Photoemission investigation of the electronic-structure changes in Zr-Ni-Cu metallic glasses upon hydrogenation

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The electronic density of states (DOS) in the valence band of $Zr_{50}Ni_{50-x}Cu_x$ metallic glasses ($x=10$, 15, 17, and 20) and their hydrides was investigated by means of ultraviolet photoemission spectroscopy (UPS). In the spectra, one could distinguish Cu-, Ni-, and Zr-derived states both before and after hydrogenation. It was found that hydrogen markedly modified the states mainly in the region of Cu-derived states whereas the Ni- and Zr-derived states were affected to a lesser extent or in a different way by hydrogen. The effect of hydrogenation on the Cu-derived $3d$ valence-band states was ascribed to a hydrogen-induced phase separation as a result of which the Zr-Ni-Cu metallic glass transformed into a nanoscale mixture of Cu-rich clusters and copper-depleted Zr-Ni-Cu-H glassy hydride regions.

I. INTRODUCTION

In recent decades, there has been a great interest in investigating the hydrides of transition-metal intermetallic compounds.[1-3] These compounds are composed of an early transition-metal (TE) such as Ti, Zr, or La and a late transition metal (TL) such as Fe, Co, Ni, Pd, or even Cu. Typical examples are the compounds TiFe or LaNi₅. The ability of absorbing a relatively large amount of hydrogen (as high as a hydrogen-to-metal atomic ratio of $H/M=1$) by these compounds is due to the fact that they contain one of the early transition metals, which can absorb hydrogen in elemental form as well.

It turned out subsequently that not only the crystalline compounds but the TE-TL-type amorphous alloys can also absorb a comparatively large amount of hydrogen.[4-6] In general, the hydrogen absorption capacity depends on two factors: (i) electronic band structure[7-8] in terms of the electronic density of states (DOS) at and below the Fermi level E_F and (ii) packing constraints,[4,5,9,10] i.e., the availability of appropriate sites with sufficiently low binding energy for the accommodation of H atoms.

In elemental metals and intermetallic compounds, hydrogen absorption is often accompanied by a change of the original crystal structure[10,11] to another one just in order to create a sufficient number of available H sites. In amorphous metals, although a quasitransformation of the original amorphous structure into a different amorphous phase upon hydrogenation cannot, in principle, be excluded, there has not yet been found any indication for this phenomenon, which could, anyway, hardly be characterized or visualized. However, even in metallic glasses there is a possibility for the hydrogen to cause

changes in order to promote the creation of a larger number of energetically favored sites than was in the as-quenched amorphous state. This phenomenon is realized via the process that we might call hydrogen-induced atomic rearrangements (HIAR).

This process, although it can be observed in intermetallic compounds such as TiFe (Ref. 12) or LaNi₅ (Ref. 13) as well and is probably the main cause for the occurrence of so-called "sloping plateaus" after repeated hydrogen cycling,[14] is especially pronounced in TE-TL-type amorphous alloys, where HIAR can already be observed even after the first hydrogen absorption process.

A very pronounced manifestation of HIAR is the observation of a phase-separation process in several TE-TL-type metallic-glass systems upon hydrogenation: in Ti-Cu,[15-18] in Ce-Cu,[19] in Zr-Ni,[20-24] and in Zr-Ni-Cu.[25-26] A common feature of all these findings is that the TL component not absorbing hydrogen in elemental form (Cu and Ni) segregates out of the matrix and forms microscopic clusters. As a driving force for this effect, we may consider mainly the large difference of hydride formation enthalpies ΔH between the TE and TL metals [e.g., $\Delta H(ZrH_2)=-165$ kJ/mol H_2 and $\Delta H(NiH_{0.5})=-6$ kJ/mol H_2 (Ref. 1)]. As a microscopic approach towards an understanding of this phenomenon, we may apply the model of Harris, Curtin, and Tenhover[27] according to which the H absorption in TE-TL glasses can be described as the accommodation of H atoms into various tetrahedra composed of TE and TL atoms (e.g., Zr_4, Zr_3Ni, Zr_2Ni_2, $ZrNi_3$, and Ni_4 in Zr-Ni glasses with the Zr_4 and Ni_4 sites having the lowest- and highest-lying energy levels, respectively). The binding energy strongly depends on the chemical composition of the tetrahedron and, at a given temperature and pressure,

only tetrahedral sites with a sufficiently deep binding energy are occupied,[6,27] whereas none of the sites with high energy are occupied. Now, if the hydrogen atoms can induce atomic rearrangements by rejecting out of the matrix some of the TL atoms, more sites with lower energy will be created. A prerequisite for the occurrence of such HIAR effects is the larger mobility of the smaller TL atoms in these amorphous hosts. This is, however, fulfilled, since it has been well established that in amorphous matrices like $Zr_{50}Ni_{50}$, because of their small atomic sizes, TL elements such as Fe, Co, Ni, or Cu diffuse much faster[28−30] than the large Zr atoms, which, even at a temperature as high as 250 °C, can be practically considered immobile.[28,30]

An important point concerning the phase separation in TE-TL glasses is also the alloy composition, since it can be expected that at higher TL contents such HIAR effects cannot efficiently contribute to increasing the available H sites; however, this effect has not yet been studied. Besides the eventual lattice transformations or other kind of atomic rearrangements, absorbed hydrogen can also induce a very drastic change of the electronic band structure of the metallic host. Therefore, it is very useful also to investigate the electronic structure of the host both before and after hydrogenation.

Although there are differences in the details characteristic for the actual structural modification, the basic features of the electronic band structure of hydrogen-free TE-TL-type alloys, either crystalline or amorphous, are very similar: the DOS curve consists of two peaks, namely, one around E_F, which derives from the d bands of the TE atoms, whereas the d bands of the TL atoms give rise to a second peak well below E_F (Ref. 31) (for a more recent review, see Ref. 32). As far as the influence of absorbed hydrogen on the DOS is concerned, it has rather common features both in elemental metals[7,33] and in transition-metal intermetallic compounds[33] as is well documented both theoretically and experimentally. Namely, hydrogen induces states in the range 5–7 eV below E_F, the d-band peaks narrow to some extent, and the value of the DOS at the Fermi level $N(E_F)$ usually decreases. An interesting conclusion of these studies was[33] that in the hydrides of the TE-TL-type compounds $LaNi_5$ and TiFe, the H atoms interacted mostly with the TL atoms (Ni,Fe), in spite of the large affinity of the TE atoms (La,Ti) for hydrogen.

The electronic structure of the hydrides of TE-TL-type metallic glasses has been studied less extensively, and, whereas theoretical work is still missing, the photoemission experiments performed on hydrides of Zr-Ni (Refs. 34–41), Zr-Pd (Refs. 34 and 37), Zr-Fe (Ref. 42), Ti-Ni (Ref. 37), and Ti-Pd (Ref. 43) glassy alloys indicates that most of the basic features concerning the influence of absorbed hydrogen on the electronic DOS are retained in such amorphous alloys as well. It was deduced from these studies that a preferential Zr-H or Ti-H bonding occurs in the corresponding glassy hydrides of Zr-Ni (Refs. 34, 37, 39, and 40), Zr-Pd (Refs. 34 and 37), Ti-Ni (Ref. 37), and Ti-Pd (Ref. 43) alloys.

In an effort for a better understanding of the behavior of hydrogen in metals, we have now extended our previous ultraviolet photoemission spectroscopy (UPS) study[40] of the electronic structure of a $Zr_{50}Ni_{50}$ glass and its hydride to the ternary Zr-Ni-Cu system both without and with absorbed hydrogen. The purpose of the present work is twofold: (i) to investigate the influence of a partial replacement of Ni by Cu on the electronic structure of $Zr_{50}Ni_{50}$ metallic glasses and (ii) to study the effect of hydrogenation on the electronic structure in the ternary $Zr_{50}Ni_{50-x}Cu_x$ amorphous alloys. The introduction of Cu into the binary $Zr_{50}Ni_{50}$ metallic glasses has led to the appearance of Cu-derived states at binding energies further below the Fermi level than the corresponding Ni and Zr states. These Cu-derived states were found to be strongly modified upon hydrogenation. It turned out that the results on the Zr-Ni-Cu hydrides can be conveniently interpreted by assuming the occurrence of a fairly pronounced hydrogen-induced phase separation for which we have previously[25] obtained some evidence on the same alloy system from magnetic measurements and TEM observations.

II. SAMPLE PREPARATION AND MEASUREMENT TECHNIQUES

Amorphous ribbons of about 15-μm thickness were quenched from $4N$ purity metals by a single-roller melt-spinning apparatus in a vacuum at 10^{-2} Pa pressure. Hydrogenation of the specimens was carried out from the gas phase at room temperature using a 50-atm overpressure. The amorphous state of the samples was checked by x-ray diffraction both before and after hydrogenation. The alloy composition was measured by atomic absorption spectroscopy. The hydrogen content of the samples was determined by weighing.

In the present work, amorphous $Zr_{50}Ni_{50-x}Cu_x$ alloys with $x = 10$, 15, 17, and 20 were investigated. The hydrogen-to-metal ratio (H/M) was about 0.8 for each Cu content; therefore, the hydrogenated alloys will simply be denoted as $Zr_{50}Ni_{50-x}Cu_x$-H.

For the photoemission investigations, the ribbons were mounted on a copper block using an In-Ga alloy. The surface oxide layer of the sample formed during the different pretreatments was removed by Ar-ion bombardment with a Kaufman ion gun at 1-keV energy before loading the sample into the electron spectrometer used for the photoemission measurements.

The valence-band density of states was investigated by measuring the energy distribution curves (EDC's) of photoelectrons. A HeI resonance discharge lamp (21.2 eV) was the photon source. A 180° spherical analyzer was used for measurement of the EDC's with an absolute energy resolution of 0.3 eV in a Kratos ES-300 spectroscope.

The samples were also cleaned *in situ* by Ar-ion bombardment with 2-keV energy before the UPS measurements. This is very important over the normal experimental requirements for a clean sample, since the presence of a surface Zr-oxide layer can significantly influence the Cu/Ni ratio at the surface because of the fact that, whereas Ni segregates out of the Zr-oxide very strongly in Zr-Ni and Zr-Ni-Cu glasses,[39,44,45] this segregation

tendency is much weaker for Cu in Zr-Ni-Cu glasses.[45] The surface composition and contaminations were checked by x-ray photoemission (XPS) with MgKα excitation with the fix retarding ratio (FRR) mode of an ES-300 spectrometer.

III. RESULTS

A. Surface composition and contamination analysis by XPS

The surface composition of a $Zr_{50}Ni_{35}Cu_{15}$-H sample was measured by XPS for the Zr $3d$, Cu $2p$, and Ni $2p_{1/2}$ atomic line emissions, and the results are shown in Fig. 1. By using excitation cross sections given by Yeh and Lindau[46] and electron transmission vs photoelectron energy dependence at the FRR mode of the hemispherical analyzer, we obtained 1.2/0.75/0.38 for the Zr/Ni/Cu intensity ratios, in relatively good agreement with the nominal bulk composition. The Zr $3d$ emission line [Fig. 1(a)] is equivalent to the spectrum given for pure, oxide-free Zr,[47] showing that our sample is free of the main source of usual contaminant, namely, ZrO_2.

B. Influence of Cu on the DOS of $Zr_{50}Ni_{50}$

The modification of the valence-band DOS of $Zr_{50}Ni_{50}$ amorphous alloys by the addition of Cu in place of Ni is shown in Fig. 2 for two Cu contents. The UPS spectrum is characterized by three large peaks at higher binding energies and by a shoulder at the Fermi edge.

The peak at 5–7 eV is related to the Zr-O interaction and the other features at 0.35 eV, 1.6 eV, and 3.8 eV binding energies correspond to Zr $4d$, Ni $3d$, and Cu $3d$ valence band states, respectively. The intensity ratios of the Ni $3d$ and Cu $3d$ peaks correspond to the differences in the alloy compositions, whereas their positions and line shapes are practically equivalent for both Cu contents.
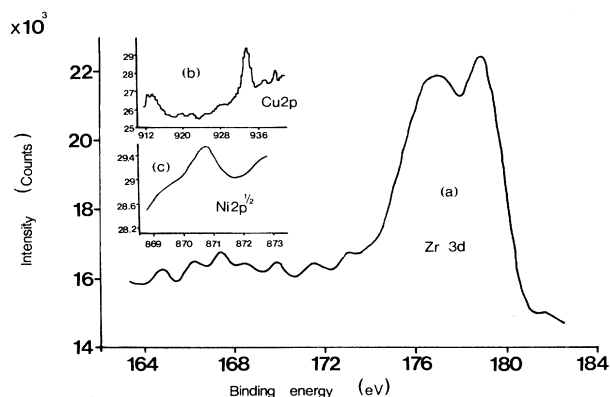
The relative positions of the Zr, Ni, and Cu valence d

FIG. 1. XPS spectra of the $Zr_{50}Ni_{35}Cu_{15}$-H amorphous alloy after Ar-ion etching: (a) Zr $3d$, (b) Cu $2p$, and (c) Ni $2p_{1/2}$ atomic lines. The recording time of each spectrum was the same and MgKα radiation was used as a photon source.
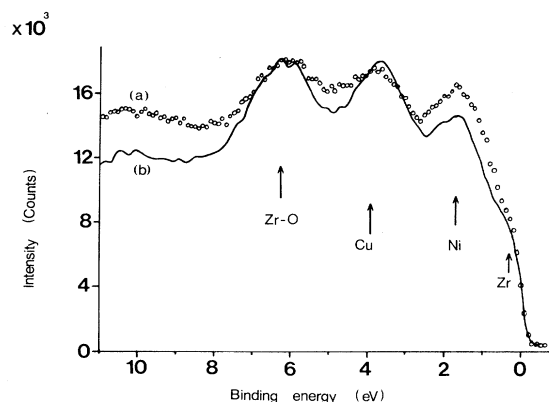
FIG. 2. Valence-band emission spectra in the hydrogen-free amorphous alloys for two Cu contents: (a) $Zr_{50}Ni_{38}Cu_{12}$ and (b) $Zr_{50}Ni_{30}Cu_{20}$.

states in the ternary Zr-Ni-Cu glasses correspond qualitatively to those of the atomic levels of the corresponding elements. It has long been demonstrated by UPS measurements[48] for binary Zr-Ni and Zr-Cu metallic glasses that, whereas the Zr $4d$ states are centered mainly around E_F for both systems, the Cu $3d$ states lie much deeper below E_F than the Ni $3d$ states. Such a relative positioning of the valence d states of Cu and Ni has also been theoretically confirmed by electronic-band-structure calculations for Zr-Ni and Zr-Cu metallic glasses[49] and for the crystalline Zr_3Ni and Zr_3Cu compounds in the Au_3Cu structure.[50] Our measurements (Fig. 2) clearly resolve separately both the Cu and Ni d-state peaks in the ternary $Zr_{50}Ni_{50-x}Cu_x$ amorphous alloys as well, and also the peak positions are approximately the same as observed experimentally[48] and calculated theoretically[49,50] for the binary Zr-Cu and Zr-Ni systems. Our results are supported by the UPS work of Zehringer et al.[51] on an amorphous $(Zr_{67}Ni_{33})_{85}Cu_{15}$ alloy who also observed the Cu and Ni d-state peaks, well resolved separately, at about 3.5 and 1.8 eV, respectively, which are fairly close to the corresponding peak positions in our Zr-Ni-Cu alloys. On the other hand, in a more recent XPS study[52] of amorphous $Zr_{67}(Ni_{1-x}Cu_x)_{33}$ alloys with $x = 0$, 0.39, 0.55, and 1.00, only a single broad DOS peak was detected, which was shifted to higher binding energies (from about 2 to 4 eV) on going from the binary Zr-Ni to the binary Zr-Cu glass.

C. Influence of H on the DOS of $Zr_{50}Ni_{50-x}Cu_x$

The emission in the binding-energy range of the valence band is given in Fig. 3 for the $Zr_{50}Ni_{35}Cu_{15}$-H sample. The spectrum consists of the same components as in Fig. 2 except that both the Zr-O and Zr-H interaction contribute now to the peak at 5–7 eV [Fig. 3(a)].

The Zr and Ni states in the present $Zr_{50}Ni_{35}Cu_{15}$-H amorphous alloy are similar to our previous results for a hydrogenated $Zr_{50}Ni_{50}$ amorphous alloy,[40] as demonstrat-

ed by the detailed spectrum shown in Fig. 3(b), where the Fermi cutoff, as well as the Zr- and Ni-derived states, are clearly visible. The Cu $3d$ states shown in Fig. 3(c) are characterized by an asymmetrical peak with a full width at half maximum (FWHM) of 1 eV.

The variation of the valence-band density of states of hydrogenated $Zr_{50}Ni_{50-x}Cu_x$-H alloys with Cu content is given in Fig. 4. The Zr peak at the Fermi level is de-

FIG. 4. Dependence of UPS spectra on Cu content for $Zr_{50}Ni_{50-x}Cu_x$-H amorphous alloys with $H/M \approx 0.8$: (a) $Zr_{50}Ni_{40}Cu_{10}$-H, (b) $Zr_{50}Ni_{33}Cu_{17}$-H, and (c) $Zr_{50}Ni_{30}Cu_{20}$-H.

creased compared to the nonhydrogenated sample, and these states remain unchanged by varying the Ni/Cu ratio similarly to the nonhydrogenated case. The Ni $3d$ band emission line of the hydrogenated alloys (Fig. 4) is also similar to the peak shape of the nonhydrogenated sample (Fig. 2).

It can be established that upon hydrogenation, there is a deformation of the Cu $3d$ peak shape and a shift of the Cu $3d$ peak position to larger binding energies. These changes in the hydrogenated alloys depend on the Cu content. Moreover, these Cu $3d$ peaks are asymmetrical, and this asymmetry is much more pronounced at larger Cu concentration as is visible in Fig. 5, where the spectra of the hydrogenated alloys with 10 and 17 at. % Cu con-
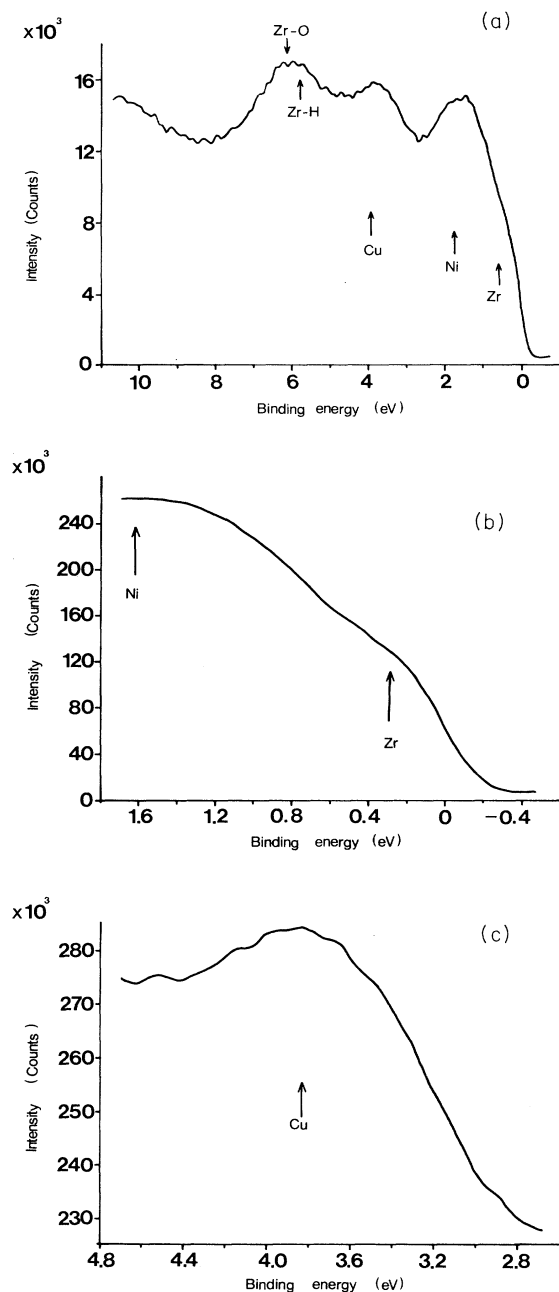
FIG. 3. Energy distribution curves of the photoelectrons excited by HeI from the $Zr_{50}Ni_{35}Cu_{15}$-H alloy with $H/M \approx 0.8$ in different binding energy regions of the valence band: (a) 0–11 eV, (b) 0–1.7 eV, and (c) 2.7–4.7 eV.
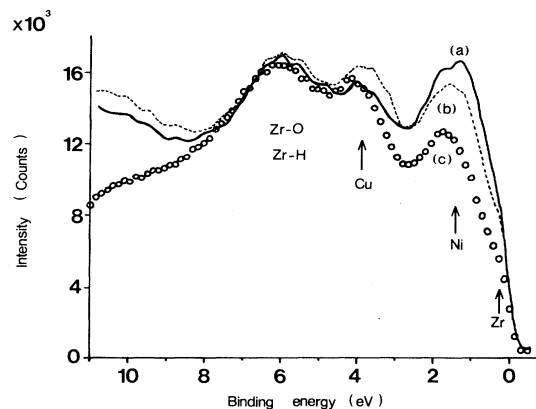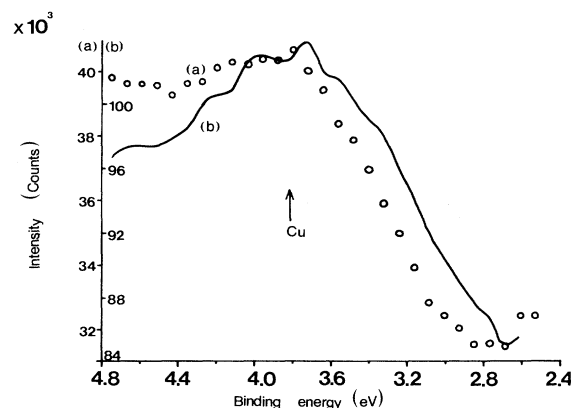
FIG. 5. Dependence of the Cu-derived emission of the UPS curves on Cu content for $Zr_{50}Ni_{50-x}Cu_x$-H amorphous alloys with $H/M \approx 0.8$: (a) $Zr_{50}Ni_{40}Cu_{10}$-H and (b) $Zr_{50}Ni_{33}Cu_{17}$-H. These spectra correspond to the Cu peaks of curves (a) and (b) in Fig. 4 but were recorded here in an independent run with improved resolution.
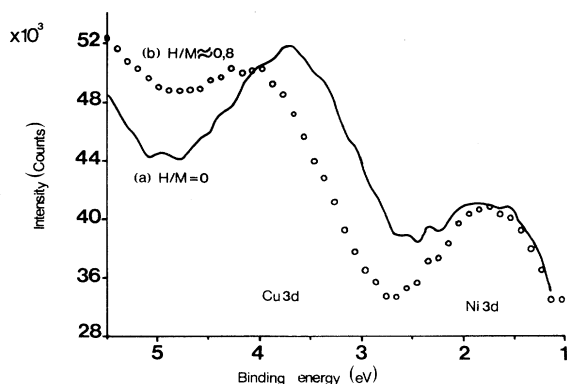
FIG. 6. Modification of Cu-derived states in the $Zr_{50}Ni_{30}Cu_{20}$ amorphous alloy upon hydriding: (a) hydrogen-free alloy ($H/M=0$) and (b) hydrogenated ally ($H/M\approx0.8$). The Cu peaks of curves (a) and (b) correspond to the Cu peaks of curve (b) in Fig. 2 and curve (c) in Fig. 4, respectively, but were recorded here in an independent run with improved resolution.

tent are shown.

The influence of hydrogenation on the Cu 3d and Ni 3d states is shown in Fig. 6, where curve (a) shows the spectrum for $Zr_{50}Ni_{30}Cu_{20}$ and curve (b) shows that for $Zr_{50}Ni_{30}Cu_{20}$-H. It is clear that the Ni-derived states are practically unchanged upon hydrogenation in comparison with the Cu 3d states, the latter of which are changed very much: they are shifted to higher binding energies by about 0.2 eV and their FWHM is larger in the hydrogenated than in the non-hydrogenated alloy (FWHM = 1.3 eV and 1 eV, respectively).

IV. DISCUSSION

A. Surface properties

The Zr-Ni-Cu amorphous alloys are very reactive materials for oxygen mostly because of the Zr component. The influence of oxidation is to change the Zr 4d states and to decrease the local Ni concentration because of the low solubility of Ni in the ZrO_2 compound.[39,44,45] Moreover, the O 2p states can drastically disturb the UPS spectra because of the very high excitation cross section.[46] Some O 2p–like emission via a Zr-O interaction can be seen on the UPS spectrum in the binding-energy range around 6 eV in Figs. 2 and 3(a), but it is far below the level that could influence the photoemission data.

It is clear from the XPS data that the amount of ZrO_2 is below the detectability level, since the Zr 4d states [Fig. 1(a)] are free of the ZrO_2-originated chemical shift, which would be at 182-eV binding energy. The bulklike Ni/Cu/Zr ratio is an independent hint for the oxidation-free state of the sample.

B. Electronic structure of $Zr_{50}Ni_{50-x}Cu_x$ glasses.

As Fig. 2 demonstrates, the peak intensities and line shapes of the Ni 3d, Cu 3d, and Zr 4d states are indepen-

dent of the Ni/Cu ratio, only the relative intensities of the Ni 3d and Cu 3d peaks are changed with Cu content. It is hard to infer any changes in the vicinity of E_F, where the Zr 4d states dominate the DOS. This is in agreement with our general knowledge[31,38,49,50] about the electronic structure of TE-TL glasses in that the TL states (here, Cu and Ni) are usually well below E_F, and, therefore, a variation of the Ni/Cu ratio should not affect the changes around E_F. As a consequence of this feature, $N(E_F)$ is also expected to remain practically unchanged when varying the Ni/Cu ratio, as has, indeed, been deduced[32] from an analysis of low-temperature specific-heat data.

Furthermore, it was established in our previous study[25] of another $Zr_{50}Ni_{50-x}Cu_x$ ($x = 0$, 5, 10, 15, 20, and 25) amorphous alloy series that the as-quenched ribbons are paramagnetic at room temperature, and their susceptibility was practically independent of the Cu content. Although the paramagnetic susceptibility of TE metals and TE-TL alloys is dominated by a Van Vleck term[53,54] mainly originating from the TE atoms, this term remains unchanged when replacing Ni by Cu. Therefore, the magnetic measurements[25] indicate that the Pauli susceptibility and, thus, also $N(E_F)$, does not depend on the Cu content in these $Zr_{50}Ni_{50-x}Cu_x$ glasses, in agreement with the present photoemission experiments.

The position of the Ni 3d peak in binary Zr-Ni glasses changes slightly with composition: it lies at 1.8-, 1.4-, and 1.25-eV binding energies for a-$Zr_{67}Ni_{33}$,[38] a-$Zr_{50}Ni_{50}$,[40] and a-$Zr_{36}Ni_{64}$,[38] respectively, i.e., the Ni 3d states more and more approach the Fermi level as the Ni content increases. According to Fig. 2, even the replacement of almost as much as half of the Ni atoms by Cu atoms changes the Ni 3d peak position to a small extent only. The position of the Cu 3d peak in the binary Zr-Cu glasses is in the vicinity of 3.5 eV,[55] but this is not influenced significantly in the ternary Zr-Ni-Cu glasses as well (see Fig. 2 and Ref. 51).

C. Electronic structure of $Zr_{50}Ni_{50-x}Cu_x$-H glasses

For the Zr-Ni-Cu amorphous alloys, the hydrogenation influences the valence-band density of states in several regions. The Zr-derived states, and, thus, the total $N(E_F)$, decreases at the Fermi level via a Zr-H chemical interaction, as has already been demonstrated earlier for binary Zr-TL glasses.[34,37−40,51] The Cu 3d states are also modified (Fig. 6): the main effect is the shift of the Cu 3d peak to larger binding energies and the development of an asymmetry. This asymmetry may be an indication for a doublet formation, which would mean that after hydrogenation the sample contains two different kinds of Cu atoms. This effect definitely changes with the Ni/Cu ratio (Fig. 5).

Unfortunately, no UPS study has been performed on glassy Zr-Cu hydrides in order to compare the influence of hydrogenation on the Cu 3d states in the binary Zr-Cu and ternary Zr-Ni-Cu glasses. On the other hand, the Ni 3d states in the Zr-Ni-Cu glasses are affected (Fig. 6) to a much less extent only upon hydrogenation than the Cu 3d states. This is in agreement with the results of previ-

ous studies[38,40,41] on Zr-Ni glasses according to which the main effect of hydrogenation on the Ni $3d$ peak is a slight change of the peak position.

As far as the features of the UPS spectra in the binding energy range 5–7 eV are concerned, it has been demonstrated for binary Zr-Ni glasses[38] that a Zr-O bonding peak can occur at about 6-eV binding energy, whereas hydrogen induces a peak at about 5 eV. Correspondingly, in properly sputter-cleaned binary Zr-Ni glasses, no UPS features were observed in this binding energy range, whereas a broad peak (extending from 4- to 8-eV binding energy) was detected in Zr-Ni-H glasses.[38,51]

In our previous study[40] of a $Zr_{50}Ni_{50}$ glass and its hydride, after sputter cleaning we observed a very small Zr-O peak only at 6 eV for $Zr_{50}Ni_{50}$ and a pronounced Zr-H peak for $Zr_{50}Ni_{50}H_{93}$ at about 5 eV. On the other hand, in the present $Zr_{50}Ni_{50-x}Cu_x$ ternary alloy samples it was not possible to get rid of the Zr-O peak completely either before or after hydrogenation. Therefore, the presence of H-derived states is indicated by a small shift, towards smaller binding energies, of the peak around 6 eV [Figs. 3(a) and 4] in comparison with the nonhydrogenated alloys (Fig. 2).

D. Influence of hydrogenation on Cu $3d$ band states

The most striking result of the present work is the change of the Cu $3d$ band states upon hydrogenation. It should be noted that the Cu-derived states are affected by hydrogenation in a different way (see Sec. III C) than the Zr $4d$ states, the intensity of which decreases as a consequence of the Zr-H interaction. We can also neglect the existence of a Cu-H interaction, since the Ni-H interaction is already very weak and it was established that (i) the solubility of H in Cu is well below the solubility of H in Ni,[56] and (ii) the formation of a metal hydride is less and less favored as more and more Cu is alloyed to Ni.[57]

As discussed in Sec. I, hydrogenation of such TE-TL-type amorphous alloys can result in hydrogen-induced atomic rearrangements. A manifestation of such HIAR effects is the occurrence of a phase separation upon hydrogenation. It has been reported[20,22–24] that in Zr-Ni glasses around the equiatomic composition a segregation of Ni atoms can be observed in the hydrogenated alloys. TEM investigations and magnetic measurements have revealed[25] that even more pronounced HIAR effects occur upon hydrogenation in $Zr_{50}Ni_{50-x}Cu_x$ amorphous alloys. The main driving force for these processes is the large difference of hydride formation enthalpies between the TE and TL atoms,[1,56] which is further promoted by the much larger diffusivity of the smaller TL atoms.[30] On the basis of diffusivity data according to which Ni has an order of magnitude higher diffusion coefficient at 573 K in a-$Zr_{50}Ni_{50}$ than Cu,[30] it would be expected that Zr-Ni glasses exhibit stronger phase separation than Zr-Ni-Cu glasses, contrary to what was observed.[25] Therefore, at this diffusivity difference between Ni and Cu, the energetics of hydride formation becomes the dominant factor in controlling the HIAR processes. This means that, whereas in the $Zr_{50}Ni_{50}$ glass a relatively small atomic rearrangement in the amorphous matrix can already re-

sult in the formation of a large number of energetically favorable sites, in the $Zr_{50}Ni_{50-x}Cu_x$ glasses, because of the lack of a significant Cu-H chemical interaction, considerable atomic rearrangements are necessary to minimize the free energy of the metal-hydrogen system. Since the gain in free energy upon proper atomic rearrangements can be higher in Zr-Ni-Cu than in Zr-Ni, the driving force for HIAR effects is also larger. This may lead to the appearance of Cu-rich and Ni-rich (Cu,Ni) segregations, as was actually observed for these ternary glasses.[25]

We believe that the modification of the Cu-derived states as revealed by the present UPS studies in the $Zr_{50}Ni_{50-x}Cu_x$ glasses upon hydriding is due to a segregation of Cu atoms, as a result of which Cu-rich clusters are formed. The size of the clusters should be in the range of a few atoms at most because DOS features characteristic for bulklike Cu cannot be detected at all.

A hint for ascribing the observed changes in the Cu-derived states to the appearance of Cu clusters may also be taken from recent UPS observations on small Cu islands deposited onto a silicon substrate.[58] This study has shown that upon decreasing the island size down to 10 nm in diameter and by about an order of magnitude smaller in height, a shift of the Cu $3d$ states towards higher binding energies occurred, very similarly to the present result.

Two points should still be mentioned. First, in the previous study[25] of Zr-Ni-Cu glassy alloys hydrogenated at 473 K, the occurrence of Ni-rich (Cu,Ni) clusters was also observed, whereas in the present UPS study we have not found a significant variation of the Ni-derived states. The reason for this might be that either the Ni states are less sensitive to changes in the atomic surroundings or the number of Ni atoms segregating is much less here than that of Cu atoms (e.g., due to the fact that the present alloys were hydrogenated at 300 and not 473 K). Second, although the thermal stability of $Zr_{50}Ni_{50}$ amorphous alloys slightly increases with the addition of Cu,[59] a crystallization upon hydrogenation might still occur. However, crystallization can be excluded (i) on the basis of the UPS data, since this would be expected also to modify the Ni- and Zr-derived states and (ii) the TEM results on the same alloy system[25] also do not confirm this possibility.

Finally, as a strong support in favor of ascribing the observed changes of Cu-derived states to the clustering of Cu atoms, the results of Rodmacq and co-workers[15–18] are mentioned. They have, namely, established that in a $Ti_{50}Cu_{50}$ amorphous alloy, hydrogenation to $H/M = 0.84$ leads to a strong phase separation, the result of which could be described as a mixture of small-sized Cu and Ti-H regions[15] on a scale of 1–1.5 nm. By analogy, we can imagine the hydrogenated Zr-Ni-Cu alloys as consisting approximately of almost pure Cu segregations and a copper-depleted Zr-Ni-Cu-H amorphous hydride phase.

In contrast to the $Ti_{50}Cu_{50}$ amorphous alloy, it should be assumed that in the case of Zr-Ni-Cu metallic glasses, not all the Cu atoms form clusters upon hydrogenation. Evidence for this comes from recent proton nuclear magnetic resonance (NMR) studies. It was established, name-

ly, that in the glassy Zr-Ni-Cu hydrides the rigid-lattice line broadening of the proton NMR spectra[60] and the diffusional correlation time of hydrogen atoms in the amorphous matrix[61] indicate that most of the hydrogen atoms (protons) are in close contact with Cu atoms in the *rigid-lattice state* and move in the vicinity of Cu atoms in the *motional-averaged state* (it should be noted that this conclusion is not in contradiction with the present UPS study).

A further check on the applicability of the above suggested model for explaining the present UPS results might be a study of these alloys after dehydrogenation. Namely, if hydrogen indeed induces a segregation of Cu, then, after H is driven out of the sample, the Cu should presumably remain segregated. Therefore, if the changes in the UPS spectra are due to Cu segregation, then they should remain after the hydrogen is evolved from the sample. Unfortunately, such an investigation cannot be performed on the Zr-Ni-Cu alloys. The reason for this is that, because of the large concentration (50 at. %) of Zr atoms in these systems, a significant fraction of the hydrogen atoms resides in Zr_4 and Zr_3Ni tetrahedral sites. Desorption of H from these deeply bound sites requires such a high temperature that, on the other hand, it induces a crystallization of the amorphous matrix. This has been firmly established for a hydrogenated a-$Zr_{50}Ni_{50}$ alloy[62] and for two independent series of $Zr_{50}Ni_{50-x}Cu_x$-H amorphous alloys.[63] These studies have also shown that the desorption of H even from the less deeply bound sites requires considerably high temperatures. At these elevated temperatures, however, the atomic diffusion would be even faster than it was during the H-absorption process performed at room temperature, and, therefore, fairly pronounced atomic rearrangements would be expected to occur, further enhanced by the presence of H. Due to this thermal cycling, obviously, the local atomic arrangements may be significantly different, at the same H content, when comparing the absorption and desorption processes, which is an interesting topic to be studied in itself. On the other hand, a comparison of the results of a variety of studies on Ti-Cu and Zr-Ni-Cu glassy hydrides suggests that it would be very informative to perform a similar UPS work on hydro-genated Ti-Cu amorphous alloys, and the microstructure of the present Zr-Ni-Cu hydrides should also be studied in more detail using TEM. These investigations might yield further justification for the proposed hydrogen-induced segregation behavior in both systems.

V. CONCLUSIONS

The valence-band density of states of $Zr_{50}Ni_{50-x}Cu_x$ amorphous alloys is characterized by Ni $3d$, Zr $4d$, and Cu $3d$ atomic states, and the main features of the valence-band density of states are practically independent of the Cu content in the investigated composition range ($10 \leq x \leq 20$). For the $Zr_{50}Ni_{50-x}Cu_x$-H amorphous alloys with $H/M \approx 0.8$, the valence-band density of states is changed at the Cu-derived states when compared to the nonhydrogenated $Zr_{50}Ni_{50-x}Cu_x$ amorphous alloys, and this change was found to depend on the Cu concentration. The Zr-derived states showed the changes characteristic for TE-TL-type glasses (reduction of DOS around E_F), whereas the Ni-derived states seemed to be quite insensitive to the hydrogenation in comparison with the Cu-derived states. The changes observed in the Cu $3d$ states may be explained by assuming a modification of the local environment of the Cu atoms upon hydrogenation. Based on the results of previously reported structural and magnetic studies of hydrogenated Zr-Ni-Cu and Ti-Cu glasses, the effects observed here by UPS in the Cu $3d$ band states were ascribed to hydrogen-induced atomic rearrangements, as a result of which the hydrogenated Zr-Ni-Cu glasses transform into a nanoscale mixture of Cu-rich clusters and amorphous Zr-Ni-Cu-H regions with reduced Cu content.

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