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Specific heat of metastable $Zr_{1-x}Si_x$ alloys

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Abstract. Non-equilibrium phases in the system $Zr_{1-x}Si_x$ prepared by liquid quenching are superconducting with intermediate electron–phonon coupling as determined from specific heat, low-field DC magnetisation, and electrical resistance measurements. Analysis of our data clearly shows that amorphous samples ($0.12 \leqslant x \leqslant 0.20$) are more homogeneous compared to samples of a metastable BCC phase ($0.08 \leqslant x \leqslant 0.11$). In the latter samples, a minority phase, presumably amorphous, strongly influences the superconducting properties. The concentration dependence of the transition temperature T_c of the majority phase is dominated by the electronic density of states. The data at very low temperatures suggest the existence of a linear specific heat contribution which may be due to the presence of two-level tunnelling states in both phases.

1. Introduction

Liquid-quenched amorphous alloys in the transition metal–metalloid system $Zr_{1-x}Si_x$ ($0.12 \leqslant x \leqslant 0.24$) are superconducting with transition temperatures T_c much higher than for pure (HCP) α-Zr. A non-equilibrium crystalline phase with a BCC structure can be obtained by the same preparation process when decreasing the metalloid concentration to $0.08 \leqslant x \leqslant 0.11$ (Inoue *et al* 1982, 1983). This metastable phase was found to exhibit superconductivity. The superconducting transition temperature T_c as measured resistively increases linearly with decreasing Si content without any discontinuity at the BCC and amorphous phase boundaries.

The aim of the present work is to further characterise the superconducting properties of these metastable alloys with specific heat and DC magnetisation measurements, and to relate them to normal state properties such as the electronic density of states N_γ at the Fermi level. In addition to yielding N_γ, specific heat measurements give information about whether superconductivity in the metastable Zr–Si alloys is a bulk effect, while the electrical resistance only probes a superconducting percolation path.

A second aspect of this work is the comparison of the thermal properties below T_c in both metastable phases. It is well known that the low-temperature thermal properties of superconducting metallic glasses are dominated by the existence of low-energy excitations, described in the model of two-level tunnelling systems (TLS) (Black 1981, von Löhneysen 1981). Some indications of TLS in quenched crystalline metastable superconductors have been reported (Lou 1976, Chevrier *et al* 1989). It is therefore of interest to look for evidence for TLS in metastable Zr–Si alloys.

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2. Experimental details and sample characterisation

Ingots of $Zr_{1-x}Si_x$ ($0.08 \leqslant x \leqslant 0.2$) were produced by melting small pieces of Zr (purity 99.95%) and Si (purity 99.999%) in an arc furnace under argon atmosphere. The samples were prepared in a splat-cooling apparatus (two-piston technique), yielding thin foils of non-uniform thickness (35–50 μm) and 15–20 mm in diameter. Each foil shows circular ripples in the central part giving evidence for a circular solidification front of the melt directed towards the centre, and a radial flow pattern in the outer region. X-ray analysis (Fe Kα radiation) of only the central part of the foils shows several diffraction patterns due to a multiphase material while the outer regions of the foils appear to be single-phase. This is confirmed by energy dispersive x-ray spectroscopy and transmission electron micrographs taken at several points of the foils. The observed microstructure and diffraction patterns in the outer and central part are quite different for each sample, but no measurable difference in composition is found. Therefore we conclude that 'non-ideal' cooling of the alloy droplet leads to different quenched-in phases due to a broad distribution of cooling rates inherent in the splat-cooling process, with a slower cooling rate in the inner part. Poon and Dowling (1984) showed that the sample homogeneity can be improved for some materials including $Zr_{1-x}Si_x$ by quenching at higher temperatures. This, however, was not possible with the present splat-cooling apparatus. Therefore, the inner circular part of each foil was discarded and only the outer circumference of the samples was investigated.

The x-ray diffraction patterns for samples with $0.12 \leqslant x \leqslant 0.2$ show a broad peak, typical for amorphous materials. The peak position corresponds to the most frequently occurring interatomic distance R (Klug and Alexander 1967), which can be estimated up to $R = 0.309$ nm. For $0.08 \leqslant x \leqslant 0.11$ relative sharp diffraction peaks were observed and indexed (JCPDS pattern 34-657) as a BCC phase with a lattice constant $d = 0.353$ nm. The corresponding nearest neighbour distance $d_{nn} = 0.306$ nm is similar to R of the amorphous phase. As pointed out by Inoue *et al* (1982), the BCC phase consists of grains with dimensions less than about 100 nm. This is in qualitative agreement with the width of the diffraction peaks of our BCC samples. The material contains amorphous regions as deduced from the broad background of the (110) peak.

The electrical resistance was determined on thin strips of width 0.6 to 1 mm cut from the outer part of the foils, using a conventional four-probe technique with a measuring current $I = 10\ \mu$A. The specific heat was measured between 0.1 K and 20 K by the standard heat-pulse method in zero field and in a magnetic field of $B = 6$ T. The mass of the heat capacity samples was about 30 mg. Details of the measuring method and the sample holder are described elsewhere (Albert *et al* 1982). The DC magnetisation $M(T)$ was determined with a SQUID magnetometer in a magnetic field of 0.1 mT for temperatures $T > 2$ K.

3. Results and discussion

Figure 1 shows the resistance ratio R/R_0, $R_0 = R(4.2\ \text{K})$, for two $Zr_{1-x}Si_x$ samples in the region of the superconducting transition. The amorphous sample $x = 0.132$ exhibits a sharp transition at $T_c^R = 3.21$ K ($\Delta T_c \simeq 30$ mK) in contrast to the BCC sample $x = 0.108$ where the transition is much broader ($\Delta T_c \simeq 210$ mK). T_c^R is the temperature for which $R/R_0 = 0.5$ and ΔT_c is defined as the temperature interval between 10% and 90% of R_0.

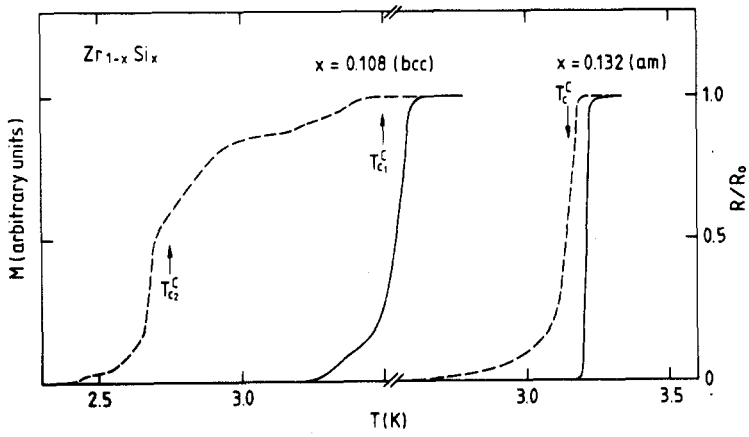

Figure 1. Electrical resistance R normalised to $R_0 = R(4.2\ \text{K})$ (full curves) and DC zero-field-cooled magnetisation M (broken curves) as a function of temperature T for $Zr_{1-x}Si_x$.

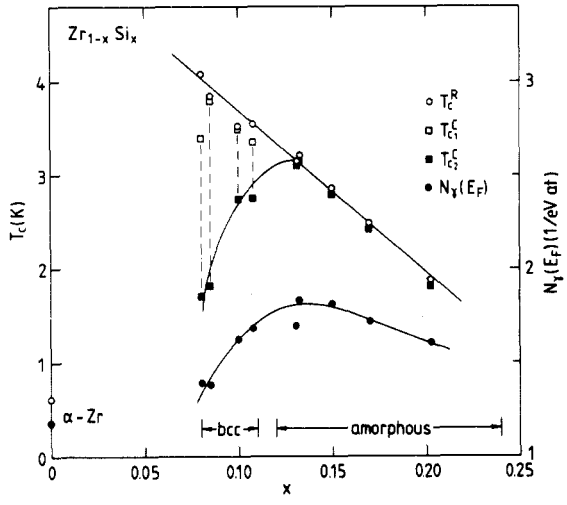

Figure 2. The superconducting transition temperature T_c as inferred from measurements of resistance (T_c^R) and specific heat (T_c^C) and density of states at the Fermi level $N_\gamma(E_F)$ of $Zr_{1-x}Si_x$ for various x. Full curves serve as visual guides. Broken lines connect transition temperatures T_{c1}^C and T_{c2}^C) of identical samples.

In order to get more information on the superconducting transition, the DC zero-field-cooled magnetisation $M(T)$ was measured for a few samples. Figure 1 shows a rather sharp drop towards diamagnetism for the amorphous sample and a broad two-step-like transition for the BCC sample, with the onset of the diamagnetic signal near $T_c^R \simeq 3.54$ K.

The compositional dependence of T_c^R is shown in figure 2 (open circles). $T_c^R(x)$ increases linearly with decreasing x and without appreciable discontinuity at the BCC and amorphous phase boundaries. The transition temperature for $x = 0$ can be extrapolated to $T_c = 5.4$ K and is much larger than for crystalline α-Zr ($T_c = 0.61$ K, Roberts 1985).

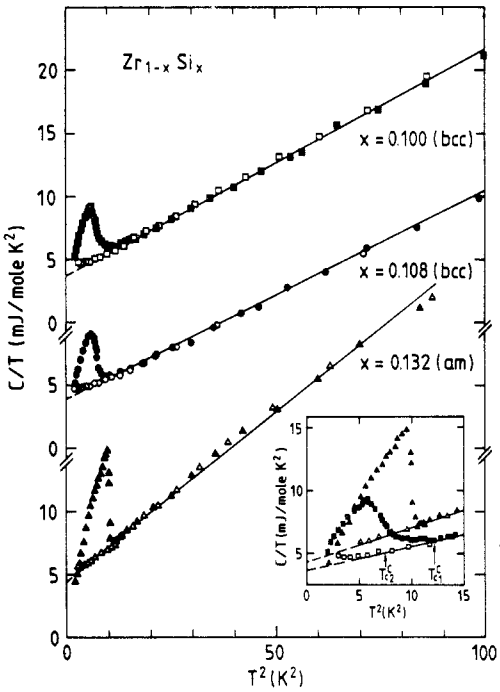

Figure 3. C/T versus T^2 plot for some $Zr_{1-x}Si_x$ samples. Closed symbols: zero-field results; open symbols: measurements in a magnetic field $B = 6$ T. Full curves indicate the best fit of $C = \gamma T + \beta T^3$ to the experimental data. Broken lines are extrapolations of the fit to lower temperatures. The inset shows the superconducting phase transitions for $x = 0.100$ (BCC) and $x = 0.132$ (amorphous).

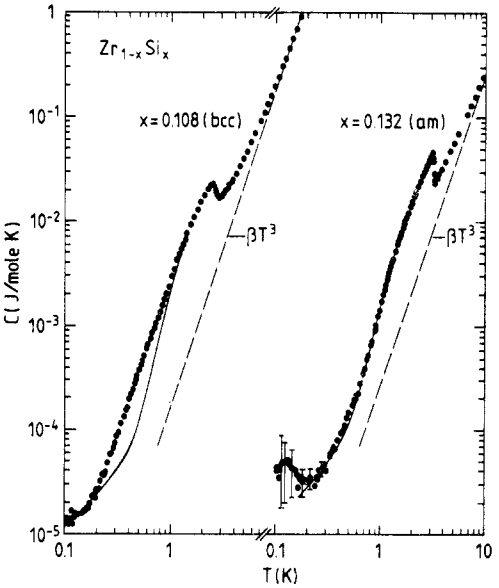

Figure 4. Specific heat C as a function of temperature T in a double-logarithmic plot for BCC $Zr_{0.892}Si_{0.108}$ and amorphous $Zr_{0.868}Si_{0.132}$. Full curves indicate a fit $C = aT + 8.5\,\gamma T_c \exp(-1.44\,T_c/T) + \beta T^3$ to the experimental data. Broken curves show the phonon contribution as calculated from figure 3.

$T_c = 5.3$ K has also been suggested for hypothetical pure BCC Zr (Inoue *et al* 1982). An earlier study of Zr_xCu_{1-x} (Samwer and von Löhneysen 1982) yields an extrapolation of $T_c = 5.6$ K for hypothetical pure amorphous Zr. Poon and Dowling (1984) extrapolated $T_c \simeq 5$ K for both amorphous and BCC Zr. As will be discussed later, this apparent similarity could be due to a small amount of amorphous material in the BCC samples, which has not been taken into consideration in the previous work. An evaluation of superconducting properties from resistance data alone must be met with caution. The sensitivity of the low-temperature specific heat to phase separation effects has been successfully demonstrated for liquid quenched Zr–Ni glasses (Kroeger *et al* 1984).

Figure 3 shows the specific heat C in a C/T versus T^2 plot for $1.5\text{ K} \leqslant T \leqslant 10$ K. In amorphous $Zr_{0.868}Si_{0.132}$ a sharp jump ΔC appears at the superconducting transition temperature T_c^C, which is slightly lower than T_c^R (see inset of figure 3). The agreement of T_c, estimated from the three different measuring methods, is better than 70 mK (figure 1). Hence, the corresponding superconducting phase sems to be rather homogeneous on a scale larger than the superconducting coherence length ($\xi \simeq 6$ nm, Inoue *et al* 1982).

The value of the reduced specific heat jump at T_c, $\Delta C/\gamma T_c = 1.87$ (BCS value: 1.43) suggests intermediate electron–phonon coupling (γ: Sommerfeld constant). Apparently the whole sample undergoes the superconducting transition.

For BCC $Zr_{1-x}Si_x$ the agreement of T_c obtained from resistance and specific heat measurements is only poor. At an onset temperature $T_{c1}^C \simeq T_c^R$, only a small part of each BCC sample becomes superconducting as can be inferred from, e.g., $x = 0.100$ in the inset of figure 3 which shows a small enhancement over the normal-state data. At a lower temperature T_{c2}^C the majority phase becomes superconducting, as evidenced by the broad, sizable jump in the specific heat. For $x = 0.108$, T_{c1}^C and T_{c2}^C agree quite well with the temperatures of the two-step transition observed in the magnetisation (figure 1). Figure 2 convincingly shows that $T_c(x)$ for the majority BCC phase, i.e. $T_{c2}^C(x)$, is suppressed with decreasing Si content in contrast to previous and present resistance data (Inoue *et al* 1982, 1983), while $T_{c1}^C(x)$ closely follows the resistance data $T_c^R(x)$. A very tempting and plausible explanation is that a small part of amorphous material leads to the transition at $T_c^R \simeq T_{c1}^C$, causing the linear increase in T_c^R with decreasing x. Indeed, evidence for some amorphous minority phase was found in the x-ray analysis for all BCC samples as mentioned earlier.

Measurements in the normal state were extended to temperatures below T_c by application of a magnetic field $B = 6$ T. At temperatures $T < \Theta_D/30$ (Θ_D: Debye temperature) the specific heat can be expressed as $C = \gamma T + \beta T^3$ (see figure 3). From a least-squares fit to the experimental data one obtains γ and hence the electronic density of states at the Fermi level $N_\gamma \equiv N_\gamma(E_F) = 3\gamma/\pi^2 k_B^2$. The TLS derived linear specific heat contribution (see below) amounts to only ~3% of γT and hence can be neglected in the normal state.

For amorphous $Zr_{1-x}Si_x$, N_γ increases linearly with decreasing x to a maximum of $1.83\ eV^{-1}\ at^{-1}$ at $x \simeq 0.13$ (see figure 2). In the BCC phase, N_γ decreases again towards the value of pure α-Zr ($N_\gamma = 1.18\ eV^{-1}\ at^{-1}$, Dummer 1965). The compositional dependence $N_\gamma(x)$ shows qualitative agreement with $T_{c2}^C(x)$ of the majority phase.

From β one gets the Debye temperature $\Theta_D = (234R/\beta)^{1/3}$, $R = 8.314\ J\ mol^{-1}\ K^{-1}$. For amorphous $Zr_{0.868}Si_{0.132}$ we obtain $\Theta_D = 194$ K, lower than the values for pure crystalline α-Zr (290 K, Dummer 1965) and Si (645 K, Flubacher *et al* 1959), due to the softening of transverse phonons in metallic glasses (Golding *et al* 1972). This is in good agreement with Θ_D of liquid quenched $Zr_{1-x}M_x$ ($x \simeq 0.25$, M = Ni, Cu, Rh, Kroeger *et al* 1984, Samwer and von Löhneysen 1982, Garoche and Johnson 1981). For the BCC phase it is obviously difficult to extract an accurate value for the Debye temperature because of the above-mentioned inhomogeneities; Θ_D varies from 221 K ($x = 0.100$) to 243 K ($x = 0.085$).

With the knowledge of T_c and Θ_D one can calculate the electron–phonon coupling constant λ and the bare density of states at the Fermi level $N_b = N_\gamma/(1 + \lambda)$ with the well known McMillan expression, taking $\mu^* = 0.13$ for transition metals (McMillan 1968). In addition to the magnitude of $\Delta C/\gamma T_c$, the value $\lambda = 0.64$ for $x = 0.132$ also indicates intermediate electron–phonon coupling in agreement with previous results for amorphous metals containing Zr (Kroeger *et al* 1984, Samwer and von Löhneysen 1982, Garoche and Johnson 1981). Since λ varies smoothly between $x = 0.08$ ($\lambda = 0.52$) and $x = 0.203$ ($\lambda = 0.52$), with a maximum at $x = 0.132$ ($\lambda = 0.64$), N_b shows the same overall concentration dependence as N_γ. The resulting roughly linear dependence of λ on N_b is compatible with the factorisation of λ after McMillan (1968), and in addition, corroborates the decisive influence of N_b on λ and T_c (or T_{c2}^C for the BCC majority phase).

Finally we want to discuss the specific heat below T_c as shown in figure 4 in a double-logarithmic plot for temperatures down to $T = 0.1$ K. For $T < T_c$ the specific heat of amorphous superconductors can be expressed as

$$C = C_{TLS} + C_{es} + \beta T^3. \tag{1}$$

In disordered solids, C_{TLS} is a contribution from low-energy excitations, which are described in the phenomenological model of two-level tunnelling states (Black 1981, von Löhneysen 1981). In general, C_{TLS} varies roughly linearly with T, $C_{TLS} = aT$ and a is of the order of 10^{-5}–10^{-4} J mol^{-1} K^{-2}. C_{es} is the electronic contribution in the superconducting state. For BCS superconductors, $C_{es} \simeq 8.5\,\gamma T_c \exp(-\varepsilon T_c/T)$ between $T/T_c = 0.167$ and 0.4, with $\varepsilon = 1.44$ (Gladstone *et al* 1969).

For $x = 0.132$, the experimental data follow the fit to (1) quite accurately down to 0.2 K with $a = 1.3 \times 10^{-4}$ J mol^{-1} K^{-2}. The experimental data for C_{es} are well described by the BCS expression with $\varepsilon = 1.44$ used for the fit, although a somewhat larger ε would be expected on the basis of the large specific heat jump. This behaviour has already been found for Zr_xCu_{1-x} alloys (Samwer and von Löhneysen 1982). The small enhancement over (1) at $T \simeq 0.6$ K could be due to a very small fraction ($\simeq 2\%$) of residual crystalline Zr (α-Zr: $T_c = 0.61$ K, ω-Zr: $T_c = 0.65 - 0.95$ K, Roberts 1985). For $T \leqslant 0.2$ K a broad anomaly appears. The large error bars illustrate the inaccuracy of the measurement in this temperature region, because of the appearance of more than one time constant in the thermal relaxation of the sample following a heat pulse. A nuclear quadrupole contribution of ^{91}Zr with a long 'spin-lattice' relaxation time (i.e. of the order of the thermal relaxation time) could cause this behaviour and also the upturn in C towards lower temperatures. The data are compatible with the linear coefficient a which is in the typical range for amorphous metals (von Löhneysen 1981, Samwer and von Löhneysen 1982).

For the BCC sample $x = 0.108$, which exhibits the sharpest jump in the specific heat (figure 3), stronger deviations from the BCS behaviour are observed (figure 4). This could be due to electronic contributions from several superconducting phases with a broad T_c-distribution. The data below 0.2 K suggest a small linear contribution with $a \simeq 1.2 \times 10^{-4}$ J mol^{-1} K^{-2}, which is of the same magnitude as in the amorphous sample. A contribution from the amorphous minority phase should be much smaller, as estimated from the magnitude of the enhancement just below T_{c1}^C (figure 3) and from a for $x = 0.132$. A linear behaviour in C has also been found in quenched crystalline Zr–Nb alloys and has been attributed to dynamical fluctuations between ω and β atomic configurations (Lou 1976). It is conceivable that similar excitations exist in BCC $Zr_{1-x}Si_x$. In a non-equilibrium crystalline solid solution of $Al_{0.94}Si_{0.06}$ a linear specific heat variation well below T_c has been measured (Chevrier *et al* 1989). Our data provide further evidence that the 'glassy' anomalies can also be found in metastable crystalline phases. However, conclusive proof for the existence of TLS with their strong phonon scattering necessitates thermal conductivity and ultrasonic measurements.

In conclusion, metastable $Zr_{1-x}Si_x$ alloys exhibit a variety of behaviour in their superconducting properties. Amorphous samples are single-phase with a sharp superconducting transition and a linear increase of T_c with decreasing Si content. At low temperatures, a linear contribution to the specific heat indicates the presence of two-level systems in the familiar range. BCC samples are phase separated into a majority phase, for which T_c decreases rapidly with decreasing x, and into a minority phase, presumably amorphous, for which T_c continues to increase with decreasing x. The

concentration dependence of T_c is governed by the concentration dependence of the electronic density of states. There is a possibility that low-energy excitations may occur in this metastable crystalline phase.

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