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X-ray photoemission spectroscopy study of zirconium hydride

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X-ray photoemission spectroscopy (XPS) measurements are reported for $ZrH_{1.65}$ and Zr metal. The valence-band measurements are compared with available band-theory density-of-states calculations for the metal and hydride. The hydride spectrum differs significantly from the metal spectrum. Most important, a strong peak associated with hydrogen s electrons appears approximately 7 eV below the Fermi level. XPS measurements of Zr $4p$ core levels show a binding-energy shift of 1 eV between Zr metal and $ZrH_{1.65}$. It is argued that this shift results from charge readjustment in the vicinity of the Zr site. With the addition of hydrogen, net charge must be transferred from the Zr site to the hydrogen site. A charge-density analysis based on simplified cluster calculations is presented.

I. INTRODUCTION

The electronic structure of transition-metal hydrides has long been a subject of considerable interest and controversy. Historically, rather simple (and contradictory) models were advocated to account for the observed electronic properties of the metallic hydrides. On the one hand, it was proposed that with the addition of hydrogen to a transition metal, electrons migrate from the hydrogen to the valence band of the metal ("protonic" model).[1] The dominant effect in this model is to produce a shift in the position of the Fermi level and attendant effects associated with filling of the conduction-band states. An alternative anionic model[2] assumed that hydrogen tends to act as an electron acceptor with the net result that electrons should shift from the vicinity of metal-atom sites toward the hydrogen sites. A third model[3] assumed that the metal and hydrogen atoms are covalently bonded. Recently, band calculations have been reported for several transition-metal hydrides.[4,5] These one-electron type calculations provide results that contradict the rigid-band ideas often invoked, where band filling (or emptying) was expected to occur with varying hydrogen concentration while otherwise leaving the band structure essentially unchanged. The recent band calculations show the appearance of a new intense peak several electron volts below the Fermi level E_F in the calculated density of states $N(E)$ for the hydride. This dominant feature, first reported by Switendick,[4] results from predominantly s-like states that are associated with hydrogen-metal and hydrogen-hydrogen bonding.

Evidence for the existence of the new bonding states has been provided with ultraviolet photoemission spectroscopy (UPS) for the Pd-H system[6] and for titanium films containing absorbed hydrogen.[7] Recently, UPS data have been reported by Weaver[8] for other transition-metal hydrides. The UPS measurements on the Pd-H system were apparently taken at room temperature where the diffusion rate of hydrogen in palladium is very high. One would expect that essentially all hydrogen would diffuse from the sample during (or before) the measurement process unless the sample has a (contaminant) surface overlayer which blocks the escape of hydrogen from the sample.[9] It seems possible that Eastman *et al.*[6] did not examine an atomically clean sample surface of Pd-H. A clean sample might retain essentially no hydrogen in which case the UPS spectrum should reproduce the spectrum for palladium metal. Our attempt to examine, at room temperature, the hydrogen bonding states in Pd-H alloys using the x-ray photoemission spectroscopy (XPS) technique was not successful, apparently because of hydrogen escape from the clean surface.

The question must be raised whether the reported peak at 5.4-eV binding energy in Pd-H is attributable to the metal-hydrogen bond or if it could be associated with surface impurities. The possibility exists that surface contamination was sufficiently heavy to block the hydrogen from escaping but was sufficiently thin to contribute insignificantly to the UPS spectrum. In this case, the data and conclusions of Eastman *et al.* are accurately represented. Nonetheless, the apparently contradictory requirements of the UPS technique and sample maintenance necessarily call into question the conclusions of Eastman *et al.* reported for the Pd-H system.

The Ti-H data[7] were acquired on deposited films of titanium which were exposed to residual or controlled hydrogen atmospheres. Thus, no estimate of the hydrogen concentration in the samples could be made. The reported data show a dominant feature at 5 eV below E_F, which has been attributed to the hydrogen-induced bonding state predicted by

Switendick.[4]

In this paper we report XPS measurements on the Zr-H system. This system was chosen because it is stable at room temperature and because hydrogen can be added to zirconium in large concentrations. Furthermore, it should be suitable to test predictions reported by Switendick[4] for the transition-metal-hydride systems.

II. EXPERIMENTAL

At least three hydrides of zirconium have been reported.[10] Rapid cooling of α-Zr–H solid solution is known to result in the formation of α-Zr+γ-ZrH. This metastable hydride has a fct sublattice of metal atoms. For $1.5 < c_H/c_{Zr} \leq 2$, two stable, nonstoichiometric hydrides are known. The metal sublattice of $ZrH_{1.6}$ is fcc, but it becomes distorted to fct for $1.8 < c_H/c_{Zr} \leq 2$. Measurements in this study were made on the fcc phase for which $a_0 \simeq 4.77$ Å.[11]

Crystal-bar zirconium was heated to 800 °C in a vacuum of 2×10^{-6} Torr and cooled to room temperature in a measured quantity of H_2 gas. Purified H_2 was obtained by thermal decomposition of UH_3. The final composition of the specimen was determined volumetrically to be $ZrH_{1.65}$.

The XPS data were acquired using a Hewlett-Packard HP 5950*A* photoelectron spectrometer equipped with a Nicollet model 1180 minicomputer. Before insertion into the spectrometer, a sample was ground to the appropriate shape. The sample was then inserted into a preparation chamber ($\sim 10^{-8}$ Torr) attached to the spectrometer where the surface was scraped with an abrasive alumina rod. Immediately after scraping, the sample was inserted into the spectrometer without exposure to air.

Zirconium (and hydrides of zirconium) are difficult to study with photoemission techniques because of the extreme surface activity. The samples must be prepared and the spectra acquired in an ultra-clean environment if no oxidation is to be encountered. The pressure in our sample chamber is in the low 10^{-9}-Torr range, not sufficiently low to avoid surface oxidation. However, at this pressure, the growth rate of the surface oxide film is sufficiently slow so that spectra with a reasonably good signal-to-noise ratio can be acquired during the growth process. Since zirconium forms only a single oxide (ZrO_2), it appears that one can obtain both "clean-metal" and ZrO_2 measurements in an "unclean" system by monitoring the growth rate of the oxide on a (nearly clean) metal sample surface. The procedure is simply to subtract, on a point-by-point basis, properly scaled spectra containing different ratios of oxide and metal contributions.

Clearly, this procedure will not generally work for binary systems or for elements which form a series of stable oxides because then one does not have a simple superposition of two spectra. Zr-H is a binary system but any effect of the hydrogen in the surface oxide of the Zr-H sample is undetectable.

In order to properly scale two sets of valence-band spectra, sequential sets of core-level Zr-3*d* spectra (taken under conditions obtained during the acquisition of the valence spectra) are weighted and subtracted to isolate the surface oxide contribution from the substrate. The scaling factor is then used for separating the valence-band data. We insure that comparable conditions for acquisition of the core and valence spectra prevail by acquiring the spectra concurrently. Computer control of the spectrometer enables us to acquire data "concurrently" in different spectral regions. Repetitive scans of a single line are always needed for an adequate signal-to-noise ratio. Two (or more) spectral regions are obtained concurrently by recording the individual scans of the different regions in alternate sequence.

This procedure was tested using pure zirconium metal, as discussed subsequently, with satisfactory results. The procedure was then applied to $ZrH_{1.65}$ again using the assumption that ZrO_2 forms slowly on the surface. The possible presence of hydrogen in the oxidized overlayer was not observed in the extracted ZrO_2 data. The extracted ZrO_2 spectra obtained from the partially oxidized zirconium metal surface and from the $ZrH_{1.65}$ surface were compared with independently measured spectra from a bulk ZrO_2 sample. The agreement among these three sets of measurements supports the assumption that, for the partially oxidized surfaces, the observed spectrum is essentially a simple superposition of two sets of spectra (one from ZrO_2, and another from the bulk substrate).

III. RESULTS AND DISCUSSION

A. Zirconium metal

Figure 1 shows several sets of spectra for Zr 3*d* levels as the oxide layer thickness increases. In Fig. 1(a), the spectrum is dominated by the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit split levels of zirconium metal. The 3*d* levels of the overlayer oxide are chemically shifted by approximately 4.2 eV to higher binding energy. For the series of spectra designated (a)–(e) in Fig. 1, the oxide coverage increases as shown by the increasing size of the high binding energy doublet. Figure 2(b) shows a measured spectrum for a partially oxidized zirconium metal surface. Curves (a) and (c) of Fig.

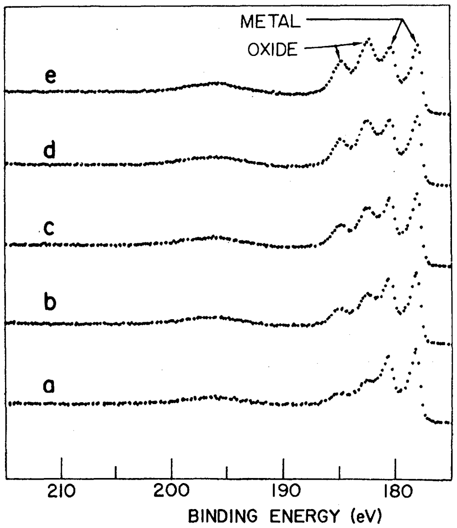

FIG. 1. Spin-orbit split Zr $3d$ core levels for Zr metal and superimposed Zr $3d$ doublet from an overlayer ZrO_2 film. Curves (a)–(e) show increasing ZrO_2 film thickness.

2 shows the separated Zr $3d$ levels for the metal and the oxide, respectively. In some cases, the separation is improved if the component spectra are shifted (less than 0.05 eV) relative to one another. Note that the separation of the adjacent points in Fig. 2 is ~0.2 eV.

Figure 3 shows a similar set of spectra for the valence-band region. Curve (b) is the measured spectrum of the oxide coated zirconium metal. Curves (a) and (c) are the separated metal and oxide valence-band spectra, respectively. These spectra were recorded "concurrently," as discussed above, with the $3d$ core level spectra using the same relative scaling factors. Again the chemical shift of the Zr $4p$ levels is seen. The O $2s$ and the molecular orbitals made up from O $2p$ and the zirconium valence electrons are separated from the measured composite spectrum and appear only in the ZrO_2 spectrum. The valence band of the metal appears at substantially lower binding energy than the O $2p$'s and, of course, is truncated at E_F by the Fermi cutoff.

We are unaware of any reported XPS measurements for the valence bands of zirconium metal. Thus, in Fig. 4, we shall compare our results with the density of states calculated by Jepsen *et al.*[12] The weak structure appearing near 7.5 eV may be a consequence of the oxide overlayer on the measured sample. The data separation technqiue may not be capable of completely eliminating all effects of the overlayer. Nonetheless, within noise limitations, the agreement between the XPS valence-band measurements and the calculation[12] is quite satisfactory.

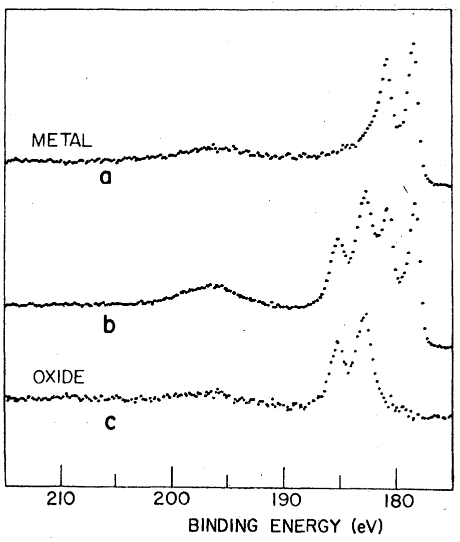

FIG. 2. Measured Zr $3d$ core levels for a partially oxidized Zr metal sample (center curve) and separated contributions from the metal and overlayer oxide.

Since the Fermi level is reasonably well defined in these experiments, we shall report binding energy measurements for prominent Zr core lines, referenced to E_F. Results for Zr and $ZrH_{1.65}$ appear in Table I. The accuracy of these measurements is limited by our ability to define the Fermi cutoff energy (see Figs. 4 and 8).

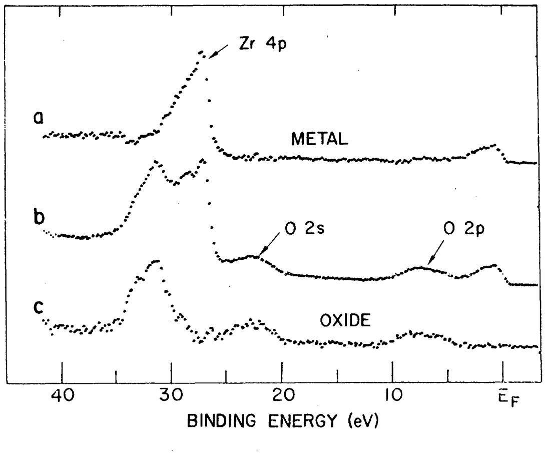

FIG. 3. Measured XPS spectrum near the Fermi level E_F for a partially oxidized Zr metal sample (center curve) and separated contributions from the metal and overlayer oxide. The metal spectrum shows no O-$2s$ or O-$2p$ contribution and the oxide spectrum does not show the peak near E_F.

TABLE I. Measured binding energies for Zr and $ZrH_{1.65}$ (eV).

	$3d_{3/2}$	$3d_{5/2}$	$4p_{1/2,3/2}$ [a]	Chemical shift $3d$	Chemical shift $4p$
Zr metal	180.8	178.4	27.0	···	···
$ZrH_{1.65}$	181.5	179.1	28.0	0.7	1.0

[a] Peak position.

B. Zirconium hydrides

Using the procedure described previously for extracting the zirconium metal data, we show in Fig. 5, the valence-band results for $ZrH_{1.65}$. Consistent with the results of Fig. 3, we find no evidence of oxygen in curve (a). In curve (c), the separated ZrO_2 spectrum, we again find the strong O-2s- and O-2p-derived peaks. Figure 6 shows a blow-up of Fig. 5 for the region near E_F. We show in Fig. 7 the ZrO_2 spectra obtained from (a) ZrO_2 powder measured directly and (b) the $ZrH_{1.65}$-ZrO_2 separation procedure. These spectra are nearly identical.

The separated valence-band spectrum of $ZrH_{1.65}$ in Fig. 6(a) shows a double peaked structure with approximately half of the intensity in the high binding energy peak centered ~7 eV below E_F. The 7-eV peak occurs at approximately the same energy as the O 2p of the overlayer. However, the complete elimination of the O-2s peak from the measured composite spectrum indicates that the strong 7-eV peak of the hydride is not a consequence of oxide contamination. This view is reinforced by the Zr metal data, which, consistent with the calculations of Jepsen *et al.*,[12] show essentially complete elimination of the 7-eV peak. The hydride spectra are very different from the valence-band spectra of zirconium metal, a result that clearly rules out use of the rigid-band model. The results are qualitatively consistent with the UPS observations of Eastman *et al.*[6] for Pd-H and for Ti-H and with the prediction of

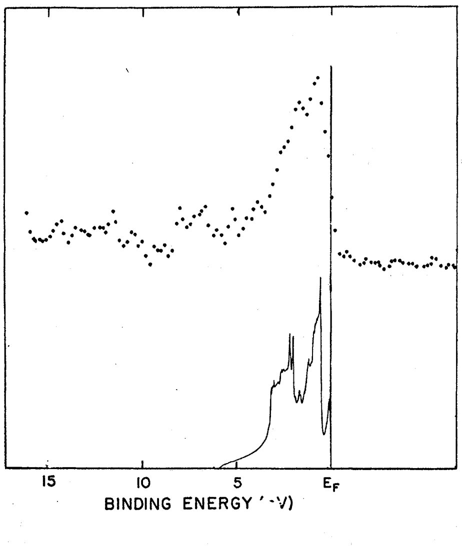

FIG. 4. Zr metal valence-band XPS spectrum (dots) compared with the density-of-states calculation of Jepsen *et al.* (Ref. 12).

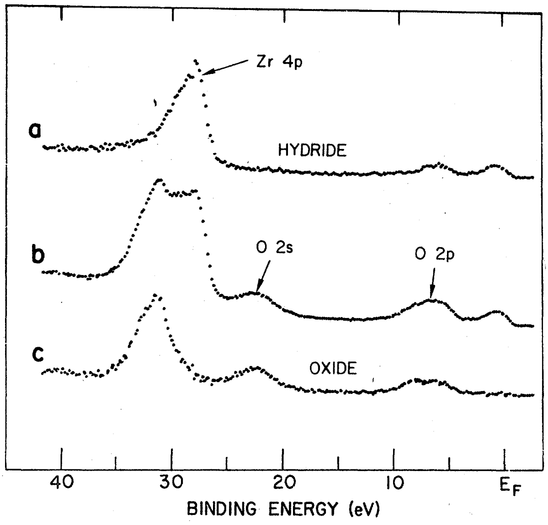

FIG. 5. Measured XPS spectrum near E_F for a partially oxidized $ZrH_{1.65}$ sample (center curve) and separated contributions from the hydride and overlayer oxide.

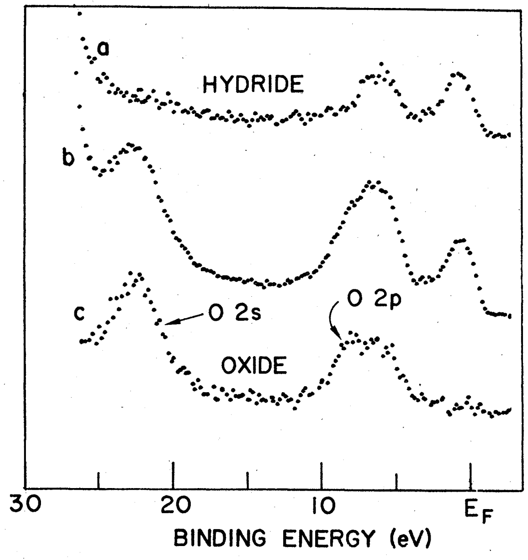

FIG. 6. Blowup of the spectra near E_F that were shown in Fig. 5. No O 2s appears in the separated hydride spectrum and the Fermi edge peak does not appear in the oxide spectrum.

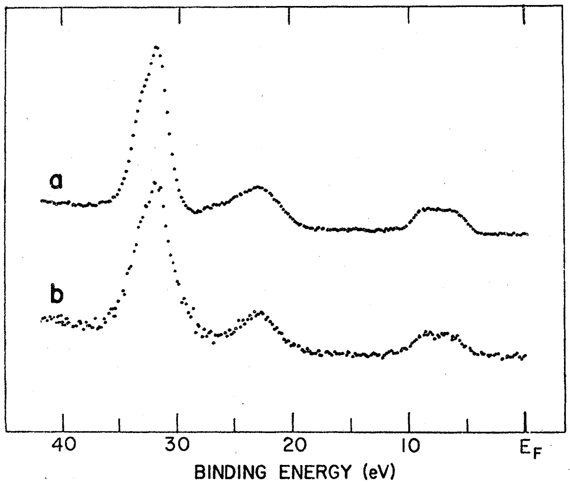

FIG. 7. Comparison of ZrO_2 XPS spectra (a) from measured bulk ZrO_2 and (b) from separating the overlayer ZrO_2 contribution from a partially oxidized $ZrH_{1.65}$ sample.

Switendick[4] based on one-electron band calculations.

Figure 8 shows our $ZrH_{1.65}$ valence-band data compared to the interpolated $N(E)$ vs E curve computed for TiH_2.[4] This comparison is made because no such calculations exist for zirconium hydride and because one would expect the titanium and zirconium hydride systems (like the pure metals)[12,13] to be very similar. The rather featureless theoretical density-of-states curve is remarkably well confirmed by experiment, especially the location of the s-like bonding peak ~7 eV below E_F and the intensity of this peak relative to the peak near the Fermi energy. Switendick's results show that the s-like peak intensity is a strong function of hydrogen concentration, growing with increasing hydrogen-to-metal ratio. The experimental H to Zr ratio is 1.65, so that the s peak, relative to the peak near E_F, should be smaller than predicted in the TiH_2 calculation, a result which is also confirmed in Fig. 8.

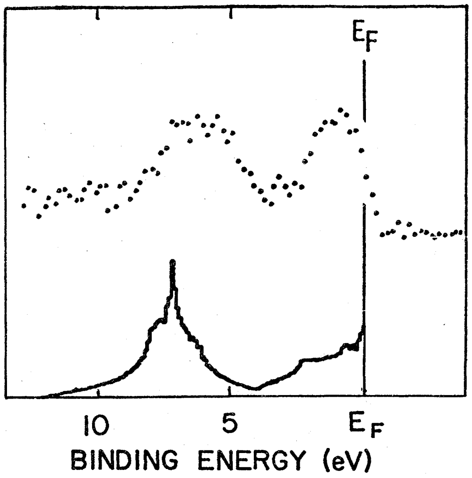

FIG. 8. $ZrH_{1.65}$ XPS valence-band spectrum (dots) compared to density of states for TiH_2 calculated by Switendick.

Figure 9 shows the zirconium hydride spectrum for the first 40 eV below E_F compared to the comparable spectrum for zirconium metal. To minimize the noise level, ZrO_2 spectra (scaled to eliminate the O-2s peak) were subtracted from the measurements for partially oxidized samples of Zr and $ZrH_{1.65}$. The energy scales are aligned to make the Zr 4p levels coincide. With this alignment, we see a significant shift in the binding energy of the Zr 4p level relative to the Fermi energy for the two metallic samples. The shift is about 1.0 eV (see also Table I).

This XPS core level shift (relative to fixed E_F) is directly related to charge distribution at the Zr atom site. However, observed shifts are difficult to interpret quantitatively, primarily because of poorly understood extra-atomic relaxation effects which contribute to the shift. Relaxation effects can be large for a core level of an element in a metallic solid because of the tendency of mobile conduction electrons to screen the core hole produced in the XPS excitation process. For this study, we need to establish that the relaxation shift of a core line in Zr metal is essentially the same as the relaxation shift in $ZrH_{1.65}$ (or, more

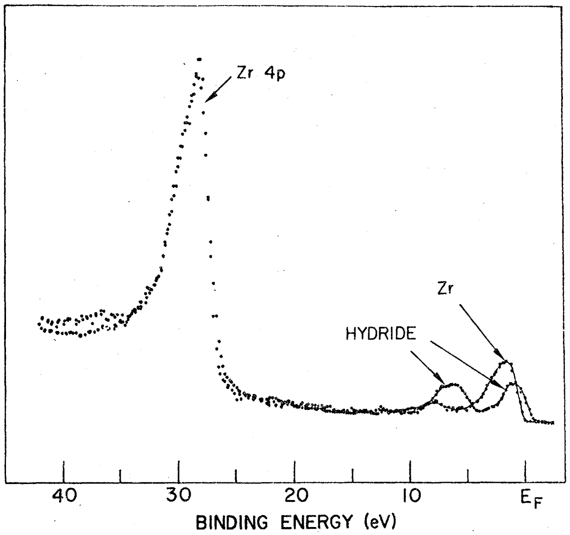

FIG. 9. XPS spectra near E_F for Zr metal and $ZrH_{1.65}$. Relative to the Fermi energy, the Zr 4p core level of $ZrH_{1.65}$ is shifted to higher binding energy. (For clarity, the spectra are displayed with the core levels aligned showing an apparent Fermi level shift.)

precisely, the difference in these relaxation shifts should be small relative to the observed core level shift). This condition cannot be indisputably established but an argument can be made that it is satisfied.

Extra-atomic relaxation has been computed[14] for the $3d$-transition metal series using a simple "excited atom" model to represent the screened core hole. The $4d$ series, which includes Zr, should show similar behavior. For titanium, the relaxation shift is about 6 eV but is insensitive to the nature of the screening electron. Similar results were obtained for $3d$ and $4s$ screening electrons. Furthermore, relaxation effects are found to be approximately constant for adjacent elements of the $3d$ series. Starting at titanium in the $3d$ series, a difference of 1 eV in relaxation energy would not be realized until one had moved three elements away.

Consistent with the "excited atom" model calculations, Lang and Williams[15] find, for atoms chemisorbed on metallic surfaces, that relaxation is quite insensitive to the density and angular character of screening electrons. However, their results indicate that relaxation is sensitive to the atomic number of the excited atom. The calculated shift for the $3d$ series is influenced by differences in the nuclear Coulomb potential as well as the valence electron concentration. For the Zr-$ZrH_{1.65}$ comparison, the Coulomb difference is not encountered—only differences in the *screening* electrons need be considered. Since the relaxation depends weakly on the screening charge, it seems likely that the observed core line shift between Zr and $ZrH_{1.65}$ is not dominated by relaxation effects.

The binding energy shift for the hydride relative to the pure metal indicates that a net charge shift has occurred in the vicinity of the zirconium atom as hydrogen is added. The hydride core level shift to higher binding energy (relative to fixed E_F) indicates that charge is transferred away from the vicinity of the zirconium atom with the addition of hydrogen. The system must, of course, be electrically neutral so that significant charge redistribution must be occurring in the hydride stimulated by the presence of the hydrogen. Presumably enough of the available charge is "tied up" in a hydrogen-metal bond so that a net reduction in electron density at the zirconium site is realized.

When hydrogen is added to zirconium, a substantial lattice expansion occurs so that the Zr-Zr separation is significantly increased. The question arises whether a charge dilution effect might occur such that the electron density at the zirconium site is reduced simply from lattice expansion (rather than charge transfer). The following simple charge-density analysis indicates that this conclusion is unlikely. If we assume that Zr contributes four valence electrons uniformly to the metal, we find that for the Zr hcp lattice (with $a=3.2312$ au and $c/a=1.5931$),[16] the electron density is 0.0255 electrons/au^3. For $ZrH_{1.65}$, if one assumes that additional 1.65 electrons are contributed by the hydrogen system, we see that this additional contribution would more than compensate for the dilution in the Zr electron density that would otherwise result from lattice expansion. Taking the metal sublattice of $ZrH_{1.65}$ as an fcc structure with $a_L=4.77$ Å, we find that the average conduction electron density in the hydride phase is increased to 0.0309 electrons/au^3. Similarly, the dilution effect can be tested if one assumes that that Zr wave functions in $ZrH_{1.65}$ are unchanged from Zr metal and the hydrogen electrons have their free-electron distribution. The tails of the added free hydrogen wave functions contribute more charge to the Zr site than the receding Zr neighbors withdraw from that site. The increase in electron density around a Zr ion in $ZrH_{1.65}$ compared to that in pure Zr would have the effect of shifting core levels of Zr in the hydride to lower binding energies. Since we observe the opposite behavior, it must be argued that chemical effects are dominant over the lattice expansion effect.

The theoretical results of Switendick provide no information regarding charge redistribution in zirconium hydride relative to Zr metal since wave functions were not computed. However, some insight into charge redistribution can be obtained from a molecular-cluster type of calculation. Jena *et al.*[17] have examined a Pd_6H cluster (a hydrogen atom surrounded octahedrally by 6 Pd atoms), and found that the charge density in the vicinity of the proton site is significantly larger than the sum of the interstitial Pd-metal charge density (calculated for Pd_6) plus the density of the free hydrogen atom. Thus, it would appear that the proton, when added to palladium metal, provides a strong attractive potential and that charge migrates from the palladium site to the proton site (rather as envisioned by proponents of the "anionic" model). This result is consistent with the XPS binding energy shift of the zirconium core lines in zirconium hydride relative to zirconium metal.

Simplified cluster calculations for Pd-H have also been reported by Jena *et al.*[18] Again, a Pd_6H cluster was considered, with the hydrogen atom octahedrally coordinated to the six surrounding metal atoms. To estimate charge transfer associated with the presence of the hydrogen atom, two calculations were performed. One calculation was simply to compute the charge density from Pd_6 at the octahedral site resulting from the overlapping atomic charge densities of the six palladium atoms. The second step was to calculate the electron density self-consistently in the density functional formalism in the vicinity of the hydrogen atom placed in the charge environment of the octahedral site of the Pd_6 cluster. It was assumed that the response of the electrons to the proton is as if the proton is situated in a homogeneous electron gas of density equal to that at the octahedral site of the Pd_6 cluster. Any charge transfer would appear as the integrated self-consistent-field (SCF) charge density (in a sphere of radius R about the proton) minus the sum of the integrated ambient charge density of the Pd_6 cluster plus the integrated free hydrogen charge density. This simple local density approximation to the molecular cluster approach agrees very well with the SCF cluster results of Jena *et al.*[17] Using the simplified cluster model for Zr_4H (appropriate for the fct lattice) Jena[17] has computed the results shown in Fig. 10. Figure 10 shows the electron charge contained in a sphere of radius R about the hydrogen atom. The dashed curve is the result for a free hydrogen atom. This integrated charge will approach the value 1 as R becomes infinite. The solid curve shows the integrated charge for Zr_4H about the tetrahedral site when the ambient zirconium metal background has been subtracted out. If we represent the total charge for Zr_4H as $Z_{tot}(R)$, then

$$Z_{tot}(R) = Z(R) + Z_{Zr}(R) ,$$

where $Z_{Zr}(R)$ is the integrated zirconium metal charge density for the Zr_4 cluster. Thus, $Z(R)$ is the integrated charge about the hydrogen site after the original intersitial charge contribution from the zirconium metal has been subtracted. For $R < 3$ Å, this integrated charge is everywhere greater than the charge associated with the free hydrogen atom. This result is also shown in plots of electron density (spherically averaged) for the two cases discussed above (shown in the inset of Fig. 10).

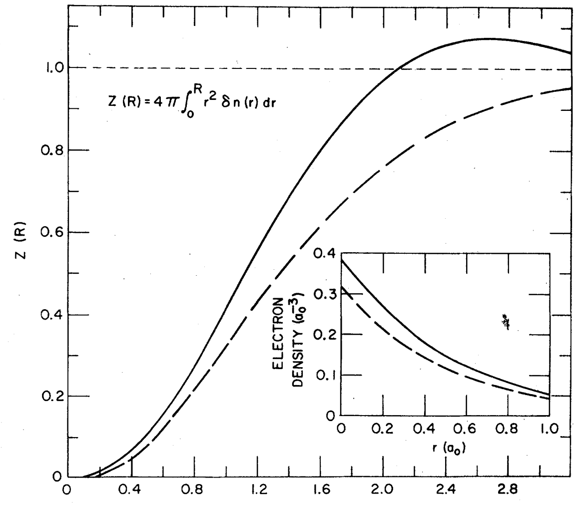

FIG. 10. (a) Dashed curve—integrated charge density about the free hydrogen atom. (b) Solid curve—integrated charge density about the hydrogen site in Zr-H calculated for a Zr_4H cluster with the contribution from the ambient Zr metal subtracted out. The larger magnitude for the hydride suggests that charge is transferred from metal to hydrogen sites when the hydride is formed. The inset shows the corresponding charge densities about the hydrogen site.

The integrated charge $Z(R)$ near the proton site exceeds the value of 1, the maximum for free hydrogen, and exhibits oscillatory behavior indicating that regions of electron depletion (relative to zirconium metal) must occur near the zirconium site. Relative depletion occurs for $R \gtrsim 2.6$ Å. The substantial increase in electron density about the proton site (relative to free hydrogen) means that charge is transferred from the vicinity of the zirconium atom leaving a net positive charge near the zirconium site. This positively charged environment will be sensed by the highly localized atomic core electrons of the zirconium atom and will be reflected as a shift in the XPS core level energies relative to the Fermi level of the material.

For the Pd-H system, Papaconstantopoulos *et al.*[5] reported self-consistent band calculations based on the augmented plane wave method. Consistent with the XPS results for Zr-H, these workers also conclude that, as hydrogen is added to palladium, charge is transferred from the transition metal to the hydrogen site. Using suitably defined muffin tin spheres, they computed the difference between the final self-consistent charge and the starting "superposed atomic" charge and concluded that, for each added hydrogen atom, from 0.1 to 0.3 electrons are transferred from the metal site to the hydrogen site.

For hydrogen in transition metals, it may be that, quite generally, hydrogen prefers to act as an electron acceptor rather than an electron donor. This tendency has now been demonstrated theoretically for hydrides of palladium and zirconium by the use of different approaches and has been experimentally confirmed for zirconium hydride.

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