge redistribution has been established by experimental and theoretical studies concerning charge transfer in Y-YH_2 and Sc-ScH_2.[16] Atomic orbital energy shifts due to charge redistribution were not, however, taken into account in the LCAO calculations. (The LCAO calculations for TiH_x were done by assuming Ti 3*d* atomic orbital energies interpolated between TiH_2 and metallic Ti with respect to x and the H 1*s* energy in TiH_2.) As a result, the positive metal ions would induce an attractive potential at hydrogen sites via the interatomic Coulomb interaction and would lower the position of the H-induced band. The positive charges on the metal atoms would increase with increasing hydrogen concentration due to metal to H charge transfer and, consequently, the H-induced band would be lowered (farther from E_F).

This second factor is indirectly supported by supercell calculations for PdH_x.[5,21] Since there is very little charge transfer between Pd and hydrogen (they have nearly the same electronegativity values and there has been no definite conclusion on the direction of the charge transfer), the only x-dependent energy shift is that due to Pd-H hybridization. In fact, the hydrogen-induced band has been predicted to shift downward with increasing x both for self-consistent[5] and non-self-consistent[21] calculations.

(3) There is a third possible source of the discrepancy between theory and experiment that is much more difficult to consider. In addition to charge transfer effects, there may also be internal stresses present around the H atom in the α-phase hydride which might contribute to the low binding energy of the H-induced band. The nearest-neighbor metal-hydrogen distance is smaller in the α phase than in the high-x phase by ≤ 0.1 Å if the hydrogen atom occupies tetrahedral sites in Y or Sc. To try to evaluate the magnitude of the resulting energy shift, we estimated the energy associated with the reduced metal-H distance in the α phases by using a nearest-neighbor metal-H force constant obtained from local H vibration frequencies in Ce.[22] The result is of the order of 0.01 eV. We therefore conclude that internal stresses around hydrogen atoms are *not* responsible for the shift of the H-induced states.

The downward shift of the H-induced band with increasing x reflects increased stabilization when going from the α phase to the high-x hydrides, as described by Gelatt *et al.*[11] They calculated the heats of formation for transition-metal monohydrides from one-electron energy

levels obtained by band-structure calculations (corrected for intra-atomic Coulomb energies on the H atom) and found that the position of the H-induced band is the most important factor for the stability of the hydride. In fact, the partial molar enthalpy of hydrogen solution has been found to be larger for YH_2 and ScH_2 than for the respective α-phases by 0.5 eV,[23,24] in rough agreement with the H-band shift. Differences in the heat of formation between high-x and low-x hydrides have been found to be smaller for the V-H and Nb-H systems where metal-to-H charge transfer is smaller and differences are vanishingly small for the Ni-H and Pd-H systems where very little charge transfer is expected (these thermodynamical data are accumulated in Ref. 11). This supports the interatomic Coulomb or ionic contribution to the stability of hydrides of electropositive metals.

Bouten and Miedema[25] recently published semiempirical calculations of the heats of formation for metal hydrides for the dihydride compositions. Their simple treatment predicted the solubility limit as a function of temperature and the heats of formation at this composition reasonably well. However, the smaller partial molar enthalpy of H solution for α phase YH_x and ScH_x compared to YH_2 and ScH_2 could not be described by their model. The smaller H solubility in the α phase or the shallower H-induced states would thus be attributed to effects not included in their model, such as lattice distortion energies or Madelung energies. The latter should be dominant because of the above discussion. Furthermore, the bonding in Y and Sc hydrides has ionic contribution from crystal chemical[22] and band theoretical[4] points of view while Miedama's semiempirical approach has been applied primarily to alloys with metallic bonding.

A similar argument should also apply for the V-H and Nb-H systems since the H-induced band has shown a similar shift relative to the V-H and Nb-H systems as a function of hydrogen concentration. (The amount of the shift is smaller than the Y-H and Sc-H systems: 0.5 eV compared to 1—1.5 eV in Y-H and Sc-H if the center of gravity of the H-induced band is considered). In fact, although the V—H and Nb—H bonds have been found to have less ionic character,[15] the electronegativity difference between V, or Nb, and H (0.5 compared to 0.8—0.9 between Y or Sc and H) would still be sufficiently large to cause some amount of metal-to-H charge transfer.

IV. SURFACE PROPERTIES OF α-PHASE HYDRIDES AND SURFACE HYDRIDE FORMATION

To compare the newly observed hydrogen bulk state with a precursor or chemisorption state, we undertook experiments involving hydrogen chemisorption onto freshly deposited Sc films. These films were "as-deposited" and, as such, they offered an array of active sites for absorption. In Fig. 3 we show results for exposures of 1, 10, and 100 L of hydrogen on Sc obtained by admitting high-purity H_2 gas into the chamber to increase the overall pressure to 10^{-8}—10^{-7} Torr with ion pumps isolated and an ion gauge on, but out of sight of the sample. The results show that 1 L exposure produces a well-defined state centered 5 eV below E_F. Comparison shows that the resulting hydrogen-induced states are indistinguishable from those of α-$ScH_{0.2}$. Further exposure produced no significant changes for coverages to 10 L. Dramatic changes were observed, however, upon exposure to 100 L of H_2, as shown in Fig. 3. Indeed, the 100 L exposure produced identical spectral features as those of bulk ScH_2, including valence-band emission (Fig. 3), Auger emission, and Sc $3p$ core binding energy (29.5 eV).[16] We conclude, therefore, that exposure of the film first produced a thin layer with limited amounts of hydrogen on the surface and in the near surface region and that this intermixed region converted spontaneously to the hydride phase at high coverage. Upon doing so, we also observe that the Sc $3p$ core level shifts to its dihydride position from that characteristic of the α phase, 28.9 eV.

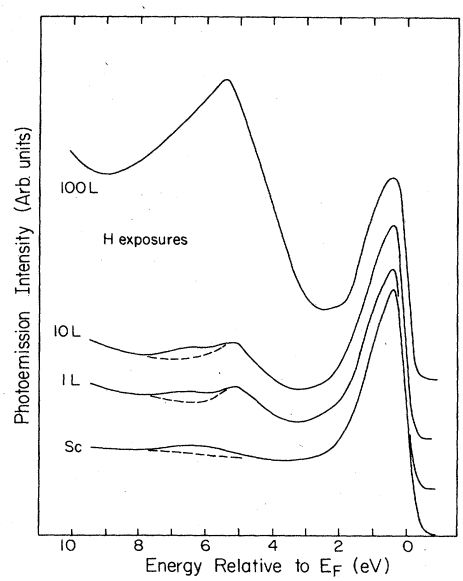

FIG. 3. EDC's showing the conversion of a clean Sc film to a hydride as the surface is exposed to H *in situ* at 300 K. Exposures are given in langmuirs where 1 L $=10^{-6}$ Torr sec.

It is important that the results obtained by hydrogen exposure were indistinguishable from those for bulk samples of the α phase and dihydride phase. Since it is unlikely that the room-temperature, spontaneously-reacted hydride would form with crystalline long-range order, these results provide further evidence for the importance of local chemical bonding. Such local bonding is apparently more important for the establishment of the gross character of the density of states than long-range order. Further support for this comes from previous results which showed that, when hydrogen outdiffuses from a hydride into a vapor-deposited metal overlayer, a system is formed with overall electronic properties identical to those of a hydride.[26] In the case of V overlayers on NbH, x-ray analysis indicated that the resulting VH overlayer had no long-range order.

In sharp contrast to hydrogen chemisorption on Sc, we have found that the H reactivity of cleaved α-phase hydride is very low and no changes were observed which could be unambiguously related to hydrogen absorption

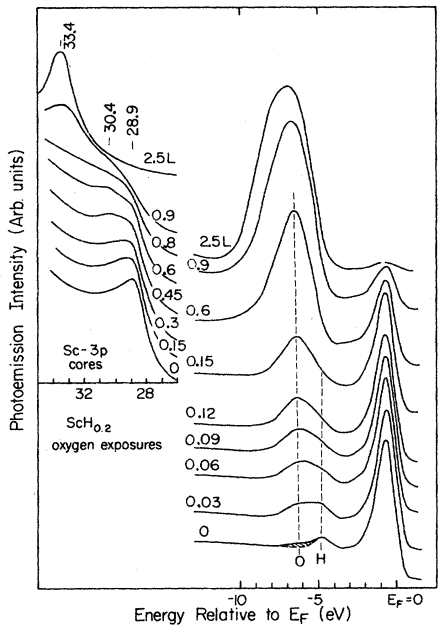

FIG. 4. EDC's showing the enormous effect of oxygen exposure on α-$ScH_{0.2}$. The presence of oxygen at the 1—2 % level can significantly disturb the appearance of the hydrogen states. At the same time, these oxygen-induced features fall at greater binding energy and can be correlated with changes in the Sc $3p$ core line shape induced by oxidation (inset).

for exposures to 1000 L of H_2. We must conclude that this is related to kinetic factors involved with the morphology of the thin Sc films.

Finally, in Fig. 4 we show the effect of oxygen exposures of $ScH_{0.2}$. These experiments were done to determine the level of sensitivity of the spectra for oxygen contamination. High-purity oxygen was admitted to the chamber sufficiently to increase the operating pressure from 5×10^{-11} Torr to 2.5×10^{-10} Torr. The ramp controlling the sweep of the analyzer energy was then started and the EDC was recorded. As each EDC was completed, the system was reset and a new trace was drawn. In this way, the dynamic behavior of oxygen/ScH_x or oxygen/YH_x system was determined. Representative spectra are shown in Fig. 4. As can be seen, these samples were extremely sensitive to oxygen. By 0.03 L exposure the hydrogen-induced feature was distorted and by 0.06 L the oxygen-induced feature was larger than that of hydrogen. If we assume a unity sticking coefficient, then we conclude that surface oxygen at the 1—2 at. % level is sufficient to produce misleading valence-band results concerning the electronic interactions of hydrogen with Sc or Y. In contrast, however, the core results were a much better indicator of the overall situation at the surface. As shown in the inset of Fig. 4, a second core feature was observed at -30.4 eV for low coverage (initial stage of oxidation). The final component did not appear until higher exposures (shifted to 33.4-eV binding energy), at which point the metal emission near E_F was very small and the probed region was converted to oxide.

V. CONCLUSION

In this paper, we have shown that the incorporation of hydrogen in small amount into a host lattice induces states 5 eV below the Fermi level. We have compared the experimental results with calculations for the electronic structure of α-phase hydrides. We have suggested that interatomic Coulomb energies (ionic cohesive energies) contribute to the stability of high-x hydrides compared to low-x solid solutions in metal-hydrogen systems with electropositive metal components. Self-consistent electronic structure calculations as a function of hydrogen concentration would be able to clarify this point. We conclude that there is general qualitative understanding of the modifications to the electronic structure of the metal induced by hydrogen. With this general understanding, the role of hydrogen in complex intermetallics can be approximated. On the other hand, there is *substantial* room for improvement and elucidation of the details of local interactions.

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