PHYSICAL REVIEW B VOLUME 37, NUMBER 11 15 APRIL 1988-I

Surface properties and electronic structure of amorphous $Zr_{75}Ni_{25}$ and $Zr_{75}Ni_{25}$ hydride studied by photoemission

Yu Xin-nan*

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

L. Schlapbach

Laboratorium für Festkörperphysik, Eidgenössische Techische Hochschule, CH-8093 Zürich, Switzerland
and Institut de Physique, Université de Fribourg, CH-1900 Fribourg, Switzerland

(Received 12 March 1987; revised manuscript received 14 September 1987)

We have studied the surface composition of melt-spun amorphous $Zr_{75}Ni_{25}$ ribbons by means of x-ray-photoelectron-spectroscopic core-level analysis and depth profiling and the electronic structure of carefully cleaned $Zr_{75}Ni_{25}$ and of $Zr_{75}Ni_{25}$ hydride by means of valence-band and core-level analysis. We observed strong oxygen-induced segregation in a surface layer on both sides of the ribbons. On ribbons which were kept in air for three years the surface layer is much thicker (≈ 60 nm) on the dark (wheel) side, suggesting enhanced corrosion. In contrast, we see no significant segregation due to hydrogen adsorption or absorption, but the appearance of the hydrogen-induced bonding band centered at 6.5 eV below E_F, a shift by 0.6 eV of the Zr 3*d* line, and a weak loss of asymmetry of the Ni 2*p* line upon hydride formation. We conclude that neither the oxygen- or hydrogen-induced segregation effects nor the electronic structure of amorphous $Zr_{75}Ni_{25}$ and $Zr_{75}Ni_{25}$ hydride differ radically from those of corresponding crystalline alloys.

I. INTRODUCTION

The effect of the absence of long-range order on the electronic and magnetic properties of bulk and surface, the possibility of a continuous variation of sample composition, the hydrogen sorption capability, and the possibility of surface modifications by selective chemisorption, annealing, and gradual recrystallization render glassy or amorphous alloys an interesting category of materials for basic and applied research.[1,2] The study of hydrides of amorphous alloys is rather new (for reviews see Refs. 3 and 4). They are reported not to disintegrate into powder upon hydride formation, in contrast to crystalline bulk alloys.

Whereas the electronic structure of amorphous alloys has been investigated extensively experimentally,[5] rather few analytical investigations of the surface chemistry are known,[6] though the amorphous alloys seem to have interesting catalytic surface properties.[7] Oxygen chemisorption and selective oxidation lead to surface segregation effects with the formation of catalytically active precipitates as in crystalline alloys.[6,8] Hydrogen absorption was reported to induce a strong Pd enrichment at the surface of amorphous $Zr_{70}Pd_{30}$ (Ref. 9) contrary to crystalline Zr-Pd alloys.[10] The chemisorption of hydrogen was found to reduce the Cu segregation in crystalline alloys.[11] The electronic structure of hydrides of some amorphous alloys was studied by means of nuclear magnetic resonance (NMR) and measurements of specific heat and magnetic susceptibility.[12] $Zr_{76}Fe_{24}H_{160}$ is the only concentrated amorphous hydride studied so far by photoemission.[13]

In this paper we report on the photoemission study of both sides of as-prepared, melt-spun amorphous $Zr_{75}Ni_{25}$ ribbons, on clean $Zr_{75}Ni_{25}$ after annealing in hydrogen atmosphere, and of $Zr_{75}Ni_{25}$ hydride. All results are comparable to those of crystalline alloys; we do not find evidence for significant hydrogen-induced surface segregation.

II. EXPERIMENT

The analysis was performed on a VG-ESCA Lab-5 spectrometer using Mg *Kα* (1254 eV) and He II (40.8 eV) radiation (Au 4*f* at 84.0 eV, full width at half maximum 1.20 eV). The base pressure was less than 1×10^{-10} mbar and the working pressure $(2-5)\times10^{-10}$ mbar (mostly Ar) after sputtering and less than 1×10^{-9} mbar (mostly H_2) after hydrogenation.

The ribbons were prepared by the melt-spin technique in a He atmosphere of technical purity. Two different ribbons of nominal composition $Zr_{75\pm1}Ni_{25\pm1}$ were studied: $Zr_{75}Ni_{25}$ ribbons prepared three years ago and stored in air and freshly prepared $Zr_{75}Ni_{25}$ ribbons. Guinier x-ray patterns of both samples showed, apart from background due to diffuse diffraction, broad very weak lines at $d=2.52$, 2.24, 1.89, 1.86, and 1.82 Å, apparently due to some ZrO_2. All samples contained at least some percentage of oxygen even after repetitive sputtering and outgassing at 470 K.

Both sides of the melt-spun ribbon (8 mm wide, 0.05 mm thick) were analyzed as prepared and after several intervals of 2-keV Ar^+ sputtering at a rate of ≈ 1 nm/min. The sputtering voltage was always reduced to 0.5 keV for the last 2 min before sample analysis to keep preferential sputtering weak. To get spectra of clean $Zr_{75}Ni_{25}$ the samples were degassed and regularly sputtered at 450 K for typically 72 h. One clean sample was exposed to 1 bar H_2 at 450 K for 16 h in the high-pressure cell of the spectrometer.

Clean samples were hydrogenated at 320 K and 40 bar for 2–5 h, cooled to 100 K before the high-pressure hydrogen was released, transferred in ultrahigh vacuum (UHV) from the high-pressure cell first to the sputtering position for a further short cleaning and then to the analyzing position, and kept at 100 K. The hydrogen to metal concentration ratio is not known; according to previous work[14] it exceeds one. Zr and Ni concentrations were evaluated from integrated Zr 3*d* and Ni 2*p* peak heights using theoretical cross sections.[15] The probing depth for these levels is 2–3 nm.

The amorphicity of the cleaned, annealed, or hydrogenated samples was checked again by Guinier x-ray diffraction. The broad weak peaks at $d = 2.52$, 2.24, 1.89, 1.86, and 1.82 Å were still present; no further reflections appeared, indicating that no crystallization had occurred during the sample treatment.

III. RESULTS

A. Depth profiles

The as-prepared ribbons show on both sides, within the probing depth of x-ray-photoelectron spectroscopy (XPS), fully oxidized Zr (Zr $3d_{5/2}$ at 183.5 eV) and hardly any Ni, i.e., the composition $Zr_{>99}Ni_{<1}$ (Fig. 1). The O 1*s* peak indicates the presence of metal oxides and hydroxides. Upon sputtering the Ni gradually appears, the O 1*s* peak changes to a purely metal oxide peak, and Zr remains fully oxidized. The Ni appears metallic but, as sputtering is known to reduce NiO, we cannot decide whether the sample also contained oxidized Ni in the outer surface layers. After prolonged sputtering metallic Zr is also found.

On the freshly prepared samples the strongly Zr-rich surface layer is less than 1 nm thick (Fig. 2) and the Zr:Ni bulk concentration ratio is almost reached on both ribbon sides after 3 nm sputtering when the oxygen concentration amounts to 2% and 10% on the dark (wheel) and shiny (free) side, respectively. The old ribbons show pronounced differences between the two ribbon sides. Whereas on the shiny side Ni and Zr are essentially metallic and the Zr:Ni concentration ratio approaches that of the bulk after 4 nm sputtering, this ratio still deviates strongly on the dark tarnished side where there is about 15% ZrO_2 left even after 5.7 nm sputtering. The differences clearly appear in the depth profile (Fig. 2). After sputtering off about 200 nm the bulk concentration is reached on both sides.

The results indicate strong surface segregation along with selective oxidation of Zr, which leads to an enrichment of Zr in the top layers and to a decomposition of $Zr_{75}Ni_{25}$ into ZrO_2 and Ni and possibly further phases. This phenomenon of surface segregation is well known in crystalline intermetallic compounds and its importance for hydrogen sorption, catalysis, getters, and rare-earth–transition-metal permanent magnets was emphasized (Refs. 6 and 16–18). Similar surface segregation effects were already found in amorphous $Zr_{36}Ni_{44}$ (Ref. 8) and Zr_9Fe_{91}.[6] Such strong segregation effects require a rather high mobility of both constituents of the alloy. Indeed it was proven recently by Rutherford backscattering that at least Ni diffuses rapidly in amorphous Zr-Ni alloys.[19]

The depth profiles found on the fresh samples, i.e.,

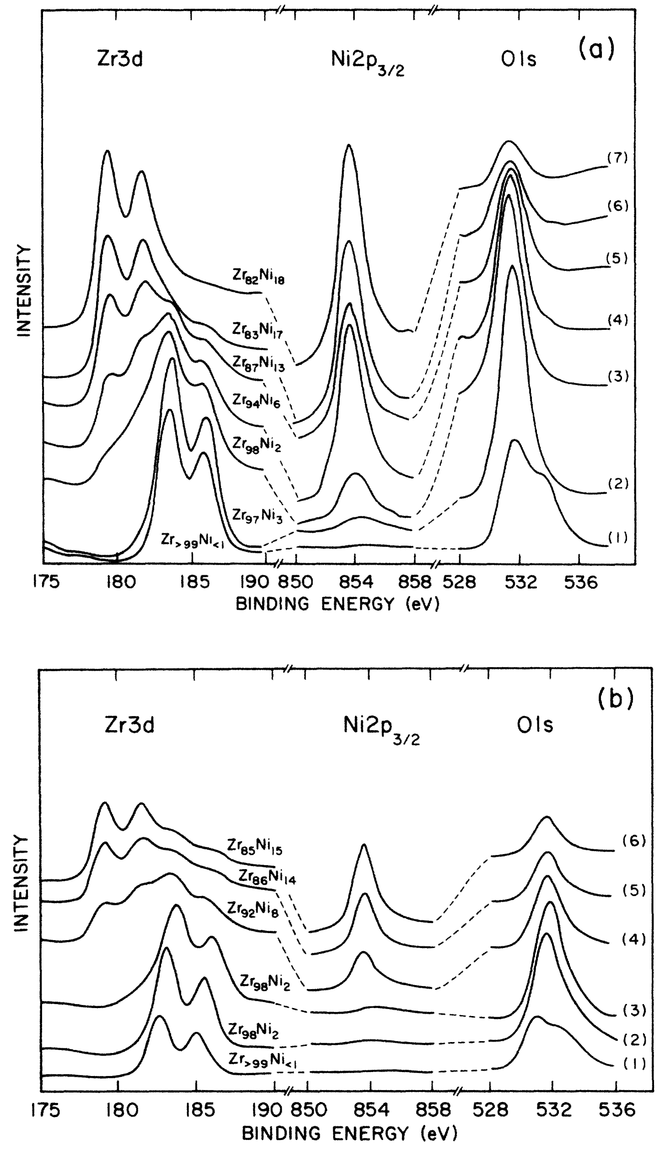

FIG. 1. (a) XPS spectra of the Zr 3*d*, Ni 2*p*, and O 1*s* core levels of the shiny side of three-year-old amorphous $Zr_{75}Ni_{25}$ as inserted (1) and after 2-keV Ar^+ sputtering for 0.5 min (2), 5 min (3), 8 min (4), 11 min (5), 15 min (6), and 40 min (7), and additional 2 min 500-eV Ar^+ sputtering before each XPS analysis. (b) XPS spectra of the Zr 3*d*, Ni 2*p*, and O 1*s* core levels of the tarnished side of the three-year-old amorphous $Zr_{75}Ni_{25}$ as inserted (1) and after 2-keV Ar^+ sputtering for 0.5 min (2), 5 min (3), 15 min (4), 25 min (5), and 57 min (6) and additional 2 min Ar^+ sputtering before each XPS analysis. Note that even after 57 min sputtering Zr is still oxydized to a large extent, contrary to Zr on the shiny side.

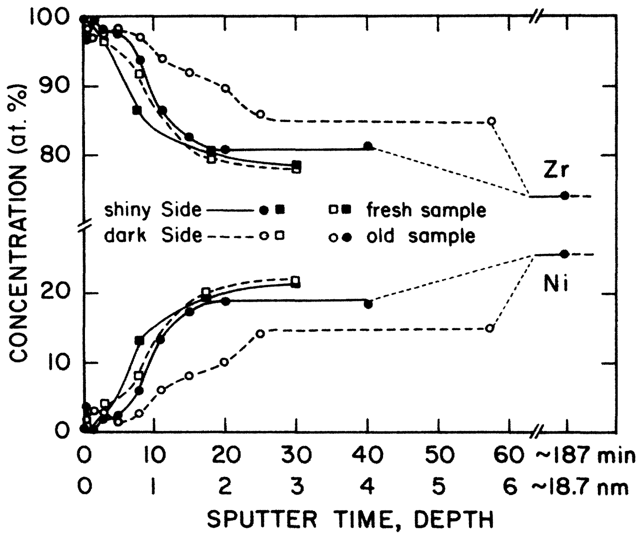

FIG. 2. XPS depth profiles of both sides of fresh (○,●) and three-year-old (□,■) melt-spun amorphous $Zr_{75}Ni_{25}$ evaluated from the Zr 3*d* and Ni 2*p* core levels using theoretical cross sections and $[Zr]+[Ni]=100\%$.

weaker or at most equal surface oxidation effects on the dark (wheel) side as on the shiny (free) side were expected. The close contact between solidifying alloy and wheel should result in a weaker contamination by oxygen from the surrounding atmosphere.

Accordingly we suggest that the unexpected depth profiles found on the old samples result from corrosion upon storage of the ribbons in air for three years rather than from the melt-spinning process. The corrosion is by far more severe on the dark (wheel) side than on the shiny (free) side. As the old ribbons were not analyzed while fresh discussions on the effect of, e.g., Cu contamination or amorphicity on corrosion rate would be very speculative.

B. Annealing in hydrogen atmosphere

The annealing of sputter-cleaned $Zr_{75}Ni_{25}$ at 450 K in a hydrogen atmosphere ($p=1$ bar) for 16 h results in a complete oxidation of Zr; Ni remained largely metallic and the Zr to Ni ratio had increased to $Zr_{91}Ni_9$, which again indicates a strong segregation of Zr. As all samples even after prolonged outgassing still contained significant oxygen concentrations ($\approx 2\%$) we assume that oxygen diffusion from bulk to surface caused this oxidation rather than the 2 ppm O_2 and H_2O impurity in 5 ml hydrogen in the pressure cell.

C. Electronic structure of $Zr_{75}Ni_{25}$ and of its hydride

The ultraviolet-photoelectron-spectroscopy (UPS) valence-band spectrum of rather clean $Zr_{75}Ni_{25}$ shows (Fig. 3, bottom) the conduction band split into two subbands with peaks at 0.7 and 2.2 eV, in agreement with earlier investigations,[5] and the emission at 6 eV due to some residual oxygen contamination. In the XPS valence-band spectrum the two subbands are not resolved (Fig. 3, top), but appear as a strong peak with an intense shoulder. The oxygen contamination is hardly visible. The Zr $3d_{5/2}$ and Ni $2p_{3/2}$ core levels appear (Fig. 4) at 178.8 and 853.5 eV, respectively, as compared to 178.8 and 852.7 eV, respectively, in elemental Zr and Ni.[20]

Surprisingly, clean $Zr_{75}Ni_{25}$ does not form a hydride rapidly. Exposures to hydrogen at 320 K and $p=40$ bar for more than 2 h were needed to obtain hydrogenated samples. Furthermore, all samples disintegrated into flakes upon hydride formation, contrary to the reported shape stability of amorphous hydrides.[21] The Zr and Ni concentration ratio of the hydride amounts to $Zr_{81}Ni_{19}$, which is close to that of the bulk, i.e., again there is no significant hydrogen-induced surface segregation.

The formation of the ternary hydride caused the appearance of additional emission centered at 6.5 eV below E_F in the XPS valence-band spectra (Fig. 3), a shift of 0.6 eV of the Zr 3*d* lines to larger binding energy (Fig. 4), and hardly any shift, but an increased symmetry of the Ni 2*p* line. The emission at 6.5 eV can be identified by the hydrogen-induced bonding band. The attractive potential of the additional protons (H) in the host metal matrix are known to pull down some *d* states already occupied in the metal. They hybridize with the hydrogen *s* states and form the hydrogen bonding band, as is well known from

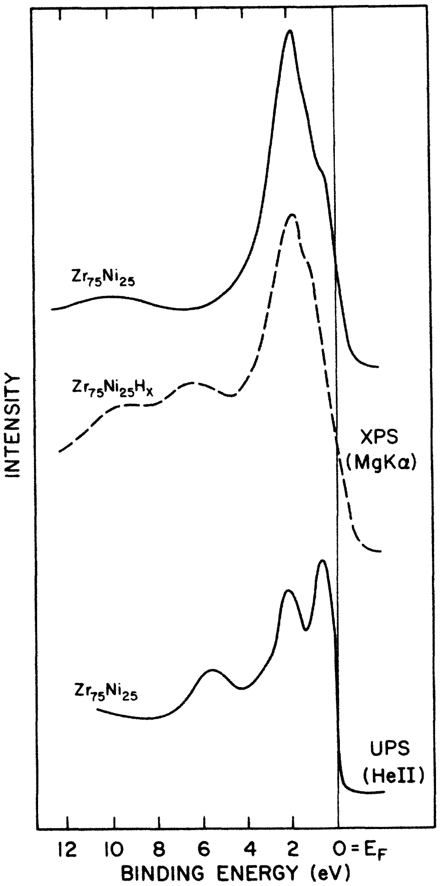

FIG. 3. XPS and UPS valence-band spectra of amorphous $Zr_{75}Ni_{25}$ and of its hydride. Note the hydrogen bonding band centered at 6.5 eV in the hydride spectrum.

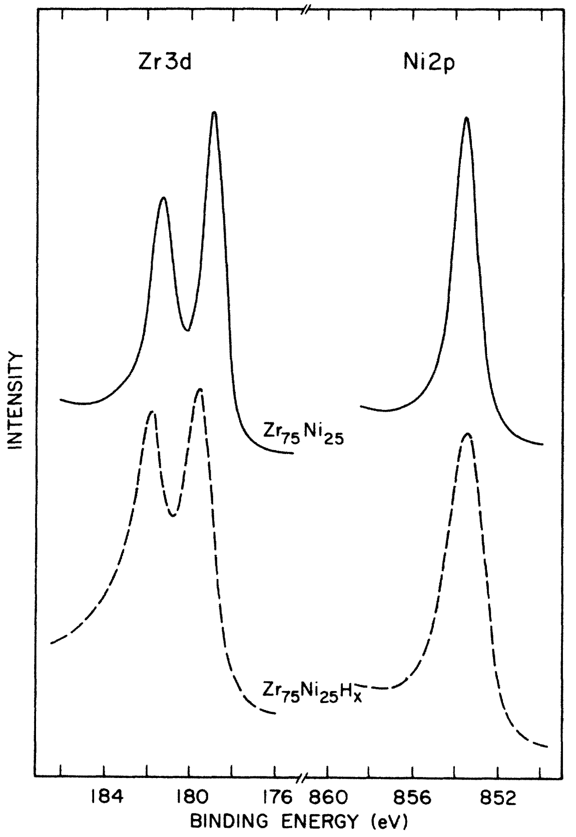

FIG. 4. XPS spectra of the Zr 3d and Ni 2p core levels of amorphous $Zr_{75}Ni_{25}$ and of its hydride.

band-structure calculations and photoemission studies of binary and ternary hydrides.[22] The position of the hydrogen-induced band as well as the Zr 3d core-level shift compare well with those of hydrides of crystalline alloys of Zr with Mn, Cr, V,[23] and Ni.[10] In hydrides of amorphous $Zr_{76}Fe_{24}$ shifts of 0.8 and 0.3 eV for Zr 3d and Fe 2p core levels, respectively, were reported.[13] The loss of asymmetry of the Ni 2p line seems to indicate a decrease of the partial density of Ni d states at E_F.[24]

IV. CONCLUSIONS

Neither the surface properties nor the electronic structure of amorphous $Zr_{75}Ni_{25}$ and $Zr_{75}Ni_{25}$ hydride are radically different from those of comparable crystalline alloys.

As-prepared melt-spun amorphous ribbons show pronounced oxygen-induced surface segregation effects. They lead to a strong Zr enrichment of the top layer and to a decomposition of $Zr_{75}Ni_{25}$ into ZrO_2 and Ni and possibly further phases in a surface layer. The thickness of this layer amounts to ≈ 10 nm on both sides of fresh ribbons and to ≈ 60 nm on the dark (wheel) side of three-year-old ribbons, pointing to a higher corrosion rate of the dark side. Annealing of sputter-cleaned ribbons in a hydrogen atmosphere results in a similar segregation (ZrO_2+Ni), probably due to the diffusion of bulk oxygen to the surface region.

The absorption of hydrogen from the gas phase by sputter-cleaned and outgassed $Zr_{75}Ni_5$ amorphous ribbons and the hydride formation are very slow and lead to disintegration of the ribbons; however, they do not produce significant surface segregation effects. We therefore assume that the reported catalytic properties of amorphous alloys are related to the oxygen-induced surface segregation effects, particularly to the decomposition into Ni and ZrO_2 in analogy to crystalline alloys (Refs. 6, 16, and 18).

In the valence-band spectra of $Zr_{75}Ni_{25}$ the Zr and Ni subbands appear at 0.7 and 2.2 eV. The Zr $3d_{5/2}$ and Ni $2p_{3/2}$ core levels appear at 178.8 and 853.8 eV, respectively, as compared to 178.8 and 852.7 eV, respectively, in elemental Zr and Ni, indicating a surprisingly large shift of 0.8 eV of the Ni $2p_{3/2}$ line.

Hydride formation results in the appearance of the hydrogen bonding band at 6.5 eV, in a shift of 0.6 eV of the Zr 3d line to larger binding energy due to charge transfer, and in a more symmetric Ni 2p line because of a weaker partial density of states of Ni and E_F.

ACKNOWLEDGMENTS

We gratefully acknowledge S. Büchler and U. Maier for technical assistance, Sulzer Brothers, Winterthur, for the delivery of some amorphous alloys, H. C. Siegmann for continuous interest and support, and the Swiss National Energy Research Foundation (NEFF) for financial support.

---

*Permanent address: Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing, China.

[1] See, e.g., *Rapidly Quenched Metals*, edited by S. Steeb and H. Warlimont (Elsevier, Amsterdam, 1985).

[2] *Glassy Metals I*, Vol. 46 of *Topics in Applied Physics*, edited by H.-J. Güntherodt and H. Beck (Springer-Verlag, Berlin, 1981); *Glassy Metals II*, Vol. 53 of *Topics in Applied Physics*, edited by H. Beck and H.-J. Güntherodt (Springer-Verlag, Berlin, 1983).

[3] *Hydrogen in Disordered and Amorphous Solids*, Vol. 136 of *NATO Advanced Study Institute, Series B; Physics*, edited by G. Bambakidis and R. C. Bowman, Jr. (Plenum, New York, 1986).

[4] H. Bernas, A. Traverse, and C. Janot, *Amorphous Metals and Semiconductors*, edited by P. Haasen and R. I. Jaffee (Pergamon, New York, 1985), p. 435; A. Traverse and H. Bernas, J. Less-Common Met. **129**, 1 (1987).

[5] P. Oelhafen, in *Glassy Metals II*, Ref. 2, p. 283.

[6] L. Schlapbach, in *Hydrogen in Disordered and Amorphous Solids*, Ref. 3, p. 397.

[7] A. Baiker, H. Baris, and H.-J. Güntherodt, Appl. Catal. **22**, 389 (1986) and references therein; R. Schlögl, in *Rapidly*

Quenched Metals, Ref. 1, p. 1723.

[8] F. Spit, K. Blok, E. Hendriks, G. Winkels, W. Turkenburg, J. W. Drijver, and S. Radelaar, in *Rapidly Quenched Metals,* edited by T. Matsumoto and K. Suzuki (Jpn. Inst. of Metals, Sendai, 1982), p. 1635.

[9] P. Oelhafen, R. Lapka, U. Gubler, J. Krieg, A. Dasgupta, H.-J. Güntherodt, T. Mizoguchi, C. Hague, J. Kübler, and S. R. Nagel, in *Rapidly Quenched Metals,* edited by T. Matsumoto and K. Suzuki (Jpn. Inst. of Metals, Sendai, 1982) p. 1259.

[10] St. Büchler (unpublished).

[11] S. Modak and B. C. Khanra, Phys. Rev. B **34**, 5909 (1986).

[12] R. C. Bowman, Jr., in *Hydrogen in Disordered and Amorphous Solids,* Ref. 3, p. 237.

[13] S. M. Fries, H. G. Wagner, S. J. Campell, U. Gonser, N. Blaes, and P. Steiner, J. Phys. F **15**, 1179 (1985).

[14] K. Tanaka and M. Higatani, J. Less-Common Met. **88**, 317 (1982).

[15] J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976).

[16] L. Schlapbach, A. Seiler, F. Stucki and H. C. Siegmann, J. Less-Common Met. **73**, 145 (1980); L. Schlapbach, *ibid.* **111**, 291 (1985).

[17] W. E. Wallace, J. Less-Common Met. **100**, 85 (1984).

[18] Yu Xin-nan, Vac. Sci. Technol. (China) **4**, 33 (1984).

[19] J. C. Barbour, M. Nastasi, and J. W. Mayer, Appl. Phys. Lett. **48**, 517 (1986).

[20] J. C. Fuggle and N. Mårtensson, J. Electron Spectrosc. Relat. Phenom. **21**, 275 (1980).

[21] A. J. Maeland, in *Hydrogen in Disordered and Amorphous Solids,* Ref. 3, p. 127, and references therein.

[22] M. Gupta and L. Schlapbach, in *Hydrogen in Intermetallic Compounds,* Vol. 63 of *Topics in Applied Physics,* edited by L. Schlapbach (Springer, Berlin, 1988), p. 139.

[23] L. Schlapbach, J. Osterwalder, and T. Riesterer, J. Less-Common Met. **103**, 295 (1984).

[24] J. C. W. Folmer and D. K. G. de Boer, Solid State Commun. **38**, 1135 (1981).