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## THE ELECTRONIC STRUCTURE OF METALLIC GLASSES

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### INTRODUCTION

The aim of this paper is to summarize the most important experimental results obtained from ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and X-ray emission spectroscopy (XES) on a great variety of metallic glasses. From this kind of measurement important information about the electronic structure of both the valence band and core electrons can be obtained. Therefore, electron spectroscopy and XES experiments are a field of increasing interest in the last few years and a great number of papers has been published after the first study of Nagel et al. in 1976 (1 - 14)

The main interest in the bulk electronic properties of the metallic glasses is twofold: first, the knowledge of the electronic structure of an alloy is the key for the understanding of many other physical properties, as e.g. magnetism or superconductivity. Second, the important question arises if there exist common electronic properties among the alloys which form metallic glasses and whether these are different from those of alloys which can not be obtained in the glassy phase.

This paper is organized in six sections and deals with [1] the glassy transition metal alloys, their d-band structure, the d-band shifts on alloying and their relation to the alloy heat of formation ( $\Delta H$ ) and the glass forming ability, [2] the glass to crystal phase transition viewed by valence band spectroscopy, [3] band structure calculations, [4] metallic glasses prepared by laser glazing, [5] glassy normal metal alloys and [6] glassy hydrides.

### 1. GLASSY TRANSITION METAL ALLOYS

In this section we discuss the binary glassy transition metal alloys, containing an early ( $T_E$ ) and late transition metal ( $T_L$ ) [the alloy constituent with the lower ( $n_d \leq 5$ ) and higher ( $n_d > 5$ ) d-electron number ( $n_d$ ), respectively].

Electron spectroscopy measurements are surface sensitive and therefore can yield information about both the bulk and surface properties. In this paper the emphasis is mainly on the bulk electronic structure of the metallic glasses. On the other hand, first measurements on glassy hydrides Pd-Zr-H show interesting surface effects which clearly show that the surface properties of the metallic glasses represent an interesting field in alloy research which has yet to be investigated.

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This alloy family is especially well suited for electron spectroscopy since the d-bands of the alloy constituents are easy to detect and to distinguish in most cases, because of the high states density in the d-bands. As a consequence, the bonding mechanism, i.e. the d-band binding energy shifts and the splitting of the alloy valence bands can directly be observed in the valence band spectra.

#### General behavior of glassy $T_L$ - $T_E$ alloys

All the binary glassy transition metal alloys prepared so far contain an early and late transition metal. The valence band structure i.e. the energetic position and width of the d-bands related to the alloy constituents are of special interest since these parameters are responsible for many physical properties, including the bonding in the alloy and the alloy heat of formation  $\Delta H$  (15).

On alloying two transition metals (3d, 4d or 5d metals) and forming a glass, the following effects can be observed in the valence band structure of the alloy:

- (i) the nearly filled d-band of the late transition metal is narrowed and its centroid position is shifted (with respect to the Fermi level  $E_F$ ) to a higher binding energy. As a consequence, the d-states density at the  $T_L$  site at  $E_F$  becomes very low, in contrast to the pure  $T_L$  metal
- (ii) the weakly filled d-band of the early transition metal is split in two main maxima, one located at  $E_F$  and the second one roughly at the same binding energy as the d-states maximum at the  $T_L$  site
- (iii) therefore, the alloy valence band consists essentially of two main maxima, the first one at a binding energy of a few eV mainly related to the d-states of  $T_L$  with an admixture

of d-states related to the  $T_E$  site, and a second one at  $E_F$ , containing mainly d-states of the early transition metal with a very small admixture of d-states related to the  $T_L$  site (6).

This behavior (i)-(iii) has been found both experimentally (by UPS, XPS, AES and XES) and theoretically by self consistent ASW (augmented spherical wave) band-structure calculations. The degree of the valence band splitting and the d-band shift depends mainly on the valence difference  $\Delta n$  of the two alloy constituents.

The dependence of the valence band splitting on the valence difference  $\Delta n$

The valence difference  $\Delta n$  (or group number difference in the periodic table) is an important parameter for the degree of valence band splitting and the d-band binding energy shift on alloying with respect to the pure alloy constituents. Valence bands with distinctly split d-bands, with two well separated d-band peaks in the valence band spectra, have been observed for e.g. Ni-Zr, Pd-Zr, Pt-Zr ( $\Delta n=6$ ) or Cu-Zr ( $\Delta n=7$ ) (14). Glassy alloys with overlapping d-bands of the two alloy constituents are e.g. Fe-Zr, Rh-Nb, Rh-Ta, Ir-Nb and Ir-Ta ( $\Delta n=3$ ) (14,16). It turned out, that for a given  $T_E$  the d-band peak binding energy related to the  $T_L$  of a given series is increasing with increasing valence difference (14). A replacement of the  $T_E$  by an element of the same group (e.g. a replacement of Ti by Zr) has almost no effect on the d-band position of the  $T_L$ . However a change of the  $T_L$  by an element of the same group (e.g. a replacement of Pd by Pt) is changing the  $T_L$  d-band peak position (14) since the d-band width is increasing in going to the heavier elements in a group of late transition metals (17).

d-band shifts on alloying and their correlation to the alloy heat of formation

Since the alloy heats of formation  $\Delta H$  are mainly determined by the d-band properties (18,19) it is tempting to try to deduce  $\Delta H$  values from photoemission data. The method described by Oelhafen (15) allows an estimate of  $\Delta H$  for  $T_L$ - $T_E$  alloys from valence band spectra and core electron binding energy shifts. The scheme is based on the following assumptions: (i)  $\Delta H$  is determined by the relative shift on alloying of the d-band binding energy with respect to the core levels. The core electrons are assumed not to contribute to  $\Delta H$  so that it is only the relative shift of the d-bands which contribute to  $\Delta H$ . (ii) the UPS spectra represent the one electron d-band density of states of both the pure components and the transition metal alloys, and (iii) the charge transfer on alloying may be neglected, i.e. the number of d-electrons of the two constituents do not change on alloying. The method is applied to a number of transition metal alloys with split d-bands for which accurate photoemission data are available. The  $\Delta H$  values deduced from photoemission data by this method are in reasonable agreement with calculated (19) or directly measured  $\Delta H$  values. For details see (15).

By examining  $\Delta H$  values for a large number of (crystalline) alloys it becomes obvious that  $\Delta H$  shows a similar dependence of  $\Delta n$  as we have observed for the d-band shift on alloying: the alloy heats of formation  $\Delta H$  are almost vanishing (or even endothermal) for alloys with  $\Delta n = 0$  or 1, and its amount is increasing with increasing  $\Delta n$  up to a value of roughly 1eV/atom for  $\Delta n=6$  and alloys with 4d transition metals (15).

The glass forming ability is also increasing with increasing  $\Delta n$ ; for low  $\Delta n$  values ( $\Delta n < 3$ ), no metallic glasses could be prepared so far by techniques with cooling rates in the  $10^6$ K/sec range (splat cooling, melt spinning). Therefore, a large (exothermal) alloy heat of formation, or in other terms, the bonding between unlike neighbors seems to be necessary for the glass forming.

By plotting  $\Delta H$  for transition metal alloys as a function of the valence difference  $\Delta n$  two ranges can be distinguished:

- (i) the low  $\Delta n$  range ( $\Delta n < 3$ ) contains alloys with almost vanishing  $\Delta H$  values, as e.g. Ag-Pd ( $\Delta n=1$ ), with very simple phase diagrams; many form solid solutions (binary random substitutional alloys) and almost no d-band shift takes place on alloying in contrast to
- (ii) the high  $\Delta n$  range ( $\Delta n > 3$ ) where we find alloys with large  $|\Delta H|$  values, as e.g. Pd-Zr, with very complicated phase diagrams, with deep eutectica and intermetallic compounds and large d-band shifts on alloying. Many of these alloys form metallic glasses.

## 2. THE GLASS TO CRYSTAL PHASE TRANSITION VIEWED BY VALENCE BAND SPECTROSCOPY

A comparison of the UPS spectra for the metallic glasses  $\text{Pd}_{35}\text{Zr}_{65}$  and  $\text{Cu}_{60}\text{Zr}_{40}$  with the corresponding results for the crystalline compounds  $\text{PdZr}_2$  and  $\text{Cu}_3\text{Zr}_2$  shows that the d-band splitting and d-band binding energy shift is not a specific property of the glassy alloys but is also found in the crystalline phase. We find essentially the same d-band peak positions for Pd and Cu in the crystalline and glassy state. However, the shape of the d-band is changed. Qualitatively the same behaviour has been observed in Pd-Si alloys (1). In the crystalline compound

$\text{Cu}_3\text{Zr}_2$  (20) the Cu d-band exhibits the covalent splitting which is typical of the pure Cu d-band spectrum, whereas in the glassy state the Cu d-band becomes more like a Gaussian. The strong similarity of the d-band positions in the crystalline and glassy state has two important consequences: i) for the positions of the d-bands realistic calculations for crystalline compounds can be used to gain insight into the position of the d-band in the glassy as well as in the crystalline state. ii) The alloy heats of formation  $\Delta H$  are mainly determined by the d-band properties. Therefore,  $\Delta H$  for the glassy state is only slightly different from the one for the crystalline state. This fact is supported by measurements of heats of crystallization which are small compared to the alloy heat of formation. This means that the glassy state lies energetically very close to the crystalline state.

### 3. BAND STRUCTURE CALCULATIONS

The photoelectron spectra of glassy transition metal alloys are mainly determined by the integrated density of states. Information about a site and angular momentum decomposed density of states can only be obtained by (i) varying the alloy concentration, (ii) a core level line shape analysis, (iii) XES measurements and in some cases from (iv) AES line shapes. In order to obtain a more complete density of states picture, a comparison with bandstructure calculations for clusters or ordered model structures are very helpful. Self consistent ASW calculations have been performed for  $\text{CuZr}_3$ ,  $\text{FeZr}_3$ ,  $\text{PdZr}_3$  (in the  $\text{AuCu}_3$  type symmetry),  $\text{NiNb}$  ( $\text{CuAu}$  and  $\text{CsCl}$  type symmetry) (21),  $\text{RhZr}_3$  ( $\text{AuCu}_3$  type symmetry) (22) and  $\text{RhNb}$  ( $\text{CuAu}$  type symmetry) (16). In most cases, especially in those with clearly split d-bands, good agreement with the experimental data has been found. In addition, cluster calculations and XES measurements on glassy  $\text{PdZr}$

alloys (23) have confirmed the admixture of Zr d-states at a binding energy of the Pd d-band peak.

### 4. METALLIC GLASSES PREPARED BY LASER GLAZING

Laser glazing is a very promising technique for preparing metallic glasses, especially in connection with electron spectroscopy measurements and in situ preparation work. Compared to the former techniques (splat cooling, melt spinning) the higher cooling rates in laser glazing, of the order of  $10^{10}$  K/sec, makes it possible to considerably extend the range of concentration in which a glassy alloy can be obtained (24, 25). First UPS/XPS/AES measurements on  $\text{Pd}_{100-x}\text{Si}_x$  ( $15 \leq x \leq 95$ ) in the glassy state prepared by laser glazing revealed the following features (26):

- (i) at concentrations at which the glassy phase can be obtained by splat cooling ( $15 \leq x \leq 22$ ), the spectra obtained from samples prepared by laser glazing and splat cooling are identical (5)
- (ii) the Pd d-band peak binding energy increases with decreasing Pd content monotonically up to a binding energy of 4.5 eV in  $\text{Pd}_5\text{Si}_{95}$
- (iii) the Pd 3d core level binding energy shift shows a maximum of about 2.1 eV at roughly  $x \sim 80$
- (iv) a transition from the glassy metallic alloy to a glassy semiconductor occurs at  $x \sim 85$

Studies of glassy silicides and other metallic glasses over almost the entire range of concentration are also very interesting with respect to the concentration dependence of the stability of the glassy phase. Measurements including UPS, XPS core level binding energy measurements and AES are in progress.

## 5. METALLIC GLASSES CONTAINING NORMAL METALS

The experimental study by electron spectroscopy of glassy normal metal (non d-metals) alloys like Ca-Al, Mg-Zn, Ca-Mg is hindered by the formation of surface oxide layers even after cleaning the sample in ultrahigh vacuum. Nevertheless, first UPS/XPS measurements on glassy Ca-Al alloys, well below room temperature in order to prevent diffusion of bulk oxygen to the surface, have been performed and stable surfaces during the measurements could be maintained. The results obtained from these measurements and the comparison with a self consistent ASW band structure calculations are exciting in two respects (27):

- (i) the valence band splits in two parts, separated by a gap of a few tenths of eV, one of them containing essentially Al 3s-states the other one Al 3p-states
- (ii) the density of states is decreasing towards  $E_F$  and  $E_F$  is close to a minimum in the density of states.

The first effect was unexpected, since the splitting of the valence band in two parts on alloying two simple free electron metals has yet to be observed. The latter effect (ii) supports the electronic model for glass formation as proposed by Tauc and Nagel (28).

## 6. GLASSY HYDRIDES: Pd-Zr-H

First UPS/XPS/AES measurements on the glassy hydride  $(Pd_{30}Zr_{70})_{100-x}H_x$  ( $x \sim 20$ ) have been performed (29,30). Although the hydrogen content was kept low, striking changes in the alloy surface properties have been observed after hydrogenation: first, the hydride shows a H induced Pd segregation at the sample surface, and second, the relative sputter yield for Zr and Pd from the glassy hydride is changed appreciable by the presence of H. Whereas

the first effect could play a crucial role for the catalytic activity of transition metal alloy catalysts, the latter one is important for quantitative alloy surface studies like SIMS (secondary ion mass spectroscopy) or photoelectron spectroscopy.

Depth profiles have been measured by AES and XPS on the pristine  $Pd_{30}Zr_{70}$  and the hydride  $(Pd_{30}Zr_{70})_{100-x}H_x$  ( $x \sim 20$ ). Without sputter cleaning the  $Pd_{30}Zr_{70}$  sample (once exposed to air) shows a very high Zr : Pd ratio  $\rho$ . That means, that almost no Pd is present in the first few atomic layers at the surface. In contrast to this behavior the hydride shows a distinct Pd Auger peak and no Zr in the corresponding surface layer. After sputtering the sample surfaces the  $Pd_{30}Zr_{70}$  sample shows a monotonic decrease of the ratio  $\rho$ , whereas the hydride reveal a maximum after a few seconds of sputtering time. This maximum corresponds to a Pd depletion (or a Zr enrichment) due to the Pd surface segregation. After further sputtering, the hydride shows a lower Zr : Pd ratio than the  $Pd_{30}Zr_{70}$  sample. This indicates that Zr is preferentially sputtered in the hydride. A quantitative estimate shows that the relative sputter yield (Zr : Pd) for pristine  $Pd_{30}Zr_{70}$  sample is near unity and is increased in the hydride, even by the very low hydrogen content, up to a value of more than 2. A calculation of the hydrogen induced Pd segregation in the hydride Pd-Zr-H based on a pair type model for the interatomic interaction has been performed (31). By this theory, a Pd segregation was obtained, which corresponds roughly to a 100% increase of the Pd concentration at the surface even for a very low hydrogen content ( $x \sim 20\%$ ), which is in reasonable agreement with our experiment.

Since we can assume that the hydrogen induced Pd segregation in Pd-Zr alloys is neither specific for Pd-Zr nor for the amorphous phase, the observed effect is

presumably an important mechanism for the catalytic activity of transition metal alloys. As long as the hydrogen content of the alloy catalysts is high enough, the surface concentration of the catalytically active alloy constituent is high enough as well. If the hydrogen content drops below to a critical value, a "poisoned" surface may result, due to a surface oxide layer of the catalytically inactive alloy component. Indeed, it is well known that the hydrogen content can play a crucial role in the catalytic activity of transition metal alloys, as e.g. in Ni-Al, which shows a decreasing catalytic activity with decreasing hydrogen content (32). Electron spectroscopy measurements on transition metal alloy catalysts combined with heterogeneous reaction rate measurements will have to clarify the role of the hydrogen induced segregation and its correlation to the catalytic activity for specific reactions and catalysts.

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