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1989 J. Phys.: Condens. Matter 1 1365

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The photoemission valence band structure of Hume-Rothery-type $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ ($x = 20, 22.5$ and 25) metallic glasses

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Received 22 July 1988

Abstract. Photoemission spectra are reported, from the valence band region, obtained through UPS He II, He I and XPS measurements, using liquid-quenched $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ metallic glass samples with Ge contents of $x = 20, 22.5$ and 25 . Band calculations performed for hypothetical (Cu_3Au) -type Ag_3Ge and Cu_3Ge compounds reveal essentially the same features in the valence band as those established from the present spectroscopic data. In addition, our data confirm that the density of states decreases smoothly towards the Fermi level without there being any indication of a distinct minimum or maximum. We conclude that the observed declining slope near the Fermi level reflects the d band tail, which is enhanced due to the sp-d hybridisation effect. Any structure-induced effect, if it exists, is too small to be detected by the UPS measurements. Combining our present results with those established previously from measurements of electronic specific heats, we are led to believe that the stability of an amorphous structure cannot be discussed solely in terms of a structure-induced perturbation on the total density of states.

1. Introduction

The fabrication of liquid-quenched metallic glasses in the noble-metal-polyvalent-metal systems has been very limited in spite of the pioneering work of Duwez and his colleagues on the Au-Si alloy (Klement *et al* 1960). The reason for this is that the crystallisation temperature is generally quite low and is close to or even below 300 K. Mizutani and Yazawa (1980) employed the Ag-Cu eutectic binary in place of Au and obtained a stable amorphous phase in the vicinity of the ternary eutectic composition in the Ag-Cu-Ge system. The crystallisation temperature was found to be near 150 °C. Later, a large number of Ag-Cu-X ternary metallic glasses have been produced by the ordinary melt-spinning technique with a third element $X = \text{Mg}, \text{Si}, \text{Ge}, \text{Sn}$ and Sb (Mizutani and Yoshino 1984). The alloys of the noble metals with polyvalent elements are often referred to as Hume-Rothery alloys after the early work by Hume-Rothery, who found that several crystalline phases appear successively in a definite electron concentration e/a -range, regardless of the solute or solvent species. Recently, the electron-transport properties have been extensively studied on Ag-Cu-X metallic glasses to test the validity

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of the generalised Faber–Ziman theory based on the Boltzmann transport equation, since the Fermi momentum $2k_F$, which plays a key role in the theory, can be uniquely defined through the Hall effect and/or the positron-annihilation measurements (Mizutani 1983). As a result, the temperature dependence of resistivity in the range 10–300 K could be consistently interpreted in terms of the generalised Faber–Ziman theory, indicating that only the sp-type electrons dominate the electron transport.

Mizutani and Yazawa also noted that these Hume-Rothery-type metallic glasses, when prepared with the liquid-quenching technique, always appear in the electron concentration range 1.7–1.8 and, thus, obey the Hume-Rothery rule regarding the role of e/a . Häussler and Baumann (1983) reached a similar conclusion, using quench-condensed Hume-Rothery-type amorphous thin-film alloys. Häussler *et al* (1983, 1984) also studied the photoemission valence band structure of quench-condensed $\text{Au}_{1-x}\text{Sn}_x$ films and observed a decrease in the UPS intensity towards the Fermi energy E_F . They attributed this to the presence of a structure-induced density of states (DOS) minimum at E_F . They further emphasised that the stability of an amorphous phase against crystallisation is maximised at compositions where the DOS below E_F possesses its steepest negative slope, leading to a minimum at E_F . However, the minimum itself was not detected. On the other hand, Mizutani and his co-workers have studied the composition dependence of the electronic specific heat coefficient in the Hume-Rothery-type metallic glasses and concluded that the DOS near E_F changes very little (Mizutani 1981, Mizutani and Yoshino 1984). There was no indication of a minimum in the composition range where the amorphous phase is most stable and can be produced by the ordinary liquid-quenching technique.

It is thus of interest, at this stage, to explore the photoemission valence band structure of the liquid-quenched Hume-Rothery-type metallic glasses, for which the composition dependence of the electronic specific heat coefficient has already been established. Here, we report on the UPS and MXPS valence band studies of liquid-quenched $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ metallic glasses and a comparison is made with the measured electronic specific heat coefficient. The detailed band structure is also discussed with the help of band-structure calculations carried out for the hypothetical Cu_3Au -type Ag_3Ge and Cu_3Ge compounds.

2. Experimental procedure and band calculations

Three $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ ($x = 20, 22.5$ and 25) alloy ingots were prepared by RF induction melting of constituent elements Ag (99.999%), Cu (99.99%) and Ge (99.999%) in an argon atmosphere. Amorphous ribbons, approximately 2 mm wide and 30 μm thick, were produced, using a single-roll spinning wheel apparatus in a reduced argon atmosphere. All samples were verified to be entirely amorphous by ordinary x-ray diffraction with Cu $K\alpha$ radiation. The photoemission experiments were performed with a combined spectrometer of monochromatised x-ray (MXPS) of Al $K\alpha$ line ($h\nu = 1485.6$ eV) and ultraviolet radiations (UPS) with He I (21.2 eV) and He II (40.8 eV) excitation energies (EA11-100 Leybold–Heraeus). The energy resolution is better than 0.1 eV for UPS and 0.5 eV for MXPS. The sample chamber of the spectrometer is always kept at pressures less than 5×10^{-10} Torr. An argon-ion sputtering was carried out for about 20–30 min prior to the photoemission measurements to remove any surface contamination. The MXPS core-level spectroscopy revealed no surface contamination after ion-sputtering. The surface composition was studied after ion sputtering by measuring the MXPS core-level intensities of the samples and of pure Ag, Cu and Ge as

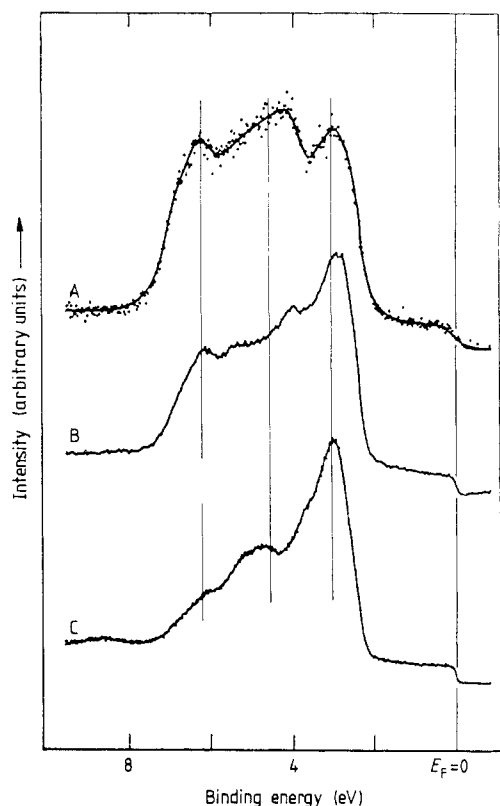


Figure 1. MXPS Al $K\alpha$ ($h\nu = 1486$ eV) (A), UPS He II ($h\nu = 40.8$ eV) (B) and UPS He I ($h\nu = 21.2$ eV) (C) spectra for $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{80}\text{Ge}_{20}$ metallic glasses. The vertical lines refer to the positions of peaks in the calculated DOS shown in figure 2.

references. The composition thus determined was shifted to slightly lower Ge and Ag contents and slightly higher Cu concentration than the nominal values for all three metallic glasses studied. These small changes are here not considered important to the main conclusions reached. The MXPS signal was accumulated over 12 h because of its low counting rate. In the UPS measurements, the accumulation time was less than 1 h and no more than 3 h with the He I and He II excitation energies, respectively.

The band calculations were made for the hypothetical Ag_3Ge and Cu_3Ge compounds in the Cu_3Au structure, using the self-consistent augmented spherical wave (ASW) method. The only input parameters to these calculations are the atomic number of the constituents and the crystal structure. The DOS is calculated for the theoretical equilibrium lattice separation obtained by energy minimisation.

3. Results and discussions

Figure 1 compares the MXPS, UPS He II and He I photoemission valence band spectra for the $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{80}\text{Ge}_{20}$ metallic glass. The UPS pattern has been corrected for both the energy dependence of the electron spectrometer transmission and the satellite contributions of the resonance discharge lamp. The valence band spectra are clearly dominated by the Cu 3d and Ag 4d states, which form the usual broad band between 2 and 7 eV in the binding energy. It is evident from the figure that the different peaks in the valence band spectra appear at about the same binding energies. This behaviour is typical of amorphous alloys (Oelhafen 1987) and justifies the interpretation of the

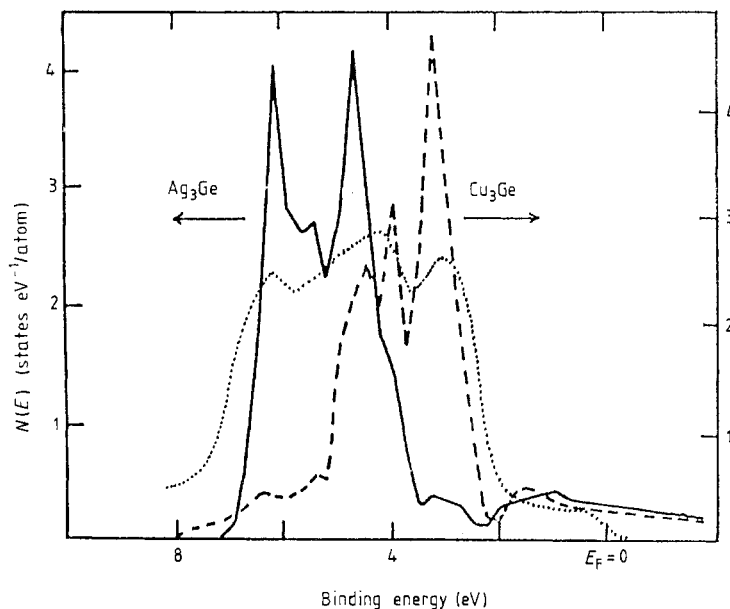


Figure 2. Calculated DOS for the Cu_3Au -type Ag_3Ge (full curve) and Cu_3Ge (broken curve) compounds. The MXPS spectrum shown in figure 1 is reproduced here as a dotted curve.

valence band spectra in terms of the DOS. Admittedly, however, for a quantitative comparison with band structure, one has to take into account the different photoionisation cross sections of the different electron states (e.g. Ag 4d, Cu 3d, Ge 4p, . . .) and also the dependence of the cross sections on the binding energy. This can be seen, for example, in the He I valence band spectrum of figure 1, in which the Ag 4d bonding states at the bottom of the valence band are strongly suppressed, as compared with the corresponding part of the valence band in the MXPS spectrum. However, we ignore, for the moment, any possible corrections associated with the cross sections. As will be seen below from the comparison with the electronic specific heats, these corrections at E_F are not likely to be important.

It is clear from figure 1 that the Fermi level is located well above the top of the d band. Firstly, we discuss the d band structure in the MXPS and the UPS He II spectra, using the calculated band structure for the hypothetical Cu_3Au -type Ag_3Ge and Cu_3Ge compounds as a guide. Figure 2 shows the valence band structures of the Ag_3Ge and Cu_3Ge compounds. It can be seen that the overall features of the observed UPS He II and MXPS spectra resemble well the calculated pattern, in spite of the fact that the structure and alloy compositions are not the same between the calculations and the experiments and, moreover, a possible interaction between Cu and Ag is neglected. The observed d band width, extending over the energy range 2.5–7.5 eV, is in good agreement with the calculated width. Furthermore, the peak observed at the binding energy of 3.2 eV can be easily assigned to the Cu 3d band. The calculated Ag 4d band is clearly split into two distinctive peaks at 4.5 and 6.2 eV. Therefore, the observed peaks at 4.2 and 6.3 eV can most likely be attributed to those associated with Ag 4d states. The observed spectra exhibit an additional peak at about 5.5 eV (see the He II spectrum in figure 1), although no peak exists in the band calculations. We consider this peak to be also related to the Ag 4d states, since a similar weak structure at about 5.5 eV is visible also in the spectrum of pure Ag (Barrie and Christensen 1976).

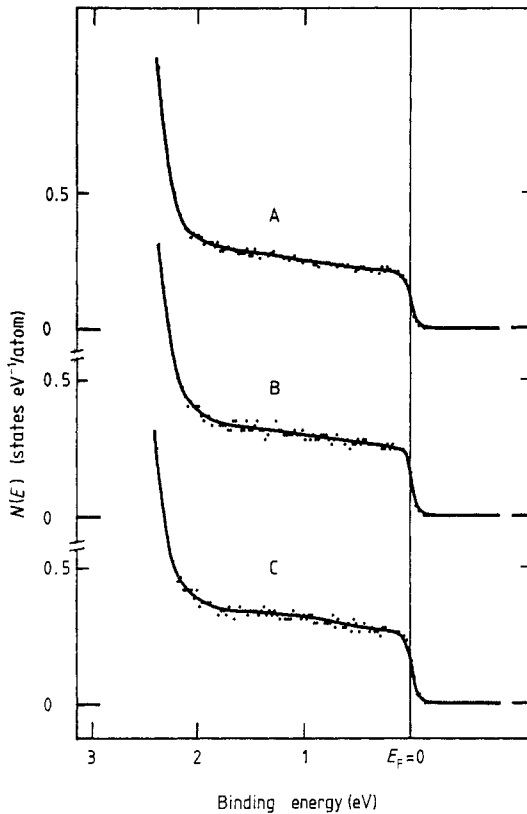


Figure 3. UPS He I spectra ($h\nu = 21.2$ eV) at low binding energies for $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{1.00-x}\text{Ge}_x$ (A, $x = 20$; B, $x = 22.5$ and C, $x = 25$) metallic glasses.

We turn our attention to the valence band structure near the Fermi level, where sp electrons dominate. Here, both UPS He I and He II spectra provide the most significant information about the structure of the DOS. We corrected the measured spectra by taking into account the energy dependence of the spectrometer transmission and subtracting first the satellite contributions and then a non-linear background, prior to the normalisation of the area under the spectrum with respect to the total number of valence electrons per atom. Here the total number of valence electrons is derived by taking a weighted mean of the valence electrons Ag $(4d)^{10} + (5s)^1$, Cu $(3d)^{10} + (4s)^1$ and Ge $(4s)^2 + (4p)^2$. Note that the Ge 3d band is located well below the valence band and can be ignored in the present discussions. In figures 3 and 4, the UPS He I and He II spectra thus derived are displayed for three metallic glasses but only in the narrow energy range of a few eV below E_F . First of all, it is obvious that the UPS intensity decreases smoothly with increasing energy without any indication of a pronounced minimum or maximum. The calculated band structure also shows a smoothly decreasing slope of the DOS in this energy range across E_F . It is important to note that the decreasing slope remains essentially unchanged for the three samples with different Ge contents. For comparison, the UPS He I spectra for the amorphous $\text{Au}_{80}\text{Sn}_{20}$ and $\text{Cu}_{80}\text{Sn}_{20}$ thin films obtained by Häußler *et al* (1983, 1984) are reproduced in figure 5. The present results resemble those of $\text{Au}_{80}\text{Sn}_{20}$, for which the DOS decreases smoothly towards E_F . The $\text{Cu}_{80}\text{Sn}_{20}$ spectrum also possesses the same feature with the presence of a small hump at 1.3 eV below E_F . As will be discussed below, the hump is most likely caused by the sp-d hybridisation effect. Nevertheless, all the data, including the present measurements, are consistent in the sense that the DOS near E_F is characterised by a decreasing slope. Here it should be

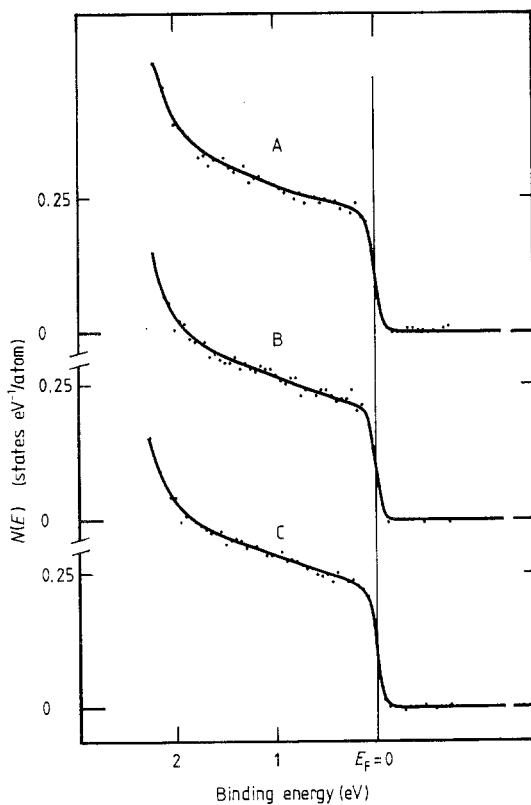


Figure 4. UPS He II spectra ($h\nu = 40.8$ eV) at low binding energies for $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Ge}_x$ (A, $x = 20$; B, $x = 22.5$ and C, $x = 25$) metallic glasses.

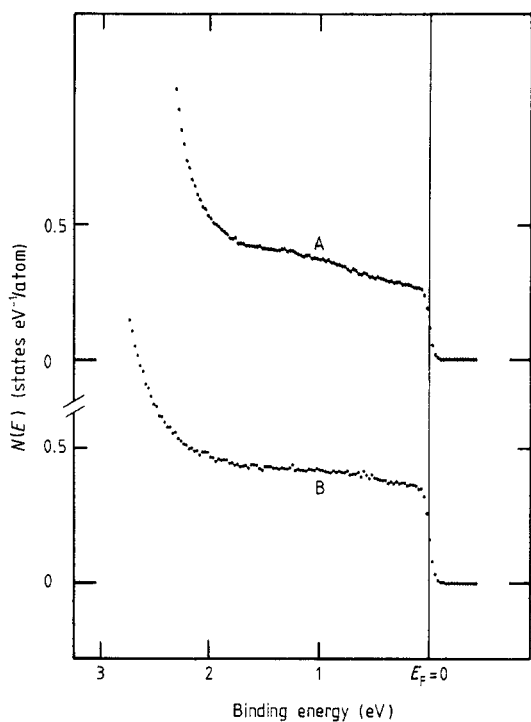


Figure 5. UPS He I ($h\nu = 21.2$ eV) spectra at low binding energies for A, $\text{Cu}_{80}\text{Sn}_{20}$ and B, $\text{Au}_{80}\text{Sn}_{20}$ amorphous thin-film alloys measured by Häussler et al (1983, 1984).

Table 1. Density of states at E_F , N (in units of states eV^{-1}/atom) deduced from photoemission spectra and low-temperature specific heats, γ_{exp} (in units of $\text{mJ mol}^{-1} \text{K}^{-2}$).

Alloy	e/a	γ_{exp}	$N(E_F)_{\text{LT}}$	$N(E_F)_{\text{UPS II}}$	$N(E_F)_{\text{UPS I}}$	$N(E_F)_{\text{MXPS}}$
$(\text{Ag}_{0.5}\text{Cu}_{0.5})_{80}\text{Ge}_{20}$	9.60	0.705 [†]	0.249	0.22	0.20	0.2
$(\text{Ag}_{0.5}\text{Cu}_{0.5})_{77.5}\text{Ge}_{22.5}$	9.425	0.730 [†]	0.258	0.22	0.25	0.2
$(\text{Ag}_{0.5}\text{Cu}_{0.5})_{75}\text{Ge}_{25}$	9.25	0.744 [†]	0.263	0.22	0.26	0.2
$\text{Cu}_{80}\text{Sn}_{20}$	9.6	—	—	—	0.30 [‡]	—

The subscript LT refers to the data deduced from the electronic specific heat coefficient $\gamma_{\text{exp}}(1 + \lambda)^{-1}$, where the value of λ is assumed to be 0.2.

[†] Mizutani (1981).

[‡] Häußler *et al* (1984).

emphasised that the presence of any structure-induced minimum at E_F cannot be deduced simply from the evidence that the slope of the DOS below E_F is negative.

Following the normalisation procedure mentioned above, approximate values of the DOS at E_F , $N(E_F)$, may be read directly from figures 3 and 4 in units of states eV^{-1}/atom . The values thus deduced from the normalised UPS He I, He II and also MXPS spectra are listed in table 1. They agree not only with each other but also show very little change with e/a . For comparison, similar information can be also extracted from the measured electronic specific heat coefficient (Mizutani 1981), provided that the electron-phonon enhancement factor is properly corrected. The enhancement factor λ in such non-superconducting metallic glasses is generally low and, hence, the value of λ may be assumed to be 0.2 for the present Ag-Cu-Ge metallic glasses. The value of γ_{band} , defined as $\gamma_{\text{exp}}(1 + \lambda)^{-1}$, should correspond to $N(E_F)$. The resulting values of $N(E_F)$ are also included in table 1, along with the measured value of γ_{exp} . One can see that the values of $N(E_F)$ deduced from the MXPS, UPS He I and He II spectra are quite similar to those derived from the electronic specific heat coefficient. Furthermore, it is seen that the value of $N(E_F)$ changes little as a function of Ge concentration, over which the amorphous phase is stable. It is indeed surprising that the MXPS, UPS He I and He II spectra, without correcting for the different photo-ionisation cross sections for different electronic states, yield similar values of the DOS at E_F deduced from the electronic specific heat coefficient. At this stage, it may be worthwhile mentioning that Indlekofer *et al* (1985) measured the photoemission spectra for a series of V-Mo solid solutions and deduced that the DOS at E_F was 2–3 times higher than that derived from the band calculations. This suggests that the UPS spectra may yield the right order of magnitude of the density of states at E_F only when dominated mainly by sp electrons.

The excellent agreement, obtained in evaluating $N(E_F)$ from both UPS spectra and the low-temperature specific heats, encourages us to believe that the decreasing UPS slope towards E_F reflects the actual band structure profile. The partial densities of states on Cu and Ag sites in both Cu_3Ge and Ag_3Ge compounds are illustrated in figure 6. It is clear that the sp-d hybridisation effects exist in both cases and contribute to enhance the decreasing slope of the d band tail in the energy range near E_F . This interaction should be a universal feature occurring in the noble-metal-rich Hume-Rothery-type alloys, regardless of the structure involved. Thus, the decreasing slope in the UPS spectra of the present Ag-Cu-Ge metallic glasses most probably reflects the decaying d states coupled with the sp states, which also decrease slowly in the vicinity of E_F . Mizutani (1981) pointed out that the electronic specific heat coefficient corrected for the electron-phonon enhancement factor in the $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{1-x}\text{Ge}_x$ metallic glasses is slightly smaller

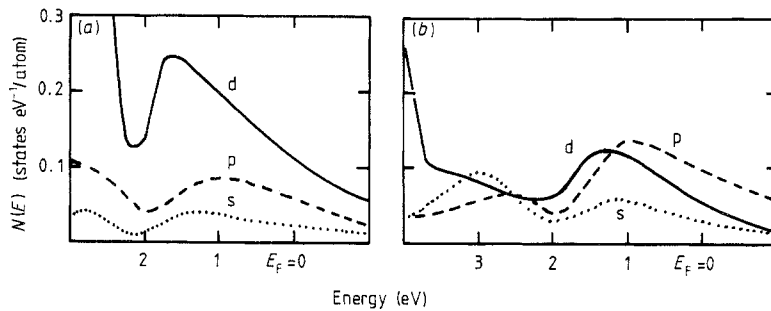


Figure 6. Calculated partial s, p and d DOS near the Fermi level E_F in Cu_3Au -type (a) Cu_3Ge and (b) Ag_3Ge compounds. All partial DOS exhibit a hump due to the sp-d hybridisation effect.

than the corresponding free-electron value. This is certainly not surprising now, since the band structure near E_F is found to be far from a free-electron-like parabola. The present interpretation means, in turn, that a structure-induced perturbation onto the DOS, if it exists, is fairly weak and masked by the d band tail in the present metallic glasses.

Upon discussing electron transport properties within the framework of the Faber-Ziman theory, we have frequently employed the parameter $2k_F/K_p$ as a key parameter, where $2k_F$ and K_p are the Fermi momentum and the wavenumber corresponding to the first peak of the structure factor, respectively. The ratio $2k_F/K_p$ was evaluated to be 1.05 for the $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{80}\text{Ge}_{20}$ metallic glass from the Hall effect and x-ray-diffraction measurements (Mizutani and Yoshida 1982). The fact that this ratio is slightly larger than unity implies that a structure-induced effect, if present, should be located below E_F . Nevertheless, there is no such indication within the accuracy of the UPS measurements. Therefore, a discussion of the stability of an amorphous structure in terms of a structure-induced effect on the total density of states is not fruitful.

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