Specific heat of amorphous Au_xSn_{100-x} at low temperatures-electrons and low-energy excitations

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Abstract. Measurements of the specific heat of amorphous Au_xSn_{100-x} films ($27 \leq x \leq 74$) between 0.35 K and 6 K in the superconducting as well as in the normal state are reported. In addition the temperature dependence of the upper critical field of these films is determined. In the superconducting state the specific heat shows a contribution proportional to the temperature which is strongly composition dependent and largest for $x = 74$. In our opinion this contribution is caused by low-energy excitations well established in amorphous solids. Taking into account this contribution the specific heat in the normal state yields the electronic density of states at the Fermi energy in agreement with the data taken from critical field measurements. Using McMillan's formula the calculated bare density of states agrees with the free electron model over the whole concentration range. This result is surprising because recent Hall-effect and photoelectron-spectroscopy measurements indicate strong deviations from the free electron model, especially for samples with high Au concentrations.

1. Introduction

The close relationship between the atomic structure and the electronic properties of amorphous metals has been subject to many investigations in recent years. Quite different theoretical approaches all came to the result that the electronic density of states (DOS) should be lowered in the region where the structure function has a maximum [1]. Of special interest is the situation when this structure-induced minimum in the DOS (MDOS) is located at the Fermi energy E_F [2].

Experimental first evidence for an MDOS at E_F has been found in amorphous Au_xSn_{100-x} films (a-Au_xSn_{100-x}) and similar alloys [3] using UPS measurements. The spectra show a decrease of the DOS towards E_F. These alloys, also called amorphous Hume–Rothery alloys, are very suitable for this type of investigation because the d electrons of the noble metals are located well below E_F, in contrast to the large group of amorphous metals and metallic glasses containing transition metal atoms. As a consequence the electronic properties can be compared with the predictions of the free electron model (FEM) and deviations can be attributed to a structural influence. In addition these alloys can be prepared easily by quench condensation over a wide

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range of concentrations [4]. All these features make them especially suitable as model substances.

From the UPS measurements it was concluded that with increasing noble metal content the density of states at E_F, $D(E_F)$, is lowered in comparison to the FEM [5]. In the case of a-Au$_{72}$Sn$_{28}$ this decrease was estimated to be about 50%. Deviations from the FEM, most pronounced for high noble metal content, were also found in the Hall effect of amorphous Hume–Rothery alloys [4] and in the electronic specific heat of a-Cu$_x$Sn$_{100-x}$ [6]. The authors report that for high Cu content $D(E_F)$ is significantly lower than the value calculated from the FEM, in agreement with the estimations from UPS data. We note that the superconductivity of the films made the determination of the electronic contribution without any magnetic field very difficult, especially for films with high transition temperatures T_c, i.e. for low Cu concentrations.

In order to test the conclusion drawn from the UPS data for a-Au$_x$Sn$_{100-x}$, we determined $D(E_F)$ by specific-heat measurements at low temperatures in the whole concentration range. In contrast to [6] the measurements were also carried out in a magnetic field larger than the perpendicular critical field $B_{c\perp}(T = 0)$. This allowed us to measure the electronic contribution to C at temperatures below the superconducting transition temperature T_c and therefore resulted in a much higher accuracy over the whole concentration range. From the coefficient γ of the linear part of the specific heat at low temperatures the enhanced or 'dressed' electronic density of states $D^*(E_F)$ can be determined from

$$\gamma = \tfrac{1}{3}\pi^2 k_B^2 D^*(E_F). \tag{1}$$

In addition to the specific heat the perpendicular critcal magnetic field $B_{c\perp}(T)$ was measured; in the case of thin superconducting films it is equal to the upper critical field $B_{c2}(T)$ [7]. For superconductors with an extremely short mean-free path, e.g. amorphous metals, $D^*(E_F)$ can be determined from $B_{c2}(T)$ from the relation [8]

$$\left.\frac{dB_{c2}(T)}{dT}\right|_{T=T_c} = \frac{4k_B e}{\pi}\rho D^*(E_F) \tag{2}$$

with the electrical resistivity ρ. Hence $D^*(E_F)$ is determined with two completely independent methods.

Amorphous metals experience a strong electron–phonon interaction [9]. For this reason the specific heat and the critical field measurements yield the enhanced or 'dressed' density of states $D^*(E_F)$ which is connected with the bare or 'undressed' density of states $D(E_F)$ by

$$D^*(E_F) = (1 + \lambda)D(E_F) \tag{3}$$

with λ describing the electron–phonon interaction. Because we need $D(E_F)$ to compare our data with the FEM we calculated λ using McMillan's equation [10]

$$\lambda = [1.04 + \mu^* \ln(\Theta_D/1.45T_c)]/[(1 - 0.62\mu^*)\ln(\Theta_D/1.45T_c) - 1.04] \tag{4}$$

where we took the transition temperatures T_c and the Debye temperatures Θ_D from our own measurements and assumed $\mu^* = 0.1$, as usual for the effective Coulomb potential.

In order to calculate the DOS according to the FEM we assumed that (i) each Au atom and each Sn atom contributes respectively, one and four electrons to the conduction band, and (ii) the atomic volumes are those of the elements in the liquid phase.

In most amorphous materials low-energy excitations (LEE) contribute to the low temperature specific heat [11]. Just like the conduction electrons, the LEE give rise to a linear contribution aT to C. Within the tunnelling model which is usually employed to describe the LEE, the coefficient a is related to the density of states of the LEE n_0 by [12]

$$a = (\pi^2/6)k_{\rm B}^2 n_0. \tag{5}$$

While in amorphous insulators this contribution can be detected directly, in normal conducting amorphous metals it appears together with that of the conduction electrons. However, in amorphous superconductors the LEE can be separated by specific-heat measurements in the superconducting state well below T_c. Usually the contribution of the LEE is small compared with that of the conduction electrons [11]. Nevertheless one has to keep in mind that in amorphous metals in the normal state the linear part of the specific heat is partly caused by LEE.

In section 2 we give some experimental details. In section 3 we report on the results of the specific-heat measurements with and without magnetic field as well as the critical field data. Finally we discuss our results in section 4 and draw some conclusions.

2. Experimental details

The amorphous films were produced by quench condensation onto a cold substrate using a flash evaporation technique where small pieces of ingots of the desired composition were thrown onto a hot tungsten filament [13]. Because the films transform from the amorphous into the crystalline state at temperatures below room temperature all measurements had to be performed *in situ*. To prevent a large increase of the temperature during the condensation process the substrate for specific-heat measurements had to be thermally well coupled to a bath held at liquid-He temperature. On the other hand most methods for measuring heat capacity require that the sample be thermally isolated. To overcome these contradictory conditions an AC-heating method was used which is described elsewhere [14]. Experimental details for the application of this method to quench-condensed thin films can be found in [6]. During the condensation process the temperature of the substrate rose typically to about 40 K. The heat capacity of the films was determined immediately after the condensation process in zero field and in a field of 1.5 T or 3 T to force the films into the normal state even at the lowest temperatures. Most films were subsequently annealed at temperatures below the crystallization temperature and the measurements were repeated. The specific heat was measured between 0.3 K and 6 K.

In addition to the heat capacity, the resistance of a simultaneously condensed film was measured using a standard four-probe method. This allowed us to determine the temperature dependence of the critical field and to compare the resistivity of the films with data known from literature.

After completion of the measurements the mass of the film was determined via atomic absorption spectroscopy. Typical masses were 1 mg. Altogether the accuracy of our measurements was about 10%.

3. Results

The specific heat C of a-$Au_x Sn_{100-x}$ for two different compositions is shown in figure 1 where $\log C$ is plotted against $\log T$. Figure 1(a) shows typical data for a film with $x \leq 60$ in the normal state as well as in the superconducting state. In a field of 1.5 T the data roughly obey a T^3 law at higher temperatures and at low temperatures a T law. In zero field one obtains the same behaviour at high temperatures. The transition temperature T_c can clearly be seen and for T well below T_c the specific heat falls below the values in the normal state and continues to follow approximately a T^3 law. It is important to note that no linear contribution to C can be seen in the superconducting state within the experimental limit of 0.1 mJ mol^{-1} K^{-2}. Figure 1(b) shows typical data for a film with high Au content ($x > 60$) in the absence of a magnetic field. Again the jump in C at T_c can be seen but in contrast to the film with $x < 60$ a linear contribution to C appears in the superconducting state. Arguments that this contribution is caused be LEE will be given below.
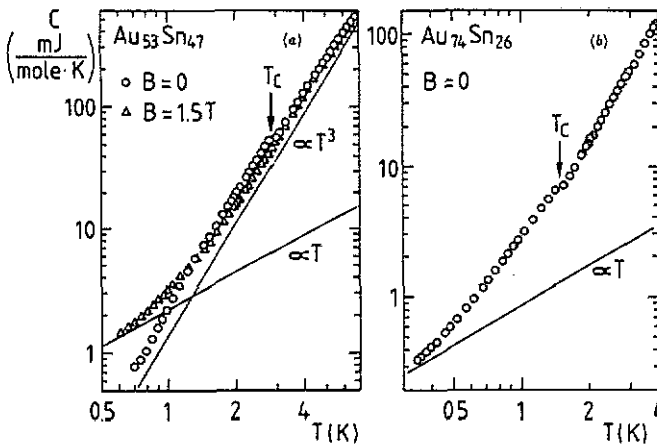

Figure 1. $\log C$ against $\log T$ for two a-$Au_x Sn_{100-x}$ films. Data are taken on the as-quenched films. (a) $x = 53$: O superconducting state, $\triangle$ normal state. (b) $x = 74$: O superconducting state The full lines are intended as guide to the eye.

Figure 2 shows the coefficient a of the linear contribution to C in the superconducting state as a function of the Au content. These data are represented by the full circles and were taken on the as-quenched films. The thin vertical lines indicate the composition range in which the films can be produced in a homogeneous amorphous phase. Up to $x \approx 60$ no linear contribution to C can be detected within the accuracy of our measurements. For $x > 60$ the coefficient a shows a very pronounced rise reaching its highest value at $x = 74$. Normal conducting regions which might appear by segregation in the superconducting films can be ruled out as the origin of this linear contribution by several arguments. First, these regions should have a minimum size of ≈ 10 nm, which is the typical size of the Ginsburg–Landau coherence length in these amorphous materials, otherwise they should become superconducting by the proximity effect [15]. A segregation on this length scale in these films is hardly to be expected because of the small diffusion at low temperatures. Second, the normal conducting regions should become larger on annealing and consequently the observed linear contribution should rise. But in contrast to this we found on a sample with

$x = 67$ that the linear contribution to C decreases on annealing. Therefore we believe that normal conducting regions cannot be the origin of the observed linear T term of C in the superconducting state. We have also estimated the possible contributions of the Zeeman splitting and the electrical quadrupole interaction [16]. While the Zeeman splitting is too small, the electrical quadrupole interaction may give a detectable effect depending on the size of the electrical field gradient. But it is impossible to fit our data with a T^{-2} law which is characteristic for this contribution. In our opinion the linear contributions to C in the superconducting state are caused by LEE. Their density of states n_0 calculated within the tunnelling model [12] has its maximum for $x = 74$ with $n_0 = 2.3 \times 10^{42}$ states $\mathrm{J}^{-1}\,\mathrm{mol}^{-1}$. For amorphous metals this value is very high [17] and is of the same order of magnitude as $D(E_\mathrm{F})$.
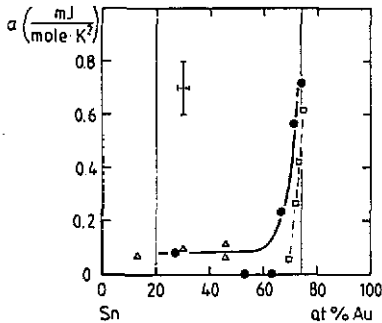

Figure 2. ●: Concentration dependence of the linear coefficient a of the specific heat of a-$\mathrm{Au}_x\mathrm{Sn}_{100-x}$ in the superconducting state. Data are taken on the as-quenched films. On the upper left experimental error bars are shown. Δ, □: a-$\mathrm{Cu}_x\mathrm{Sn}_{100-x}$ [6, 18], explained in the discussion.

We now turn to the specific heat in the normal state. A typical result is shown in figure 3 where C/T is plotted against T^2 up to $T \approx 3$ K for a film with $x = 53$. The data are taken in a field of 1.5 T in which superconductivity is completely suppressed. The upper curve shows the data in the as-quenched state and the lower one those after annealing to 60 K. To each set of data a fit to the relation

$$C = AT + \beta T^3 + \delta T^5 \tag{6}$$

is shown by the full curves. The linear coefficient A contains contributions from electrons and LEE ($A = a + \gamma$). One can see that the data cannot be described by a linear and a cubic term in T alone. The additional T^5 term was also observed in other amorphous metals [6] and indicates deviations of the phonon spectrum from a Debye-like behaviour. Annealing the films in the amorphous state always lowers the linear and the cubic contributions. This behaviour was observed in all films. The T^5 term which was of the same order of magnitude ($\delta \approx 0.1$ mJ mol^{-1} K^{-6}) in all investigated films, did not show a systematic annealing behaviour.

In order to calculate $D^*(E_\mathrm{F})$ according to equation (1) we determined $\gamma = A - a$ where a was taken from measurements in the superconducting state. The data for $D^*(E_\mathrm{F})$ obtained in this way on the as-quenched films are shown in figure 4 as full circles. In addition $D^*(E_\mathrm{F})$ from our critical field measurements and from those of [18] is shown by the full curve. Within the accuracy of our measurements both methods give identical results. But this is true only if the LEE are subtracted in the way mentioned above. The contributions of the LEE are indicated by the vertical bars in figure 4. The concentration dependence of $D^*(E_\mathrm{F})$ can be understood by the change of the mean number of valence electrons on alloying.
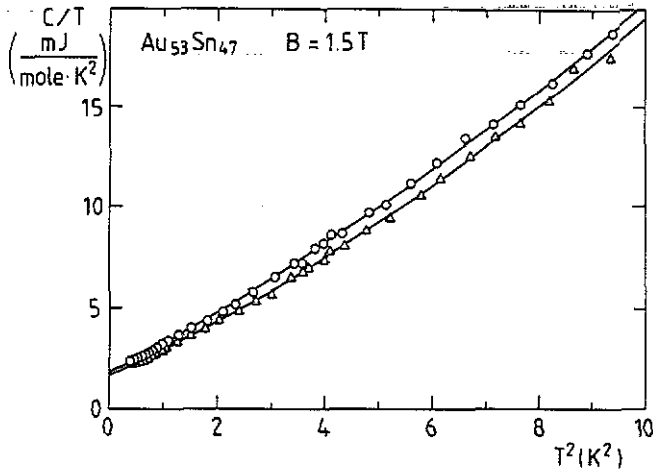
Figure 3. C/T against T^2 for a-Au$_{53}$Sn$_{47}$ measured in a field of 1.5 T. Upper curve: as-quenched state. Lower curve: after annealing at 60 K. Fits according to equation (6) are shown as full curves.

In order to compare our results with the FEM we first have to calculate the electron-phonon coupling parameter λ according to equation (4). The Debye temperatures Θ_D of our films were determined to $\Theta_D \approx 120$ K nearly independent of the composition. This led to values for λ between 0.6 and 0.8. In figure 5 $D(E_F)$ is given in the as-quenched state as well as in the annealed state. As already mentioned annealing always lowers $D(E_F)$ a little. $D(E_F)$ according to the FEM is included as a full line. The most important conclusion to be drawn from figure 5 is that $D(E_F)$ agrees with the FEM in the whole concentration range. Values for $D(E_F)$ estimated from UPS data are shown as triangles [5] which clearly lie below the FEM values.

4. Discussion

In this section two points will be discussed. First the behaviour of the LEE as a function of the composition and second the agreement of our $D(E_F)$ data with the FEM.

The most striking feature of the LEE in a-Au$_x$Sn$_{100-x}$ is the strong increase of their density of states in the region $x \approx 70$. Probably a-Cu$_x$Sn$_{100-x}$ behaves in the same way. Measurements of the specific heat in the superconducting state well below T_c carried out on a-Cu$_x$Sn$_{100-x}$ with low Cu content showed small contributions of the LEE [17]. These data are shown in figure 2 as open triangles. Unfortunately such measurements do not exist for samples with high Cu content. But measurements without magnetic field at temperatures $T > T_c$ give a linear part of C which rises with increasing Cu content in the range $x \approx 70$ [6]. If we assume that this rise is caused by LEE as it is in a-Au$_x$Sn$_{100-x}$, we can estimate their density of states. This gives the data which are shown in figure 2 by open squares. So for both alloys the concentration dependence of n_0 seems to be very similar.

Although the physical effects connected with the LEE are well described in the framework of the tunnelling model [12], not much is known about the microscopic nature and the physical origin of the LEE. Therefore it is worthwhile to look for
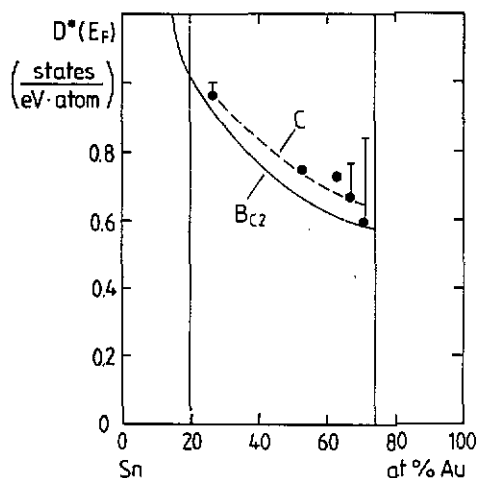
Figure 4. 'Dressed' electronic density of states $D^*(E_F)$ of a-Au$_x$Sn$_{100-x}$. ●: $D^*(E_F)$ calculated from the specific heat C. Vertical bars indicate the respective LEE contributions. The full curve summarizes data of this work and [18] taken from $B_{c2}(T)$. The broken curve is intended as guide to the eye.
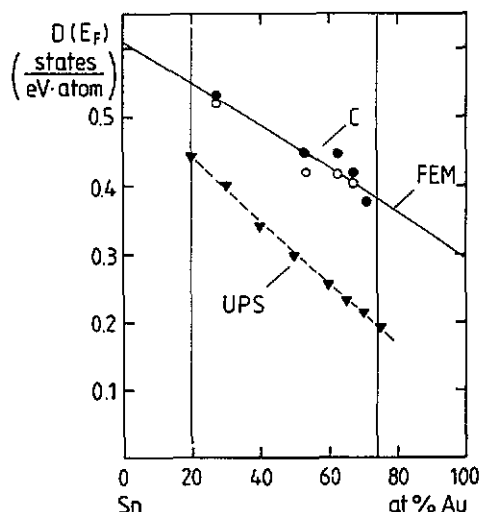
Figure 5. 'Bare' density of states $D(E_F)$ of a-Au$_x$Sn$_{100-x}$ calculated from specific heat. ●: as-quenched, ○: annealed at temperatures below the crystallization temperature for some hours. The full line corresponds to the free electron model. ∇: estimations from UPS data [5]. The broken line is intended as guide to the eye.

correlations between the LEE and other physical properties of the material under consideration. The pronounced concentration dependence of the density of states n_0 of the LEE with a maximum at $x \approx 70$ correlates with the concentration dependence of many properties of amorphous Hume–Rothery phases. For $x \approx 70$ the electrical resistivity and the crystallization temperature of these materials have their highest values [4]. In addition the Hall effect deviates from the FEM and the concentration dependence of these deviations is very similar to that of n_0 [4]. Furthermore the UPS spectra of these materials show a decrease of the DOS towards E_F which gets stronger with increasing noble metal content and is largest for $x \approx 70$ [5]. All this is connected with the fact that for $x \approx 70$ the position k_p of the main peak in the structure function coincides with the diameter $2k_F$ of the Fermi sphere [19] and clearly reflects the interplay between the structural and the electronic properties of amorphous metals which has often been discussed in the literature [5]. We believe that the pronounced concentration dependence of n_0 in a-Au$_x$Sn$_{100-x}$ is also caused by the interrelation between the structure and the electronic states. It should be added that phase separation which was observed to be the reason for LEE in a crystalline Pd–Si–Cu alloy [20] can be excluded in a-AuSn. As already mentioned during annealing and crystallization of an a-Au$_{67}$Sn$_{33}$ film the density n_0 of the LEE was strongly reduced. Hence the pronounced concentration dependence of n_0 shown in figure 2 cannot be caused by crystalline material embedded in an amorphous matrix.

We now turn to the electronic density of states $D(E_F)$. In our measurements of the specific heat as well as of the critical magnetic field we find good agreement of $D(E_F)$ with the FEM in the whole concentration range. This is quite surprising considering the results just discussed and it is obviously in disagreement with the values taken from UPS measurements. For a comparison these values are shown in figure 5 as triangles. It is interesting that their largest deviation from the FEM occurs for $x \approx 70$.

Although we cannot give any explanation for this disagreement, we want to mention two points concerning the evaluation of $D(E_F)$. Firstly, UPS measurements give the DOS only in arbitrary units. To compare the data with the FEM a normalization procedure has to be used which is not free of uncertainties. Therefore $D(E_F)$ taken from the UPS measurements may be systematically too small. The second point concerns the specific heat and the critical field data and arises from the calculation of $D(E_F)$ from $D^*(E_F)$ using the electron–phonon interaction parameter λ. McMillan's relation is known to give, sometimes, too small values in the case of amorphous metals [21]. Therefore the values for $D(E_F)$ taken from our data may be somewhat too large, but we do not believe them to be significantly so [22].

Finally we add that some structural influence on the DOS is also seen in specific-heat measurements. Annealing of a-$Au_x Sn_{100-x}$ always lowers $D(E_F)$. The thermal relaxation is expected to produce sharper peaks in the structure function and therefore more pronounced minima in the DOS.

Using the relation $A = \alpha + \gamma$ in our analysis of the specific-heat data we have ignored any mutual influence between electrons and LEE. Such an effect has been found recently to be manifested as a decrease of the LEE density of states due to the presence of quasiparticles in the superconducting state of a-ZrCu alloys [23]. Assuming the same influence in a-$Au_x Sn_{100-x}$ this would result in an increase of $D^*(E_F)$, which would lead to a disagreement between our specific-heat and our critical-field measurements and would make the disagreement with the UPS data even larger.

It has to be mentioned once more that in the case of a-$Cu_x Sn_{100-x}$, $D(E_F)$ taken from UPS and specific-heat measurements agree and are well below the value calculated from the FEM [5,6]. This is in contrast to a-$Au_x Sn_{100-x}$ while otherwise both alloys behave very similarly in many respects. Our results presented in this paper are quite unexpected and will certainly stimulate further investigations.

5. Summary

We report on measurements of the specific heat of a-$Au_x Sn_{100-x}$ at low temperatures in the superconducting and in the normal state. In the superconducting state a contribution proportional to T is observed which is caused by LEE and is largest for $x = 74$ for which $k_p = 2k_F$ also holds. The 'bare' density of states $D(E_F)$ determined from specific-heat and critical-field measurements agrees well with the free electron model in the whole concentration range. This result is in disagreement with conclusions drawn from UPS measurements.

Acknowledgments

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