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The electrical resistivity and electron–phonon interaction of Cu substitutionally alloyed with Ti

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Abstract. The electrical resistivity ρ and its temperature and concentration derivatives $d\rho/dT$, $d\rho/dc$ and $d^2\rho/dT\,dc$ are reviewed and measured for Cu substitutionally alloyed with Ti. The **Cu**Ti samples are prepared by a conventional method with heat-treatments as well as by melt-spinning. Heat-treatments are found to deplete the Cu matrix of Ti. From the values of $d\rho/dT$ we conclude that the electron–phonon interaction remains almost constant when Cu is alloyed with Ti. FCC **Cu**Ti is therefore non-superconducting.

1. Introduction

Dilute Cu-based **Cu**Ti alloys have been proposed to be superconducting with transition temperatures well above 5 mK [1]. This was based on the well known relation between the electron–phonon interaction constant λ and the temperature derivative of the electrical resistivity $d\rho/dT$, $\lambda = k(d\rho/dT)$ (see e.g. [2]), and the assumption that k was of similar magnitude as in other noble metal based alloys. There have, however, been no reports on superconductivity in this alloy system and our own measurements down to 20 mK have not given any positive result.

One other intriguing question in this alloy system is the problem of getting well defined values for ρ, $d\rho/dT$, $d\rho/dc$ and $d^2\rho/dT\,dc$. The published data give a rather confused picture, with large differences between results of different workers. This indicates problems in the sample preparation process.

In § 2 we show that the Cu matrix is depleted of Ti during heat-treatments. This gives rise to a concentration gradient of Ti with small or vanishing values for the dissolved Ti concentration at the sample surface. In the resistivity measurements this depletion will result in virtual values which are too low for ρ and $d\rho/dc$ and too high for $d\rho/dT$ and $d^2\rho/dT\,dc$. In § 3 we review the literature results and give estimates for $d\rho/dc$ and $d^2\rho/dT\,dc$ at $c = 0$.

2. Sample preparation and related problems

We have prepared samples by a conventional method with heat treatments and by melt-spinning. Wires with diameter 0.4–0.5 mm and nominal Ti concentrations 0.86 and 4.0 at.% were prepared by the following method: (i) Cu and Ti were induction melted

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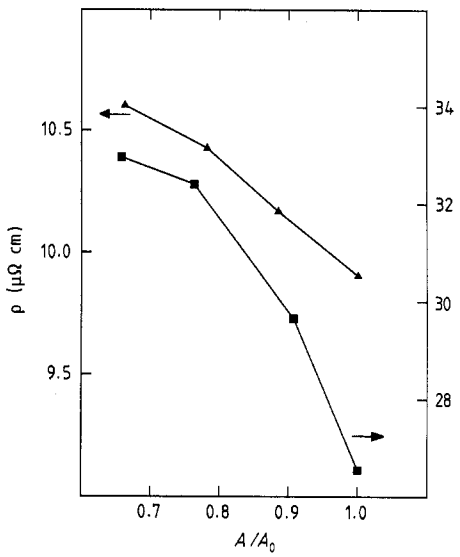

Figure 1. Resistivity ρ versus sample cross section area normalised to the area before the etching procedure for dilute **Cu**Ti alloys around room temperature. ▲, 0.86 at.% Ti; ■, 4.0 at.% Ti.

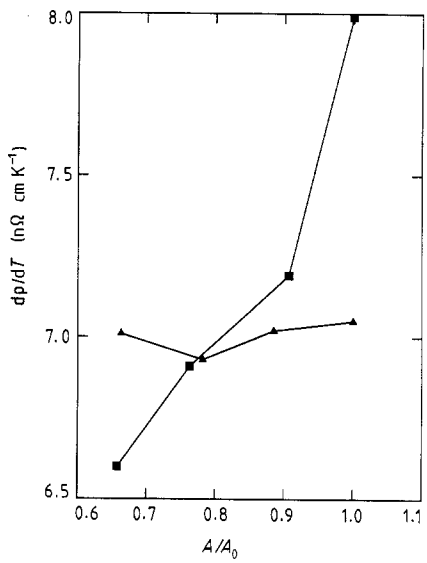

Figure 2. $d\rho/dT$ versus sample cross section area normalised to the area before the etching procedure. ▲, 0.86 at.% Ti; ■, 4.0 at.% Ti.

and cold-rolled to form a rod of cross section 3×3 mm^2; (ii) this was heat treated at 870 °C for 12–16 h. (iii) Wires were produced by cold-drawing to a diameter of 0.4–0.5 mm. (iv) These were then heat treated at 870 °C for 2.5 h. The wires were heat treated in evacuated silica ampoules and quenched by throwing the ampoules into water. The temperature for the heat treatment was chosen from the solubility maximum of Ti in Cu [3]. Even after careful evaporation of the ampoules, the samples were somewhat black on the surface. This surface layer was removed by grinding prior to further investigations. Ribbons with composition 0.29 (0.49, 0.29), 0.86 (0.86, —), 0.95 (0.95, 1.03) and 1.95 (1.95, 1.99) at.% were prepared by melt spinning. The values in brackets are respectively the nominal analysed concentrations. The analyses were made by atomic absorption spectroscopy and are correct within 5–10%. The melt-spinning method may reduce the Ti content. We have therefore used the lowest value. ρ and $d\rho/dT$ were measured for all samples at temperatures around room temperature. To investigate the homogeneity of the wires, they were etched in a number of steps. ρ and $d\rho/dT$ were controlled after each step. The lattice constant was also measured by x-ray diffraction in order to correlate the Ti concentration at the surface of the samples with measured values of ρ and $d\rho/dT$. Published results for the lattice parameter [4] provide some guide for this procedure.

In figure 1 we show ρ for the wires as a function of cross section area normalised to the value of the area before the etching procedure. ρ increases systematically during the etching. This is correlated with an increase in the lattice parameter. Thus the heat treatment seems to cause an inhomogeneous distribution of Ti, with a Ti concentration gradient perpendicular to the sample surface and Ti precipitation at the surface. This is only possible if the diffusing Ti atoms stick to the surface when they reach it. A similar phenomenon has been described for dilute **Cu**Mn [5]. The FCC phase at the surface is

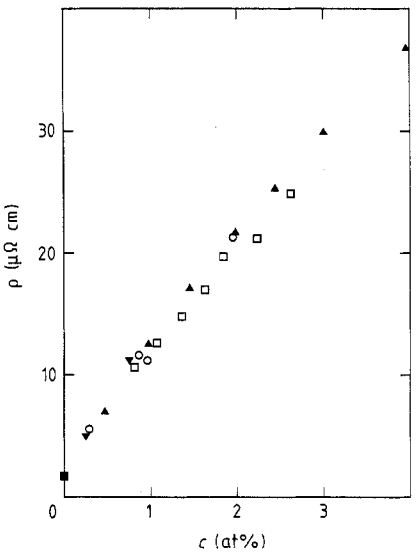

Figure 3. ρ versus Ti concentration. ▼, Linde [6]; ▲, Hahlbohm [7]; □, Sato and Doi [9]; ○, ribbon samples of present work.

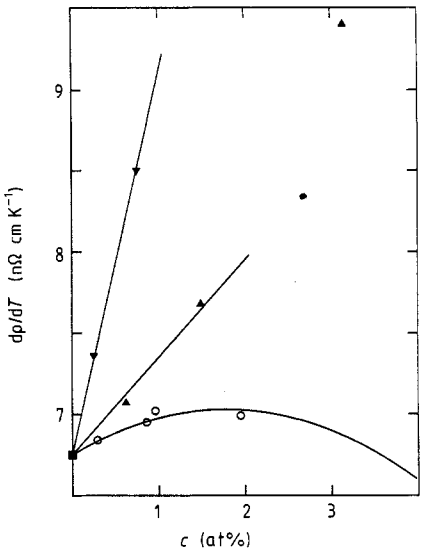

Figure 4. $d\rho/dT$ versus Ti concentration. ▼, Linde [6]; ▲, Hahlbohm [7]; ○, ribbon samples of present work. The straight lines give the values of $d^2\rho/dT\,dc$ in table 1. The curved line for our data above 2 at.% Ti indicates a possible behaviour of $d\rho/dT$ as suggested by the 4 at.% Ti wire sample.

thus lower in Ti than the nominal composition. If we calculate the average resistivity in the area which is removed in the first etch step, we obtain 8.3 $\mu\Omega$ cm and 13.1 $\mu\Omega$ cm for the 0.86 at.% and 4.0 at.% Ti samples, respectively. These are respectively only 78% and 40% of the ρ values we measure after the last etch step.

The inhomogeneity in the Ti concentration of the wire samples also affect the measured $d\rho/dT$. When the temperature is changed the current distribution in the sample is changed as well. This can result in a value of $d\rho/dT$ much larger than the actual $d\rho/dT$. This can be understood by modelling a simple system of two concentric conductors of equal areas with resistivity ρ_1 in the inner section and $\rho_2 < \rho_1$ in the outer section corresponding to the depleted region. We assume for simplicity that $d\rho/dT$ is equal in both conductors. This is not a restrictive assumption in CuTi where $(1/\rho)d\rho/dc$ is larger than $(dT/d\rho)d^2\rho/dT\,dc$ by a factor of 200. One then finds that the measured $d\rho/dT$ is greater than the true value by a factor $2(\rho_1^2 + \rho_2^2)/(\rho_1 + \rho_2)^2$, which is between 1 and 2. It can be seen from figure 2 that the change of the measured $d\rho/dT$ with area reduction is within 2% for 0.86 at.% Ti and more than 15% for 4.0 at.% Ti. The variation of ρ with c is shown in figure 3. One interesting fact is that $d\rho/dT$ for the 4.0 at.% Ti sample is lower than for pure Cu (6.75 nΩ cm K^{-1}) (see figure 4). This indicates that $d^2\rho/dT\,dc$ is negative in this concentration range.

From figures 3 and 4 the 0.86 at.% Ti ribbon sample has $\rho = 11.6\ \mu\Omega$ cm and $d\rho/dT = 6.95$ nΩ cm K^{-1}. These values fit well with the values we can extrapolate from the corresponding wire sample, namely $\rho = 11.3 \pm 0.3\ \mu\Omega$ cm and $d\rho/dT = 7.0 \pm 0.05$ nΩ cm K^{-1}. The melt-spinning technique thus provides an alternative to the conventional method.

Table 1. Concentration derivatives of the resistivity in dilute **Cu**Ti alloys at $c = 0$ around room temperature.

$d\rho/dc$ ($\mu\Omega$ cm (at.%)$^{-1}$)	$d^2\rho/dT\,dc$ (nΩ cm K^{-1} (at.%)$^{-1}$)	Reference
12.7[a]	2.35[a]	Linde [6]
11.9[b]	0.60[a]	Hahlbohm [7]
16[c]	—	Pawlek and Riechel [8]
11.0[d]	—	Sato and Doi [9]
>7.0	—	Vassel [10]
11.5	0.23[e]	Present work

[a] Straight line fit
[b] Second degree polynomial fit
[c] Claimed uncertain
[d] Straight line through $c = 0.81$ at.% Ti
[e] $c < 1$ at.%

3. Short review and results

The resistivity of Cu substitutionally alloyed with Ti has been measured a few times over the last 50 years. Starting with the measurements of Linde in 1939 [6], we have found five reports in the literature mainly from the late 1950s and early 1960s. We have evaluated $d\rho/dc$ close to $c = 0$ in these papers. When these data are of sufficient quality, a second-order polynomial in c was used. This may result in a considerable correction of $d\rho/dc$; this can be illustrated by the value 8.8 $\mu\Omega$ cm (at.%)$^{-1}$ given by Hahlbohm [7] and 11.9 $\mu\Omega$ cm (at.%)$^{-1}$ obtained by us from his data. When no primary data was given, the quoted value of $d\rho/dc$ is used. These results and ours are collected in table 1. $d\rho/dc$ ranges from 7 to 16 $\mu\Omega$ cm (at.%)$^{-1}$, with a group of values around 12 $\mu\Omega$ cm (at.%)$^{-1}$. Only two of the papers give results for $d\rho/dT$. From the data of Linde [6] we obtain $d^2\rho/dT\,dc = 2.35$ nΩ cm K^{-1} (at.%)$^{-1}$ and from those of Hahlbohm $d^2\rho/dT\,dc = 0.60$ nΩ cm K^{-1} (at.%)$^{-1}$. Our measurements give 0.23 nΩ cm K^{-1} (at.%)$^{-1}$ when $c < 1$ at.% Ti and smaller values for larger Ti concentrations.

The literature values can now be examined in the light of § 2. Almost all published values are affected by the depletion effect. The resistivity data of Linde [6] give a $d\rho/dc$ which is larger than ours and a value of $d^2\rho/dT\,dc$ which is much larger. This trend is opposite to that observed by us and is not understood. Another anomalous literature result is the high value of $d\rho/dc$ of 16 $\mu\Omega$ cm (at.%)$^{-1}$ given in [8]. This value was claimed to be uncertain, but despite this it has apparently been quoted in a text book [11].

The prediction of superconductivity was based on the data of Linde [6]. With $k = 0.03$ K nΩ^{-1} cm^{-1} [12] and using McMillan's formula this gives superconducting samples with $T_c > 5$ mK for $c > 1$ at.% Ti. With our data, λ will never increase beyond 0.23, and therefore, from any set of reasonable parameters in McMillan's formula, superconductivity will not be observed above 1 mK. The electron–phonon interaction strength thus seems first to increase slightly and then starts to decrease as the Ti concentration is increased.

4. Summary

Dilute **Cu**Ti samples in the FCC phase have been produced by a conventional method and by melt-spinning. The conventionally made samples were found to be depleted of

Ti during the heat-treatments. This depletion is present in all published data. The melt-spinning technique provides a means of producing homogeneous samples. We recommend $d\rho/dc|_{c=0} = 11.5 \pm 0.5\ \mu\Omega$ cm, the upper limit being the more likely for any deviations. The electron–phonon interaction increases only slightly for small Ti concentrations. The alloys are therefore not expected to be superconductors.

Acknowledgments

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