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ELECTRON SPECTROSCOPY OF LIQUID ALLOYS CONTAINING TRANSITION METALS

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Several liquid alloys containing transition metals (Ni, Pd, Ag) have been investigated by means of photoelectron spectroscopy (UPS and XPS). In Pd-Si the d band exhibits a temperature dependent shift towards lower binding energy with increasing temperature. A similar temperature dependence of the d band positions and core level binding energies has been found in liquid Au-Sn alloys. The valence band (VB) spectra of liquid Pd-Si are compared with corresponding measurements on glassy Pd-Si. The great similarity of the VB spectra of the liquid and amorphous phases indicates a close resemblance of the atomic structure.

The comparison of photoemission results of the liquid and the amorphous state is of great interest as concerns the influence of the atomic structure on the electronic density of states (DOS). Whilst the electronic structure of amorphous metals has been the subject of many photoemission studies, the corresponding liquid phases have been investigated only scarcely mainly because of experimental difficulties in preparing clean liquid surfaces. The low evaporation rates just above the melting point of the present systems offer the possibility to perform photoemission studies in the liquid state as well and therefore a direct comparison of the electronic structures of the two phases is possible.

Liquid sample surfaces have been prepared in ultrahigh vacuum by the wire cleaning technique [1]. Photoelectron spectra have been measured with a Leybold EA 10/100 electron spectrometer. Atomically clean surfaces have been obtained as characterized by XPS core level analysis.

Fig. 1a shows the UPS HeI spectra of liquid alloys containing Pd. In the case of the Bi-based alloys the VB is mainly dominated by the split Bi $6p$ band giving rise to two peaks one located at 3.4 eV the second forming the shoulder close to E_F [2]. The Pd $4d$ band is superimposed on the Bi derived electron states and its maximum density is located at 2.7 eV. The comparison of the Pd $4d$ peak positions in Bi-based alloys and $Pd_{84.5}Si_{15.5}$ clearly indicates a concentration dependent shift towards lower binding energy (BE) with increasing amount of Pd. However the increase of the Pd content leads to an increase of the melting temperature. Therefore the VB spectrum of liquid $Pd_{84.5}Si_{15.5}$ has been measured at 800 °C which itself leads to a decrease in BE of the $4d$ band structure. The temperature dependence of the d band position can be observed by comparing the spectra of liquid and amorphous Pd-Si measured at room temperature (Fig. 1a). A similar temperature dependence has been observed in liquid Au-Sn alloys. The VB spectra of $Au_{25}Sn_{75}$ (Fig. 1b) are dominated by the double peak structure of the Au $5d$ band. Upon cooling the $5d$ peaks are shifted towards higher BE. A linear temperature dependence of -0.6 meV K^{-1} in the case of $Au_{25}Sn_{75}$ is found which turns out to fit even the $5d$ band position of the amorphous alloy at 77 K [3]. Within the experimental accuracy the same temperature dependence of -0.6 meV K^{-1} has been found in the case of the Pd-Si alloy whereas this effect is less pronounced for the Pd $3d$ core states which amounts -0.3 meV K^{-1}.

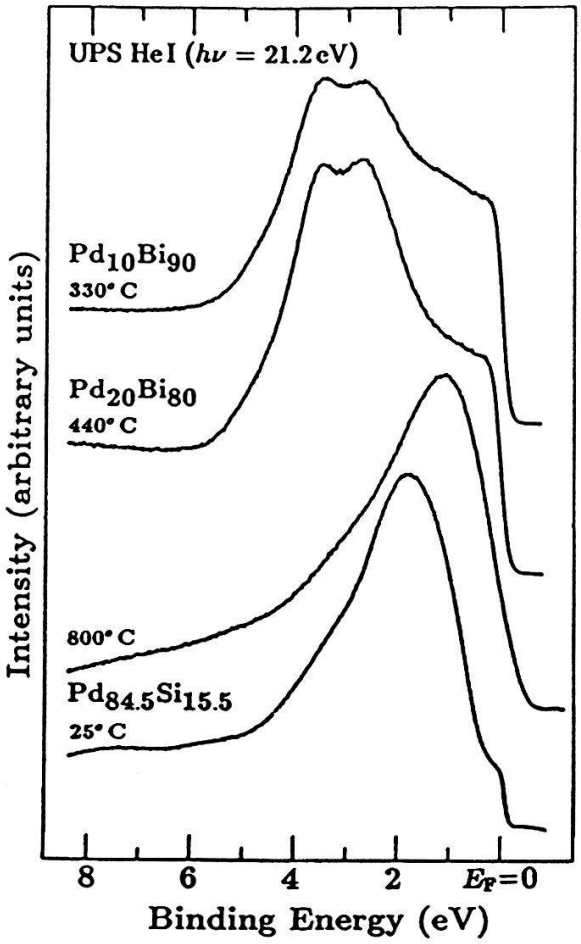

Fig. 1a: UPS HeI spectra of the liquid alloys $Pd_{10}Bi_{90}$, $Pd_{20}Bi_{80}$, $Pd_{84.5}Si_{15.5}$ and amorphous $Pd_{84.5}Si_{15.5}$.

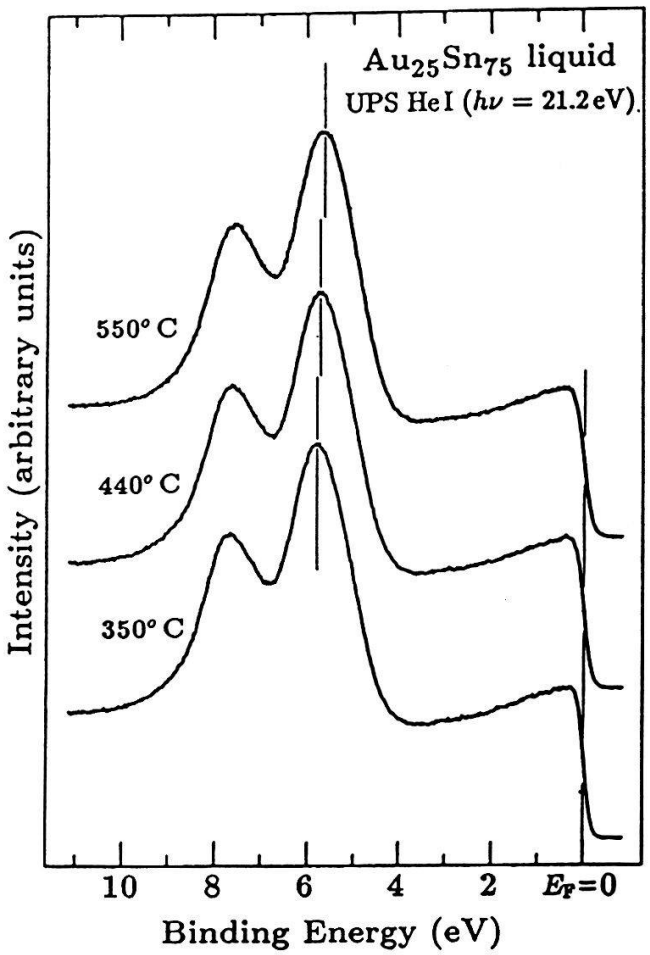

Fig. 1b: UPS HeI spectra of liquid $Au_{25}Sn_{75}$ at different temperatures.

The temperature dependence of the *d* band BE has been explained on the basis of atomic and electronic density changes [3] which are accompanied with corresponding changes of the mean bond length between neighboring atoms.

In conclusion, we have shown that in liquid alloys containing a transition metal, a temperature induced *d* band shift is observed which is superimposed on a concentration dependent shift.

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