Mössbauer Effect of $^{119}$Sn in Amorphous Superconducting Metals

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Abstract. Mössbauer spectra for $^{119}$Sn in crystalline and disordered Sn, as well as in crystalline and liquid-like amorphous Sn$_{1-x}$Cu$_x$ ($x=0.10-0.18$), have been measured at $2.6 \, K \leq T \leq 10 \, K$. The Debye-Waller-Factor (DWF) obtained from the spectra is identical for the crystalline and for the disordered phase. The DWF of the amorphous phase is smaller than the DWF of the crystalline phase at high temperatures, but it shows a stronger temperature dependence than the DWF of the crystalline phase and reaches the latter one at about 4 K. From this low-temperature result we conclude that the differences of the Eliashberg function $\alpha^2 F(\omega)$ and of the superconducting transition temperature $T_c$ in these two phases cannot be related to changes in the phonon spectrum $F(\omega)$, but must result from changes of the interaction parameter $\alpha^2$. A comparison between DWF, $\alpha^2 F$, and specific heat data is performed. From the values for the isomeric shift of the Mössbauer line we can show that the hybridisation and covalency of the electronic bonds present in the crystalline and in the disordered phases are destroyed in the amorphous phase. Both, the DWF and the isomer shift demonstrate that the electronic properties of crystalline and amorphous Sn(Cu) differ appreciably. The electronic and superconducting properties of amorphous Sn(Cu) are similar to the properties of the high pressure phase of tin.

I. Introduction

Many metals can be obtained in a disordered state by condensing their vapour onto a cold substrate [1, 2]. Whereas the strongly covalent semi-metals Bi and Ga are produced even in an amorphous phase by this method [2], one has to add impurities to less covalent metals if one wants to obtain them in a liquid-like amorphous state by quenched condensation [3-5]. A well known amorphous system showing liquid-like X-ray [3] and electron diffraction [4] patterns is Sn with at least 8 at. % Cu. After condensation the metal films show a high electric resistance which decreases irreversibly at a characteristic annealing temperature which depends on the Cu-concentration [6, 7]. Another remarkable property of amorphous films is the significant change of the gap parameter $\Delta$ and of the superconducting transition temperature $T_c$. For Sn, $T_c$ increases from the value 3.7 K of the crystalline state to 4.5 K for the disordered state [1], and up to 7 K for the amorphous state [4-7]. Similar shifts in $T_c$ have been seen for cold-worked Sn [1], indicating that the disorder is responsible for the shift in $T_c$. In McMillan's extension of the BCS-theory [8] for the case of strong-coupling superconductors the transition temperature is given by

$$T_c = \frac{\theta}{1.45} \exp \left( \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right)$$

(\theta = \text{Debye-temperature}; \lambda = \text{electron-phonon coupling parameter}; \mu^* = \text{Coulomb pseudo potential}.)
Because $\lambda \gg \mu^*$, the essential parameter in this equation is the electron-phonon coupling parameter $\lambda$ defined as

$$\lambda = 2 \int_0^\infty (\omega^2 F(\omega)/\omega) d\omega$$  \hspace{1cm} (2)

($F(\omega)$= phonon density of states; $\omega^2$= electron-phonon interaction; $\omega$= phonon frequency).

The product $\omega^2 F(\omega)$, as well as $\mu^*$, can be determined from tunnel spectra, which account for the observed shift in $T_c$ for the amorphous metals mainly by an increase of $\omega^2 F$ at low energies [9]. But it remained an unsolved question whether the coupling parameter $\omega^2 (\omega)$ [10], or the phonon density of states $F(\omega)$ [8, 11] is predominantly responsible for the increase of the Eliashberg function $\omega^2 F$ at small $\omega$, and therefore for the enhanced $T_c$.

Whereas other properties cannot be measured on thin films (neutron scattering), weight the phonon spectrum differently than $\lambda$ (specific heat), or give only the product $\omega^2 F$ (tunneling), a measurement of the Debye-Waller-Factor (DWF) seems to be capable of solving the above question. The DWF is given by

$$f(T) = \exp - (2R/3h) \int_0^\infty (F(\omega)/\omega) (n+1/2) d\omega$$ \hspace{1cm} (3)

($R$= recoil energy due to $\gamma$-emission or absorption; $n$= phonon occupation number).

The logarithm of the DWF at $T=0$ K,

$$\ln f(0) = - (2R/3h) \int_0^\infty (F(\omega)/\omega) d\omega,$$ \hspace{1cm} (4)

corresponds to the same moment of the phonon spectrum as $\lambda$ does, and should therefore allow to distinguish between a change of $\omega^2 F$ and a change of $F(\omega)$ in going from the crystalline to the amorphous phase. If the "softening" of $\omega^2 F$ results from a softening of the lattice one should see a corresponding change in $\ln f$. If, for example, $\omega^2 = \text{constant}$, then $\ln f(0) \propto \lambda$.

In this paper we report determinations of the DWF of crystalline and disordered Sn, and of crystalline and amorphous Sn(Cu) from measurements of the Mössbauer spectra of $^{119}$Sn in these substances. The behaviour of the DWF demonstrates that the observed changes of $\omega^2 F$ and of $T_c$ cannot be related to a change of lattice properties. A detailed comparison between DWF, $\omega^2 F$ obtained from tunneling experiments, and specific heat data is performed calculating one property from the others. In addition, we obtain information about electronic properties from the isomeric shift of the Mössbauer line. We show that in the quenched condensed amorphous films hybridisation or covalent bonds between the tin atoms are not present. In the amorphous phase the atoms have an effective electronic configuration identical to the configuration of the free atom ($5s^2 5p^2$), quite different from the hybridised configuration in the crystalline metal ($5s^{2-\gamma} 5p^{2-\gamma}$, $\gamma \approx 0.3$). The electronic and superconducting properties of the amorphous phase show similarities to the properties of the high pressure phase of Sn ($P > 110$ kbar).

II. Experimental Set-Up

1. Cryogenics

The low-temperature part of our experimental set-up is shown schematically in Fig. 1. The samples were evaporated from a small molybdenum crucible onto an oxidized aluminum foil (0.5 mm thick). The aluminum foil was clamped into a copper block (sample holder) thermally anchored by a copper strip to the bottom of the helium vessel of our cryostat. During evaporation the copper block had an additional Cu-In press contact to the helium bath to keep down the temperature increase of the substrate (due to radiation and heat of condensation). After condensing the sample this contact was opened, and the sample holder was moved inside the cryostat to the region where the Mössbauer effect was measured. The copper block contained holes into which a germanium, a platinum, and a carbon resistor were fitted. Temperatures below 30 K were measured with the germanium resistor, above 30 K the platinum resistor served as a thermometer. The temperature of the sample could be regulated to better than 0.1 K in our temperature range using the carbon resistor as a sensor. Its value was measured in a dc-bridge, any deviation from a preset value amplified and fed back into a heater wound onto the copper sample holder.

![Fig. 1. Experimental set-up](image-url)