Experimental Evidence for a Structure-Induced Minimum of the Density of States at the Fermi Energy in Amorphous Alloys

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First photoemission spectra are reported for the valence bands and core levels of quench-condensed $\mathrm{Au}_x\mathrm{Sn}_{100-x}$ ($0 \leq x \leq 100$) films in the amorphous and the crystalline state. It is found that (1) the valence-band spectra for the $20 \leq x \leq 80$ region, measured just after condensation, exhibit a decrease in intensity towards the Fermi energy E_{F} which can be understood in terms of a minimum in the density of states near E_{F} and (2) the minimum near E_{F} is most pronounced at an alloy concentration where the highest stability for the amorphous phase has been found.

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There has been a long-standing interest in the question as to how the main peak in the static structure factor $S(k)$ located at a wave number k_p influences the properties of liquid and amorphous metals.[1] Recent examples in this respect, out of many, are concerned with the electronic density of states (DOS). Evidence for a structure-induced minimum in the DOS of liquid and amorphous metals has been provided by theoretical investigations.[2,3] According to the Nagel and Tauc model,[4] amorphous metallic alloys with concentrations such that k_p is equal to $2k_{\mathrm{F}}$, the diameter of the Fermi sphere, should have a minimum in the DOS at the Fermi energy E_{F} and their stability against crystallization should be at a maximum.

So far all investigations, such as photoemission measurements,[5] made in order to confirm this hypothesis have been carried out on metallic glasses containing elements which are dominated by d states close to E_{F} and, thus, the nearly free-electron model of Nagel and Tauc cannot be applied. Therefore the structure-induced minimum in the DOS at E_{F} had not yet been observed in a convincing manner.

Undoubtedly quench-condensed tin–noble-metal films which are amorphous between 20- and 70-at.% noble-metal content[6] are the most promising candidates for examining the problem under consideration. Binary alloys such as Cu-Sn can be viewed as good models both in the liquid[7] and the amorphous state. In addition to several experimental advantages these films have well-known structural[8] and transport properties.[6] These amorphous films behave almost according to the free-electron model (FEM) for small noble-metal content but not for higher noble-metal concentrations. In the latter range the Hall coefficient[6] shows distinct deviations from the value calculated according to FEM. Specific-heat measurements carried out on amorphous Cu-Sn films led to smaller values of the DOS at E_{F} compared with the FEM in the range between 50- and 75-at.% Cu.[9]

We report, in this paper, photoemission measurements on quench-condensed Au-Sn films in the amorphous and the crystalline state. According to detailed investigations, quench-condensed tin–noble-metal films with about 20- to 70-at.% noble-metal content grow in a homogeneous amorphous state.[6] To our knowledge these are the first photoemission measurements carried out on this kind of an amorphous alloy. The measurements were performed with a combined x-ray photoemission/ultraviolet photoemission/Auger electron spectroscopy spectrometer EA 10-100 (Leybold-Heraeus). The energy resolution for ultraviolet photoelectron spectroscopy (UPS) ($h\nu = 21.2$ eV) and x-ray photoelectron spectroscopy (XPS) ($h\nu = 1253.6$ eV) was 0.1 and 0.9 eV, respectively. All films were evaporated, as described elsewhere,[10] onto a crystalline quartz plate held at temperatures between 80 and 100 K. The condensation took place in the preparation chamber of the spectrometer at pressures less than 5×10^{-9} mbar. After condensation the samples were transfered to the measuring chamber and measurements carried out. The films could be annealed under ultrahigh vacuum to temperatures well above their crystallization temperatures. An argon-ion bombardment for a short time did not influence the spectra of the amorphous and the crystalline films. In addition (XPS) core-level spectroscopy did not show any surface contamination.

Figures 1(a) and 2(a) show the UPS spectra of the valence band measured in the quenched and the well-annealed crystalline state. The He I-satellite components have been removed from the spectra in such a way that the intensity above E_F disappears completely. The data close to E_F are shown enlarged in Figs. 1(b) and 2(b). The parameters indicate the Au concentration in atomic percent. All curves have been smoothed numerically. Except for the curves of Fig. 2(a), all curves are normalized at a binding energy $E_B = 1$ eV to the DOS calculated for the liquid alloys according to the FEM. The spectra of the alloy films show the typical 5*d* band of gold which is split by spin-orbit interaction.

First of all we focus on Fig. 1(b). All spectra of the quenched films with a gold content between 20 and 80 at.% show a pronounced fall in intensity as the binding energy decreases from $E_B = 1$ eV to E_F. We relate this decrease in DOS just mentioned to the main peak in the structure factor at k_p. The structure factor of the quench-condensed Au-Sn films show two main peaks at k_{p1} and k_{p2}.[6,8] With increasing Au concentration the height of the first peak decreases, while that of the second one increases and becomes dominant. In addition to the UPS spectra we show in Fig. 1(b) a curve through three points, which represents the energy $E(k_{p2}/2)$ as a function of gold concentration calculated for free electrons with wave number $k_{p2}/2$. For amorphous $Au_{70}Sn_{30}$ films k_{p2} is equal to $2k_F$.[6] For higher gold concentrations the values of $E(k_{p2}/2)$ are above E_F and are not shown in Fig. 1(b). It is very interesting to note that the increase in the height of the peak in the structure factor at k_{p2} with increasing Au content is correlated with the decrease in the intensity of the spectra around E_F. Therefore we see in this, evidence that there exists a minimum in the DOS near E_F. We interpret this minimum as being

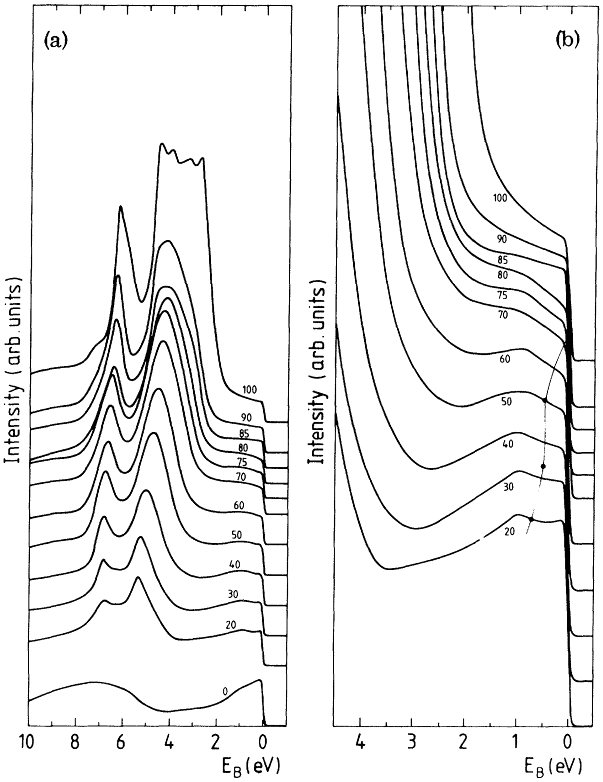

FIG. 1. UPS spectra of the Au_xSn_{100-x} valence band measured after condensation between 80 and 100 K.

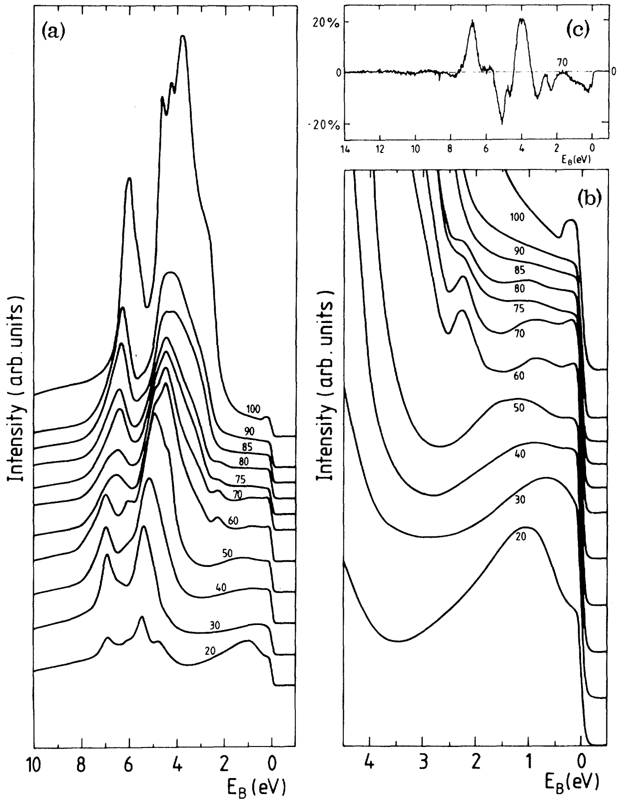

FIG. 2. UPS spectra of the Au_xSn_{100-x} valence band measured after annealing above the crystallization temperatures. The difference spectrum (top right) shows a relative difference in the spectrum of the amorphous state minus the spectrum of the crystalline state.

structure induced in accordance with previous theoretical investigations.[2,3] Preliminary measurements on quench-condensed Ag-Sn and Cu-Sn films show similar results to those reported here. From this we conclude that final-state effects are not important in this respect which allows us to pursue the interpretation along the lines mentioned above.

As can be seen in Fig. 1(a) it is interesting to note that the alloy films with less than about 80-at.% Au possess very similar spectra after quenching. The spectra are smooth and the intensity distribution around the two peaks is quite symmetrical. At higher gold concentrations the films condensing partly in the crystalline state show a shoulder around $E_B = 3$ eV. However, after annealing as shown in Fig. 2, the spectra between 20- and 75-at.% Au are drastically changed and new structures appear. Obviously the shape of the spectra is strongly concentration dependent and especially between 50- and 60-at.% Au there is an abrupt change. We interpret these pronounced changes in the UPS spectra as evidence for the occurrence of thermally stable phases and compounds during annealing according to the equilibrium phase diagram. For direct comparison in one case the UPS spectrum taken in the amorphous state minus the spectrum in the crystalline state is also shown in Fig. 2. In order to calculate this difference the intensities are normalized in such a way that the areas under the spectra are made equal in both cases. The difference spectra show a lower DOS at E_F in the amorphous phase compared with the crystalline phase.

Figure 3 shows the concentration dependence of the Sn $3d_{5/2}$ and the Au $4f_{7/2}$ core levels measured with respect to E_F. All data are slightly higher than the values taken by Friedman *et al.*[11] and are in better agreement with those of Ichikawa.[12] The quenched films show a continuous decrease in the binding energy of the Au $4f_{7/2}$ core levels with increasing gold content. In contrast to this the corresponding values of the annealed films exhibit a discontinuity between 50- and 60-at.% Au. There is also a change in the binding energy of the Sn $3d_{5/2}$ levels on crystallization in the concentration range between 20- and 70-at.% Au. This is the composition region where the quenched films grow in a homogeneous amorphous phase. Similar results have been observed also in the case of Sn $4d_{3/2}$ and Sn $4d_{5/2}$ core levels. Apparently the changes in binding energy are largest at the composition of the thermally stable compound SnAu. In our opinion most of the changes in the valence-band spectra and the changes in the core levels are caused by modifications in the short-range order due to crystallization. Changes in the long-range order may be responsible for changes in the valence-band spectra in pure Au films near E_F as can be seen from Figs. 1 and 2. We believe that the peak near E_F in the pure Au film, which was extremely thin (<5 nm) shown in Fig. 2 is a bulk effect since a similar peak has been observed in angle-resolved energy-distribution curves.[13]

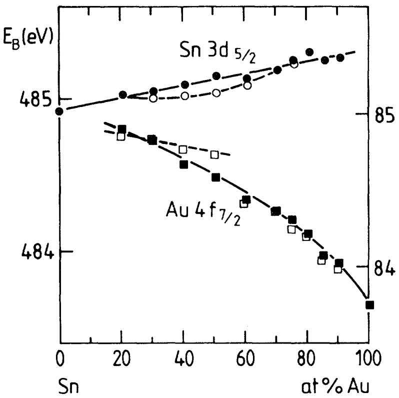

FIG. 3. XPS data of some core levels as indicated. Full and open symbols represent data taken in the quenched and the well-annealed state, respectively.

In conclusion we found experimental evidence for a structure-induced minimum in the DOS near E_F in amorphous Au-Sn films and in addition strong indications for distinct differences in the short-range order of amorphous and crystalline Au-Sn films. Preliminary measurements on quench-condensed Ag-Sn and Cu-Sn films show similar results. The observed minimum in the DOS seems nicely related to the observed deviations from the FEM in the Hall coefficient[6] and the electronic specific heat.[9] We also would like to emphasize that the stability against crystallization of the amorphous Au-Sn films has its maximum at 70-at.% Au[6] at which the DOS has its most pronounced minimum. However, the stability against crystallization of these metastable amorphous films is a rather complex problem which cannot be explained only in terms of the minimum in the DOS.

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