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## Photoemission valence-band structure of Hume-Rothery-type metallic glasses

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**Abstract.** Photoemission spectra of the valence-band of Hume-Rothery-type  $\text{Ag}_{45}\text{Cu}_{35}\text{Ge}_{20}$  and  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  metallic glasses are reported. In the present measurements and in contrast to previous measurements on liquid-quenched samples of these alloys we avoid any sputter-cleaning procedure prior to the spectroscopy by vapour quenching the samples in the preparation chamber of the spectrometer. Whereas in the liquid-quenched samples no indications of distinct structure-induced effects in the electronic density of states near  $E_F$  have been observed, in the new samples the existence of a minimum can clearly be seen and so the earlier conclusion is partly corrected by this paper. Structural influences on the density of states exist and can be detected by photoelectron spectroscopy in electronic states with large dispersion such as s and p states. In addition we show that the decrease of the density of states towards  $E_F$  cannot be discussed in terms of sp-d hybridization effects as stated previously.

### 1. Introduction

Ever since Nagel and Tauc [1] proposed a structure-induced minimum in the electronic density of states (MDOS) near the Fermi energy  $E_F$  of amorphous systems in order to explain their stability this behaviour has been a focus of interest. Beck and Oberle [2] as well as Hafner [3] have given a reinterpretation of this model in terms of the indirect ion-ion interaction mediated by the conduction electrons. This interaction causes oscillations in the effective pair potential and therefore gives rise to an electron-induced sensitivity of the ion positions. Structural consequences as well as consequences for phase stability and electronic transport properties have been studied extensively [2–5]. Although the stability of metallic glasses cannot convincingly be described within the framework proposed originally by Nagel and Tauc, an MDOS is assumed to indicate the electron-structure interrelations even in its reinterpretation [6, 7]. Photoelectron spectroscopy (XPS/UPS) as well as specific heat measurements have failed to prove the existence of an MDOS in many cases due to the use of transition elements with high d-state densities at  $E_F$  [8, 9]. Electron-structure interrelations and their influences on phase

stability, on the other hand, are common in crystalline Hume-Rothery phases [10]. In these phases the effect of the Fermi sphere–Brillouin zone interaction on the DOS is often detected and minima in the DOS are well established [11]. After establishing that a large class of amorphous noble-metal/polyvalent-element alloys with d states well below  $E_F$  belong to Hume-Rothery phases [12, 4] some of the authors have focused on these alloys because of their interest concerning the MDOS problem [13, 14, 5]. UPS measurements performed on  $\text{Au}_{100-x}\text{M}_x$  alloys ( $M = \text{Sn, Al, Sb, Si}$ ) revealed an MDOS over large concentration ranges [5, 13–15]. Similar results have been found in  $\text{Ag}_{100-x}\text{Sn}_x$  as well as  $\text{Cu}_{100-x}\text{Sn}_x$  [5, 14] and therefore an MDOS is expected to be a general feature of the noble-metal-containing amorphous Hume-Rothery phase [5, 14].

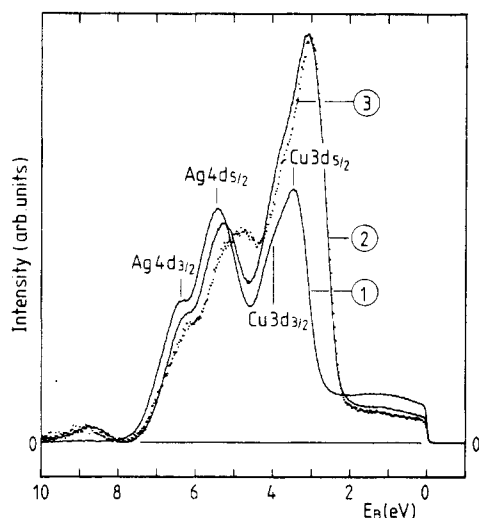
The structural and the electronic transport properties of  $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$  alloys have already been studied [16–19] and results similar to those of the alloys just mentioned have been observed. In the light of these measurements the absence of the MDOS in liquid-quenched (LQ) amorphous  $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$  ( $x = 20, 22.5, 25$ ), recently published by some of us [20], was unexpected. In these earlier measurements a long sputter procedure was applied in order to remove surface contaminations. The measurements were performed with a Leybold spectrometer (EA11-100). The analyser transmission sensitivity turned out later to be influenced by aberrations of the electron optics, and hence did not allow an accurate quantitative elemental analysis. A Cu enrichment, accompanied by a decreasing content of Ge and Ag after sputtering, was recognized but considered negligible. Here a sequential flash vapour-quenching technique (VQ) onto liquid- $\text{N}_2$ -cooled substrates placed inside the preparation chamber of the spectrometer was used. Sputter cleaning prior to the measurements was not needed.

## 2. Experimental procedures

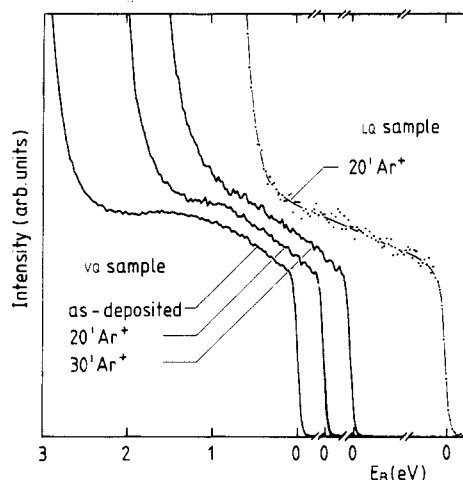
The UPS measurements were all performed at  $T = 77$  K within a Leybold spectrometer (EA10-100) which, as will be shown below, gives excellent agreement between the XPS core-level analysis and nominal composition. In the present samples contaminations are found to be negligible. Prior to any sputtering  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  shows an oxygen content of less than approximately 1% and for  $\text{Ag}_{45}\text{Cu}_{35}\text{Ge}_{20}$  the oxygen content could not be observed within the experimental resolution. All spectra are corrected for satellite contributions of the He I discharge lamp as well as for secondary-electron contributions. Both corrections were performed in a conventional manner described elsewhere [5]. Subsequent use of sputtering allowed us to observe surface composition changes. In the present paper we show that sputter-induced composition changes at the surface are much larger than assumed. These changes are found to be responsible for the failure of finding the MDOS in the LQ samples.

## 3. Results and discussion

In figure 1 we show UPS-spectra of vapour-quenched  $\text{Ag}_{45}\text{Cu}_{35}\text{Ge}_{20}$  immediately after deposition (curve 1) and after a sputter procedure (curve 2) similar to the previous work (20 min,  $3 \times 10^{16} \text{Ar}^+$  ions  $\text{cm}^{-2}$ ). Neither spectra are normalized and they clearly indicate, due to preferential sputtering, a large increase of the Cu 3d states and a large decrease near  $E_F$ , where the noble-metal s states and Ge 4p states dominate. The increase of the Cu 4s states at  $E_F$  seems to be compensated by a large decrease due to



**Figure 1.** Vapour-quenched sample prepared and measured at 77 K: 1: before sputtering (composition:  $\text{Ag}_{45}\text{Cu}_{35}\text{Ge}_{20}$ ), 2: after a long sputter procedure (composition:  $\text{Ag}_{35}\text{Cu}_{55}\text{Ge}_{10}$ ). Liquid-quenched sample (dots) after a long sputter-cleaning procedure (nominal composition  $\text{Ag}_{40}\text{Cu}_{40}\text{Ge}_{20}$ ) [20]. The intensity of curve 3 is normalized to curve 2 at the  $\text{Cu } 3d_{5/2}$  peak.



**Figure 2.** Enlarged region near  $E_F$ . The spectra are normalized at  $E_B = 1.5$  eV to equal amplitudes. The full curves show a vapour-quenched  $\text{Ag}_{45}\text{Cu}_{35}\text{Ge}_{20}$  sample, as-quenched and sputtered for 20 and 30 min, respectively. The dotted spectrum represents the LQ sample after sputtering for 20 min. The curves are shifted slightly with respect to each other.

the loss of Ge. The composition change is quite obvious and the core-level analysis confirms drastic changes within the first five minutes from 45 to 35 at. % Ag, 35 to 55 at. % Cu, and 20 to 10 at. % Ge, respectively, indicating a loss of half of the Ge at the surface. Support for the change of composition can be seen in characteristic changes of the d bands. The positions of the d states as well as their splittings, caused by spin-orbit interaction, are close to those of amorphous  $\text{Ag}_{100-x}\text{Sn}_x$  or  $\text{Cu}_{100-x}\text{Sn}_x$  [5]. The shift of the d states during sputtering is similar to that observed in these alloys when the composition has been changed. Comparing the LQ sample (curve 3) with the VQ sample after sputtering (curve 2) we find good agreement of the  $\text{Cu } 3d$  state position as well as the intensity ratios between the d states and the states close to  $E_F$ . Even a tiny peak of unknown origin, occurring at  $E_B = 8.8$  eV after sputtering, is in good agreement. The new measurements hence indicate that the earlier measurements were distinctly off the nominal composition. The older sample with the nominal composition of  $\text{Ag}_{40}\text{Cu}_{40}\text{Ge}_{20}$ , for example, might have been changed to  $\text{Ag}_{35}\text{Cu}_{55}\text{Ge}_{10}$ .

Whereas the present samples have been prepared, sputtered and measured at 77 K, roughly 300 K below the crystallization temperature  $T_c$  [17], the older ones were prepared at room temperature, only 85 K below  $T_c$ , and had been stored at room temperature for weeks. The loss of Ge and the Cu enrichment during sputtering shifts the surface composition into a region where  $T_c$  is even lower. A difference of approximately 35 K is left between the measuring temperature and  $T_c$  with obvious consequences on the shape of the noble-metal d states due to partial crystallization. Whereas in the VQ sample the Ag 4d and Cu 3d states are well separated, in excellent agreement with the liquid state [21], this is not true for the LQ sample. The Ag  $4d_{5/2}$  peak is much broader

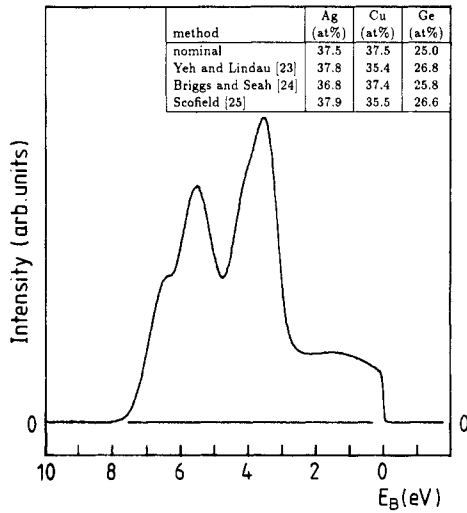
and closer to the Cu 3d states. Similar intensities occur in the present vQ samples after partial crystallization and therefore we assume the existence of crystalline segregations in the LQ samples (although they were found to be entirely amorphous by x-ray diffraction prior to the sputtering [20]). The previous samples can therefore not be seen as representative for the amorphous state.

In the following we focus on details near  $E_F$ . In figure 2 the enlarged region near  $E_F$ , normalized at  $E_B = 1.5$  eV, is shown immediately after deposition as well as after sputtering for 20 and 30 min respectively. Data on the LQ sample are again included for comparison. The shift of the Cu 3d states closer to  $E_F$  caused by the change of composition seems to overlap a stationary feature near  $E_F$ . In the partly crystalline LQ sample the slope is slightly different but still shows the decrease towards  $E_F$ . This, on the other hand, does not necessarily mean that the DOS at  $E_F$  shows similar features in both the amorphous and the partly crystalline state: polycrystalline Cu segregations, unfortunately, show also a decreasing intensity towards  $E_F$  [5, 14] and hence are indistinguishable near  $E_F$  from a decreasing intensity due to an MDOS.

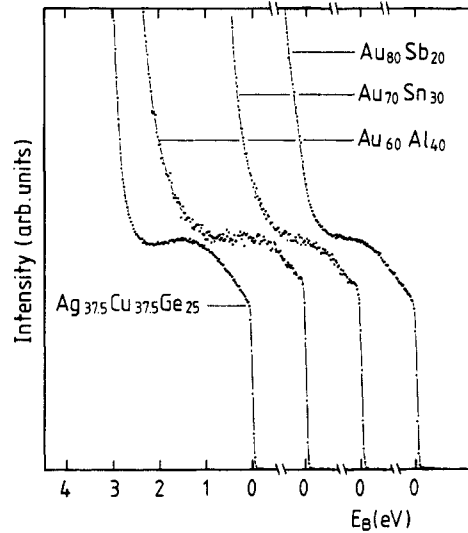
In the earlier study band-structure calculations based on hypothetical (crystalline)  $\text{Cu}_3\text{Au}$ -type  $\text{Ag}_3\text{Ge}$  and  $\text{Cu}_3\text{Ge}$  compounds were presented [20]. Following these calculations the decrease in intensity of the DOS near  $E_F$  was ascribed to an sp-d hybridization effect. In most simple approximations those effects should couple to the d-state intensities as well as to their position. In figures 1 and 2 of the present paper we show that neither the increasing Cu content nor the shift of the d states seem to have any effect on the stationary feature near  $E_F$  and hence are in contradiction with an interpretation in terms of sp-d hybridization effects. As shown by one of us [5] the depth of the MDOS correlates with the height of a peak in the structure factor  $S(K)$ . The position of this peak ( $K_{pe}$ ) is in general close to  $2k_F$  over large concentration regions due to a shift of the structure peak nearly parallel to  $2k_F$ . In  $\text{Au}_{100-x}\text{Al}_x$ , for example,  $S(2k_F)$  has a nearly constant height over the whole amorphous region [22] while the MDOS has a constant depth [14, 5]. The maximum in the structure function stays very close to  $2k_F$  over the same region and so the MDOS in this system remains at a constant position relative to  $E_F$ . The Au 5d state intensities in this system vary by factors and the shift of their binding energy is  $\Delta E_B = 2.5$  eV.  $\text{Au}_{100-x}\text{Sn}_x$  alloys show a changing  $S(2k_F)$ -value with composition and, correspondingly, a changing depth of the MDOS [5, 13]. In  $\text{Mg}_{70}\text{Zn}_{30}$  metallic glasses, an alloy without any d states close to  $E_F$ , very recently the MDOS has both been found theoretically [6] as well as experimentally [7]. Hence these results support the interpretation of the features near  $E_F$  in terms of a structure-induced MDOS.

The structure factor of the alloys presented in this paper has also an intense peak at  $2k_F$  [17, 4]. Under those conditions only part of the structure-induced MDOS is expected to be positioned below  $E_F$  and the whole minimum cannot be observed by UPS alone. In figure 3 we also show results for a  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  sample which has been vapour-quenched. The inset shows the nominal composition as confirmed by the XPS core-level analysis. The decrease in the DOS towards  $E_F$  is considered as revealing the part of the MDOS which lies below  $E_F$  [4, 5]. The region above  $E_F$ , where increasing intensity is expected, would have to be measured by methods which are sensitive to the unoccupied states such as inverse photoemission.

We emphasize that the existence of an MDOS is independent of the use of covalently bonded elements like Ge. As mentioned above, alloys with no Ge behave quite similarly. In figure 4, for example, we compare  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  with three other systems. The compositions are such that  $K_{pe}$  equals  $2k_F$ , the *ideal* composition for the amorphous Hume-Rothery phase concerning the MDOS [5] or phase stability [4]. The evidence for an MDOS at  $E_F$  in all these systems is obvious.



**Figure 3.**  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  vapour-quenched at 77 K, without applied sputtering. The inset shows a comparison between the nominal composition and those determined by means of the XPS core-level analysis using various photoionisation cross-section tables [23–25].



**Figure 4.**  $\text{Ag}_{37.5}\text{Cu}_{37.5}\text{Ge}_{25}$  vapour-quenched at 77 K in comparison with other amorphous Hume-Rothery alloys [13, 14, 5]. The spectra are normalized at  $E_B = 1.5$  eV to the same amplitude.

Other methods applied to Hume-Rothery-type alloys partly support and partly contradict the existence of a structure-induced MDOS at  $E_F$ . Measurements of the magnetic susceptibility of  $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ , for example, by one of us [18] clearly show a minimum in the range of  $20 \leq x \leq 30$  in the amorphous as well as in the liquid state. The minimum gets weaker and tends to be smeared out as temperature increases well into the liquid state. This behaviour led to the conclusion that the free-electron value of the DOS at  $E_F$  is valid in the liquid state at high temperatures well above the melting point and that a depression becomes evident when the temperature is lowered. This finding would agree with the existence of an MDOS as presented for the amorphous state in the present paper. It might even agree with the fact that an MDOS has not been revealed by UPS in the liquid state of the same [21] or similar systems [26, 27] if the MDOS is much weaker compared to the amorphous state. A close agreement of the measured electronic specific heat coefficient of the  $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$  metallic glasses ( $20 \leq x \leq 25$ ) with the free electron value has already been taken as an indication that the DOS at  $E_F$  is at least 20–30% lower than the free electron value [12]. It has been stated that amorphous  $\text{Cu}_{100-x}\text{Sn}_x$  also shows a depressed electronic density of states at  $E_F$  [28]. However, recent specific heat measurements on  $\text{Au}_{100-x}\text{Sn}_x$ , with and without magnetic field, and a careful correction for non-electronic contributions due to low-lying excitations and for electron–phonon enhancement effects show excellent agreement with the free electron value [29]. In contrast to this, susceptibility measurements in the liquid state just above the melting point still show indications of an MDOS at  $E_F$  for both Sn alloys [30, 5].

In conclusion we emphasize that structure-induced effects on s or p states can be detected by UPS in amorphous alloys of the type considered in this paper. The stability of the amorphous Hume-Rothery phase can be discussed in terms of an electron-structure interrelation which itself gives rise to the structure-induced minimum in the

electronic density of states [13, 14, 5] as well as to an electronic-induced peak in the structure function near  $2k_F$ , well known in the field of amorphous metals [2–5]. The MDOS at  $E_F$ , correlated to structure, electronic transport, and stability is discussed in detail elsewhere [5].

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