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Time-resolved valence band photoelectron spectroscopy of liquid AuSn

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Abstract. The solid–liquid–solid-phase transitions of a Au₅₀Sn₅₀ alloy have been investigated by means of the recently developed method of time-resolved photoelectron spectroscopy, using dye laser pulses to melt the sample surface on a microsecond scale. Starting at a temperature of the liquid sample just above the melting point (740 K), the laser pulse heating allowed us to obtain, for the first time, valence band spectra of an alloy at temperatures of up to 1620 K, distinctly above the vapour pressure limit of steady-state photoelectron spectroscopy. The photoemission results of the liquid at different temperatures are compared with data from the corresponding amorphous alloy, prepared by vapour condensation at liquid-nitrogen temperature. By increasing the temperature of the disordered phase, the Au 5d band is found to shift continuously toward a lower binding energy, showing a linear behaviour over the whole temperature range. Our measurements confirm earlier results obtained with conventional photoemission within a restricted temperature range. The results presented here clearly show the potential of the new technique to investigate the electronic structure of alloys at conditions under which standard photoemission experiments cannot be performed.

1. Introduction

The new method of time-resolved photoelectron spectroscopy following pulsed-laser heating was originally developed to perform photoelectron spectroscopy of liquid elements with a high vapour pressure but additionally allows the investigation of surfaces at very high temperatures. It gives the possibility of locally heating a sample to temperatures at which conventional experiments would fail owing to problems such as chemical reactions of the sample with the crucible or an overflow as a result of wetting of the container by the liquid. In this contribution, we present the first time-resolved experiments of an intermetallic compound. The alloy Au₅₀Sn₅₀ has a low evaporation rate up to its melting temperature of only 692 K [1] and can therefore be used to test the applicability of our new technique on an alloy. This results from the possibility of performing conventional photoemission experiments, at least at temperatures near the melting point, which serve as a reference for the time-resolved method.

2. Experiment

The ultraviolet photoelectron spectroscopy was performed in a Fisons ESCALAB 210 spectrometer with the electron energy analyser set at a constant energy resolution of 80 meV

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(FWHM). The sample was kept in a heatable molybdenum crucible. The base temperature was monitored by a thermocouple in contact with the crucible. The Au₅₀Sn₅₀ alloy was prepared by melting high-purity (Au, 99.99%; Sn, 99.999%) elements under ultrahigh-vacuum conditions, followed by the removal of slag at the sample surface using the wire cleaning technique [2, 3]. This method produced atomically clean surfaces as proved by x-ray photoelectron spectroscopy.

The time-resolved measurement of the solid–liquid–phase transition is achieved by melting a sample surface area of about 2 mm² for several microseconds by irradiation with flashlamp-pumped dye laser pulses of 2 μ s pulse width (FWHM), 2.1 eV photon energy and a maximum repetition rate of 10 Hz. The photoelectrons are excited by a continuous UV source ($h\nu = 21.2$ eV) which illuminates a spot of about 0.8 mm diameter concentric to the melt area. The spectra are recorded in eight different time windows of variable duration and delay relative to the laser pulse, thus allowing the investigation of the electronic structure at different surface temperatures. The latter is determined on the basis of a lineshape analysis of the thermal Fermi edge broadening by fitting a Fermi distribution function to the experimental data, convoluted with the instrumental resolution function. Using conventionally recorded photoemission data, the fitting procedure has been tested for temperatures up to the melting point, showing deviations between the extracted values and the temperatures as measured by the thermocouple of less than 40 K. Each of the time-resolved measurements presented below was recorded by applying 2.1×10^5 laser pulses. Further details about the experimental set-up of the new dynamic method have been given elsewhere [4, 5].

3. Results and discussion

Figure 1 shows the evolution of the valence band spectra during the solid–liquid–solid-phase transitions. W1–W8 denote consecutive acquisition time windows and the corresponding spectra of the dynamic photoemission measurement. W1–W7 have a duration of 2 μ s each. W1 starts 1.5 μ s before the beginning of the laser pulse, which has an energy density of 2.6 J cm⁻². Between W7 and W8 there is a delay of 20 ms, before W8 is acquired with a duration of 4 ms. Starting at a temperature slightly above room temperature, reversible changes in the electronic structure can be observed for the different phase transitions as the laser pulses repeatedly melt the sample. The valence band is dominated by two peaks, which originate from Au 5d band states and the Sn 5p band at lower binding energies. In W8 the sample was cooled to 360 K, giving the reference spectrum of the crystalline sample in the irradiated area. During W2 the sample is heated by the main part of the laser pulse, resulting at the end in a liquid surface. Spectrum W2 can be interpreted as a combination of two spectra, representing the properties of both the solid and the liquid alloy. In the case of W3 the sample remains liquid, heated by the tail of the laser pulse and the latent heat of deeper parts of the sample. This spectrum is very similar to that of the conventionally measured liquid (dotted curve), except for minor differences due to the contribution of inelastically scattered electrons at higher binding energies. The main differences between the liquid and the crystalline alloy can be summarized as follows.

- (i) In contrast with the crystalline phase the two peaks of the Au 5d band are highly symmetric in the liquid.
- (ii) Both Au derived intensity maxima shift to lower binding energies in the liquid.
- (iii) In the crystalline state, a kink is visible at a binding energy of about 1.2 eV, which disappears in the liquid phase (see figure 1(b)).

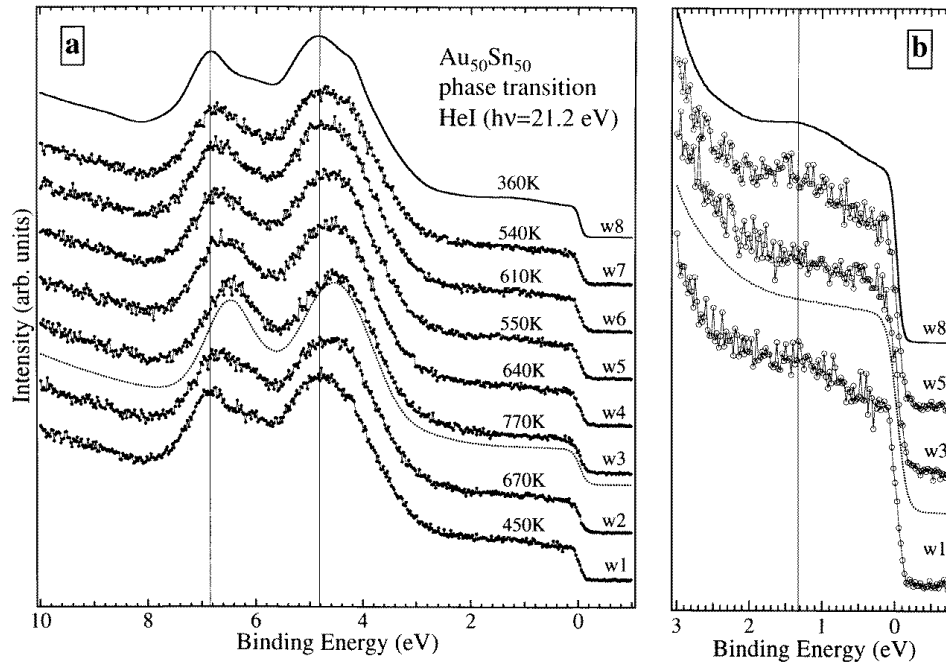


Figure 1. He I ultraviolet photoelectron valence band spectra of $\text{Au}_{50}\text{Sn}_{50}$ during melting and recrystallization by a laser pulse with an energy density of 2.6 J cm^{-2} . W1–W8 denote consecutive acquisition time windows of the time-resolved measurement. W1–W7 are acquired during $2 \mu\text{s}$ each, starting with W1 $1.5 \mu\text{s}$ before the beginning of the laser pulse. Between W7 and W8 there is a delay of 20 ms, before W8 is acquired with a duration of 4 ms.

After the decay of the laser beam, the melted area cools again, gradually showing all the valence band features observed before the irradiation.

The time-resolved measurement shown in figure 2 was performed during the irradiation of a pre-heated liquid sample with a laser pulse energy density of 11.7 J cm^{-2} . The sequence of time windows is identical with that in figure 1, having the spectrum related to the lowest temperature of 740 K in W8. Again, the highest temperature is reached in W3, which is even visually evident from the Fermi level broadening. The numerical fitting of spectrum W3 yields a value of 1620 K, which gives the possibility of comparing the electronic structure of liquid $\text{Au}_{50}\text{Sn}_{50}$ over an extended temperature range. The spectra corresponding to different temperatures look very similar; however, an increasing d-band peak shift towards the Fermi energy is clearly visible with rising temperature.

The binding-energy dependence of the Au 5d subbands on temperature is summarized in figure 2(b), together with the values of the corresponding amorphous phase [6]. Obviously, the low-temperature data of the amorphous sample can be extrapolated from the temperature region of the liquid phase, providing additional support for the interpretation of the amorphous phase as a frozen liquid. This has also been suggested on the basis of electron diffraction experiments on liquid and amorphous Au–Sn alloys, revealing almost identical static structure factors $S(K)$ [7].

Our new data also agree with earlier photoemission results [8], measured with conventional photoelectron spectroscopy within a restricted temperature range. A significant

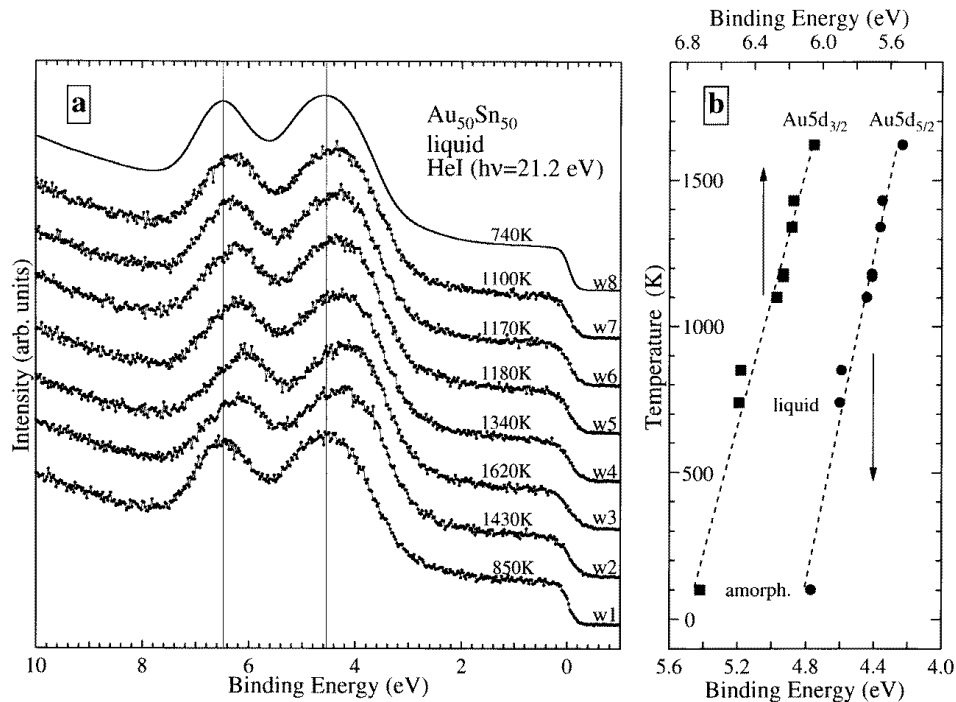


Figure 2. Time-resolved He I ultraviolet photoelectron valence band spectra of pre-heated liquid $\text{Au}_{50}\text{Sn}_{50}$ during irradiation with a laser pulse of an energy density of 11.7 J cm^{-2} . The sequence of time windows is the same as in figure 1. The temperature dependence of the energy position of the Au 5d subbands is summarized in (b), including the values of the amorphous phase [6].

temperature-induced shift of the Au 5d band towards lower binding energies was also found for different stoichiometries of the $\text{Au}_x\text{Sn}_{100-x}$ alloys, indicating the existence of a general temperature effect in the band structure of these alloys. This shift can, at least partly, be interpreted as being due to a temperature-induced decrease in the atomic (and therefore electron) density, leading to a decreasing diameter of the Fermi sphere within a free-electron approximation. However, binding-energy shifts of localized core electrons in metallic systems are influenced by final state screening effects [9] which, in similar alloy systems [10], are of the same order of magnitude as ground-state-induced binding energy shifts, e.g. due to alloying. Since the Au 5d valence band states reflect, to some extent, the properties of localized electronic states, final state screening of the photoionized hole state has also to be included in the discussion of temperature-induced binding-energy shifts. To clarify this problem, more experiments have to be performed on this subject, taking advantage of the significantly increased temperature range accessible with the laser pulse method.

In conclusion, the first dynamic photoemission experiments on $\text{Au}_{50}\text{Sn}_{50}$ have shown the potential of this method to access the electronic properties of alloys at temperatures well beyond the limit of conventional photoelectron spectroscopy.

Acknowledgment

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