Enhanced superconductivity in Hf-base metallic glasses

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Abstract
A systematic study of electrical resistivity of $Hf_{100-x}Fe_x$ ($x = 20, 25$), $Hf_{100-x}Cu_x$
($x = 30, 40, 50$) and $Ti_{65}Cu_{35}$ metallic glasses has been done in the temperature range
0.3–290 K, and in magnetic fields $B \leqslant 5$ T. All Hf-base alloys are superconducting with
$T_c \geqslant 0.44$ K, which is well above the T_c of pure crystalline Hf (0.13 K). From the initial slopes
of the upper critical fields, $(dH_{c2}/dT)_{T_c}$, and resistivities we determined the dressed electronic
densities of states, $N_\gamma(E_F)$, for all alloys. Both T_c and $N_\gamma(E_F)$ decrease with increasing x
(Fe and Cu content). The results are compared with those for corresponding Zr-base metallic
glasses and ion-implanted Hf films.

1. Introduction

Glassy TE–TL alloys (TE and TL being the early and late transition metal, respectively) have been extensively studied in recent decades [1] and the interest in these alloys further increased after the discovery of TE–TL-base bulk metallic glasses [2–4]. These studies revealed several unusual phenomena [5–8], which has led to the development of novel concepts for the calculation of their properties [9, 10]. In TE–TL alloys the composition range for the formation of the amorphous state by rapid quenching from the melt is quite wide and in favourable cases it spans from 20 to 70 at.% of the TL component. Such a broad composition range enables a detailed study of the changes in the electronic band structure and properties on alloying through a comparison between the model and experiment [1, 11, 12].

In nonmagnetic amorphous TE–TL alloys, several properties which are related to the electronic density of states (DOS) show a simple, sometimes linear, variation with TL content [1, 6, 7, 11–16]. These simple variations of the properties correlate with ultraviolet photoemission spectroscopy (UPS) results for the same alloy systems [1, 17], which showed that DOS at the Fermi level (E_F), $N(E_F)$, is dominated by TE d-states. Accordingly, in amorphous TE–TL alloys, the effect of alloying with TL can be approximated with the dilution of amorphous TE [13]. So far, a majority of the results on TE–TL alloys has been obtained for Zr–TL metallic glasses, rendering a comparison between alloy systems based on different TE (e.g. Ti, Zr, Hf) rarely possible [11, 12, 18].

This is particularly true for superconductivity, with only a few results for superconducting transition temperatures T_c of Ti-[19] and Hf-base [20, 21] metallic glasses.

Here we report the first, to the best of our knowledge, systematic study of superconductivity in Hf–Fe and Hf–Cu metallic glasses. Our results show that the variation of T_c with x in $Hf_{100-x}Fe_x$ and $Hf_{100-x}Cu_x$ glassy alloys is quite similar to that observed in the corresponding $Zr_{100-x}Fe_x$ and $Zr_{100-x}Cu_x$ metallic glasses [14, 15, 22]. In particular T_c decreases with x and the rate of decrease is much faster for $x =$ Fe than for Cu. The magnitudes of T_c in Hf-base alloys are about two times lower than those in the corresponding Zr-base alloys [14, 15, 22]. The dressed density of states at the Fermi level, $N_\gamma(E_F)$, also decreases with increasing x. Thus, superconductivity in Hf-base alloys is consistent with the 'split-band' electronic structure of glassy TE–TL alloys [1, 17, 20].

2. Experimental details

$Hf_{100-x}Fe_x$ ($x = 20, 25$), $Hf_{100-x}Cu_x$ ($x = 30, 40, 50$) and $Ti_{65}Cu_{35}$ amorphous ribbons were prepared by melt spinning of master alloys with the predetermined concentration in either a pure Ar [23] or He [24] atmosphere. The ribbons were typically 10 μm (Hf–Fe) and 20 μm (all other alloys) thick and their amorphousness was verified by x-ray diffraction [23, 25]. About 9 mm long samples for resistivity measurements were glued by GE varnish on the sample holder of a ^{3}He cryostat inserted into a 16/18 T superconducting magnet. The current

Table 1. Measured and calculated parameters for Hf–Fe and Hf–Cu metallic glasses. ρ is resistivity at 2 K, α is the temperature coefficient of resistivity, T_c is the superconducting transition temperature, $(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ is the initial slope of the upper critical field and $N_\gamma(E_F)$ is the dressed density of states obtained from (1).

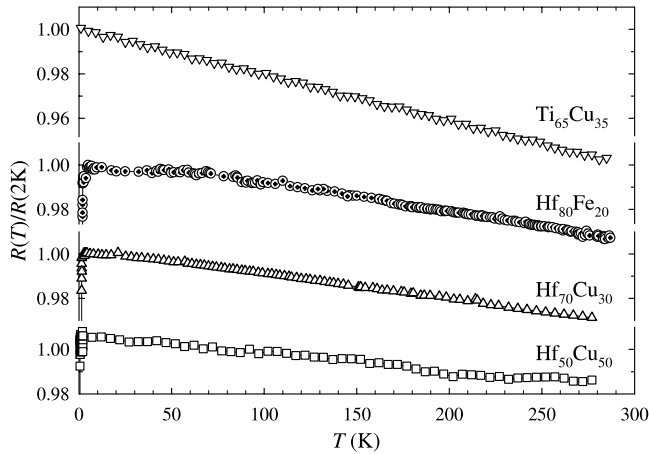| Alloy	ρ ($\mu\Omega$ cm)	α (10^{-4} K^{-1})	T_c (K)	$(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ (kOe K^{-1})	$N_\gamma(E_F)$ (states/eV atom)
Hf$_{80}$Fe$_{20}$	206	-1.2	1.86	38	2.27
Hf$_{75}$Fe$_{25}$	200	-2.0	1.12	35	2.14
Hf$_{70}$Cu$_{30}$	206	-1.3	1.36	28.5	1.64
Hf$_{60}$Cu$_{40}$	212	-1.2	0.82	26.1	1.40
Hf$_{50}$Cu$_{50}$	210	-1.1	0.44	23.7	1.16

Figure 1. Temperature dependence of normalized resistance for representative Hf-based metallic glasses and Ti$_{65}$Cu$_{35}$ amorphous alloy.

Figure 2. Resistive transitions for Hf-based metallic glasses. For Hf$_{75}$Fe$_{25}$ alloy transitions curves in a magnetic field 0 and 0.5 T are shown.

and voltage wires were glued with silver paste onto the samples. The resistivity measurements were performed by the low frequency (22 Hz) ac method with rms current $I = 0.1$ mA in the temperature range 0.3–290 K in a magnetic field $B \leqslant 5$ T, perpendicular to the broad surface of the ribbon and to the current direction. The temperature was measured with a calibrated Cernox thermometer situated close to the samples. The resistivity was determined from the measurements of resistance, length, mass and density of samples [13–15]. Due to the finite width of the silver paste contacts the uncertainty in the absolute resistivity values was about 5%. This uncertainty propagated into the values of the density of states $N_\gamma(E_F)$. Some data relevant to our samples are given in table 1.

3. Results and discussion

Figure 1 shows the variation of resistance with temperature for Ti$_{65}$Cu$_{35}$ and selected Hf–Cu, Fe glassy alloys. As is usual for glassy TE$_{100-x}$TL$_x$ alloys with high resistivity ($\rho \geqslant 140$ $\mu\Omega$ cm) [6, 13, 26] all our samples had negative temperature coefficients of resistivity (TCR). The literature values for resistivities and TCRs of the corresponding Hf–Cu and Ti$_{65}$Cu$_{35}$ [6, 26] agree quite well with our results (table 1). In particular, our $T = 2$ K resistivities, $\rho(2\,\text{K})$, are a few per cent higher than the room temperature resistivities, $\rho(290\,\text{K})$, of other authors [6, 26, 27].

Figure 2 shows the variations of normalized resistance $R(T)/R(2\,\text{K})$ with temperature below 2.5 K for all studied
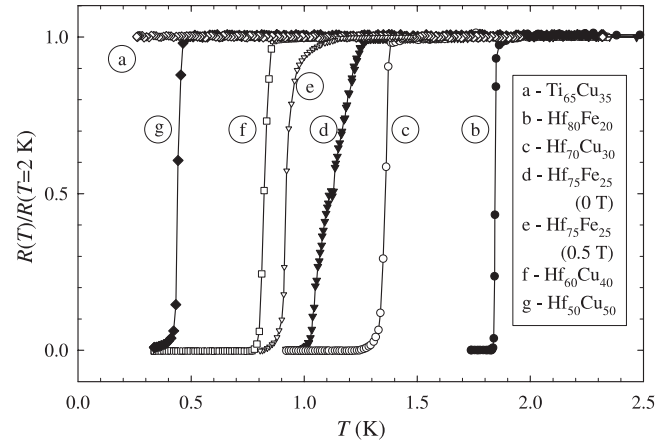
alloys. All Hf–Cu, Fe samples become superconducting within the explored temperature range ($T \geqslant 0.3$ K). Except for the Hf$_{75}$Fe$_{25}$ alloy, all other samples show very narrow superconducting transitions with typical widths (from 0.1 to $0.9\rho(2\,\text{K})$) $\Delta T_c \leqslant 0.04$ K, which can be regarded as an indication of good quality (homogeneity) of the studied samples [13–15, 20, 27]. The transition width for the Hf$_{75}$Fe$_{25}$ alloy, $\Delta T_c \cong 0.14$ K, is somewhat larger but not unusual for amorphous alloys. As illustrated in figure 2 the resistive transition of this alloy became narrower in an applied field, which allowed reliable determination of the variation of the upper critical field with temperature, $H_{c2}(T)$, also for this alloy. The values of superconducting transition temperatures (defined as midpoints of resistive transitions) are given in table 1. Sample Ti$_{65}$Cu$_{35}$ showed no sign of superconductivity down to 0.3 K, which is consistent with the reported $T_c \cong 0.06$ K for this alloy [19].

In figure 3 we compare the variations of zero-field T_cs with concentration x for our Hf$_{100-x}$Fe$_x$ and Hf$_{100-x}$Cu$_x$ alloys, with the literature results for Zr–Fe and Zr–Cu alloys [14, 15, 22]. Also shown are the maximum T_cs (i.e. the highest attainable T_c in the given TE$_{100-x}$Cu$_x$ series) of presumably amorphous Ti–Cu, Hf–Cu and Zr–Cu thin films, obtained by low temperature ion implantation [28], which seem to extrapolate the results for metallic glasses quite well to lower Cu contents. Since there are no previous results for T_c of Hf–Fe, Cu glassy alloys, we can compare our results only with those for splat cooled Hf$_{70}$Ni$_{30}$ foil [20] with $T_c = 1.5$ K.
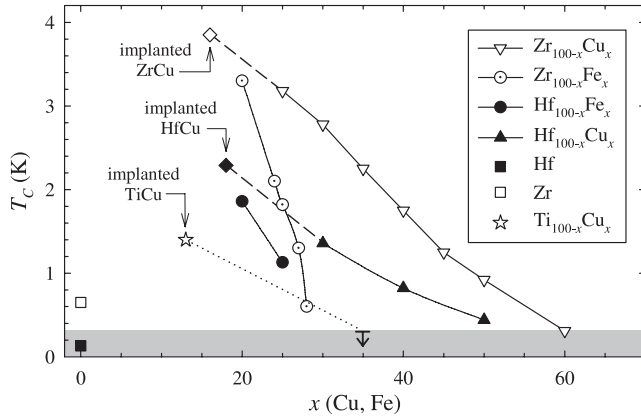
Figure 3. Superconducting transition temperature T_c for Hf-base (closed symbols; our work) and Zr-base (open symbols; [14]) metallic glasses. Maximum T_c for Cu–ion-implanted Ti (open star), Zr (◇) and Hf (◆) films [28], and for crystalline Zr (□) and Hf (■) [29], are also shown. The shaded area denotes temperatures unattainable in our experiment.

Figure 4. Upper critical field H_{c2} of representative Hf-based metallic glasses. See text for definition of H_{c2}.

Judging by the relation between T_cs of similar Zr–Ni and Zr–Cu alloys [12, 14, 15, 22], T_c of the $Hf_{70}Ni_{30}$ alloy [20] is consistent with $T_c = 1.36$ K for our $Hf_{70}Cu_{30}$ alloy. The transition temperatures of pure crystalline (hcp) Zr and Hf (figure 3) are about an order of magnitude lower than the maximum T_cs of Zr–Cu and Hf–Cu amorphous alloys. This is qualitatively consistent with the observed [1, 12, 16, 17] and calculated [11, 12] higher $N(E_F)$ in dilute amorphous TE–TL alloys than those of pure crystalline (hcp) TE metals. As seen from figure 3 the variations of T_c with x in Zr–Fe, Cu and Hf–Fe, Cu amorphous alloys are qualitatively very similar; the main difference is that T_cs of Hf–Fe, Cu alloys are about two times lower than those of the corresponding Zr–Fe, Cu alloys. Like in Zr-base alloys the rate of decrease of T_c with x in Hf-base alloys is much faster for Fe than for Cu alloy. This is due to the onset of magnetic correlations such as the spin fluctuations and/or formation of magnetic moments/clusters which cause strong pair-breaking [14, 15, 20, 25].

Lower T_cs of Hf–Fe, Cu alloys, compared to those of Zr–Fe, Cu, are consistent with a decrease of $N(E_F)$ on going from Zr to Hf (due to the increase of the bandwidth), but may also be affected [29] by the different Debye temperatures of Zr- and Hf-base alloys. Unfortunately, there are no measurements of the low temperature specific heat (LTSH) of Hf-base metallic glasses [12] which are necessary in order to explain the difference between T_cs of Zr-base and Hf-base alloy systems. In the absence of LTSH, useful information about the nature of superconductivity in metallic glasses can be obtained from the measurements of upper critical field $H_{c2}(T)$ [14, 15, 20–22, 27, 30]. The variation of H_{c2} with temperature in TE–TL metallic glasses is usually well described by the Werthamer–Helfand–Hohenberg theory [31] and a fit of experimental results to the model enables one to determine the spin–orbit interaction parameter, λ_{so}, and the Maki paramagnetic limitation parameter α [32]. However, such fits yield reliable results for the above parameters (especially λ_{so}) only if the measurements extend to sufficiently
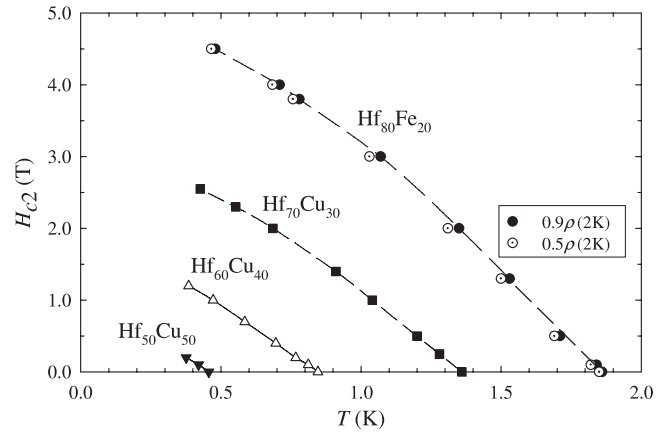
low temperature, $T/T_c \leqslant 0.1$ [21]. The $H_{c2}(T)$ variations for our Hf–Fe, Cu alloys are shown in figure 4. H_{c2} was defined with $0.9\rho(2\,\text{K})$, but—as illustrated for the $Hf_{80}Fe_{20}$ alloy—the variation of H_{c2} with T for the $0.5\rho(2\,\text{K})$ criterion was virtually the same. Due to the low T_cs of alloys we have studied, our measurements are limited to $T/T_c \geqslant 0.2$ which is not sufficient for the accurate estimate of both λ_{so} and α. Instead, we can use rather well-defined initial slopes of H_{c2}, $(\text{d}H_{c2}/\text{d}T)_{T_c}$, for our alloys (table 1) in order to estimate their dressed densities of states, $N_\gamma(E_F)$ [14, 15, 20, 22, 27]. $N_\gamma(E_F)$ can be calculated from [31]

$$N_\gamma(E_F) = -\frac{\pi M}{4 k_B N_A \rho d}\left(\frac{\text{d}H_{c2}}{\text{d}t}\right)_{t=1}, \qquad (1)$$

where k_B is the Boltzmann constant, N_A the Avogadro number, M the molecular weight, d the mass density and $t = T/T_c$. The product ρd can be expressed via resistance R, length l and mass m of the sample, $\rho d = (m R/l^2)$ [14, 15, 27]. The values of $N_\gamma(E_F)$ for Hf–Cu, Fe alloys calculated by using (1) decrease with increasing Fe, Cu content (table 1) in the same fashion as $N_\gamma(E_F)$ in the corresponding Zr–Fe, Cu alloys [14, 15]. However, the magnitudes of $N_\gamma(E_F)$ in Hf-base alloys are some 10–12% lower than those in the corresponding Zr-base alloys [14, 15]. As in Zr-base alloys [14, 15, 20] a clear correlation exists between the values of $N_\gamma(E_F)$ and T_c. In metallic glasses the values of $N_\gamma(E_F)$ calculated from (1) usually agree well with those obtained more directly from the coefficient of a linear term in LTSH, γ [12, 14, 15, 20–22, 27, 30]:

$$N_\gamma(E_F)_{\text{LTSH}} = \frac{3\gamma}{\pi^2 k_B^2}. \qquad (2)$$

The dressed density of states is enhanced by many-body interactions in respect to a band (bare) density of states, $N(E_F)$. In particular, $N_\gamma(E_F) = (1 + \lambda_{ep} + \lambda_{esf})N(E_F)$, where λ_{ep} and λ_{esf} are the electron–phonon and electron–spin fluctuation interaction parameters, respectively. Since our Hf-base alloys were paramagnetic [25] with magnetic susceptibilities well below of those for the corresponding Zr-base alloys [14, 15] we expect λ_{esf} to be small for Hf–Fe, and

negligible for Hf–Cu alloys. For a reliable estimate of λ_{ep} the LTSH measurements are required [12]. Since at present no LTSH results for Hf-base glassy alloys exist [12] we cannot make accurate estimates of $N(E_F)$ for the alloys studied.

In amorphous TE–TL alloys the electron–phonon enhancement factor can also be estimated from the temperature variation of the thermopower, $S(T)$ [6]. Such an estimate for the amorphous $Hf_{50}Cu_{50}$ alloy yields $N_\gamma(E_F)/N(E_F) \cong 1.4$, nearly the same as that obtained for the $Zr_{50}Cu_{50}$ alloy [33]. Another estimate of λ_{ep} in Hf–Cu glassy alloys can be obtained by dividing our results for $N_\gamma(E_F)$ with the calculated values of $N(E_F)$ for amorphous $Hf_{100-x}Cu_x$ alloys [12, 34]. The ratio between our $N_\gamma(E_F)$ and (interpolated) values of $N(E_F)$ decreased from about 1.4 ($x = 30$) to $\cong 1.2$ ($x = 50$). This calculation gave $N(E_F)$ values for amorphous Hf–Cu alloys about 10% lower than the values of $N(E_F)$ in the corresponding Zr–Cu alloys [12].

In principle, λ_{ep} can also be obtained from the approximate proportionality between λ_{ep} and $N(E_F)$ derived for disordered transition metal alloys of a given series [35] which was found applicable to several 4d (Zr, Mo)-base metallic glasses [20]. There, the coefficient of λ_{ep} versus $N(E_F)$ variation for 4d and 5d series was found to be quite similar [35], whereas that for 3d series was sizeably smaller. This result is in qualitative agreement with the estimates of λ_{ep} from $S(T)$ [33] for equiatomic Ti–Cu, Zr–Cu and Hf–Cu amorphous alloys. Thus, the electron–phonon enhancement in Hf–Cu glassy alloys is probably quite similar to that in Zr–Cu alloys and the main reason for lower T_cs in the former system may be higher ionic mass of Hf (lower Debye temperature, Θ_D [36]) and lower $N(E_F)$ [12].

The near absence of superconductivity in Ti-base metallic glasses [12, 19], also confirmed by us (figures 2 and 3), is puzzling. Since in these systems both $N_\gamma(E_F)$ and Θ_D are higher than those in the corresponding Zr-base and Hf-base metallic glasses [12], an inefficient electron–phonon coupling is required to explain their low T_cs [34].

4. Conclusion

The first systematic study of superconductivity in Hf-based metallic glasses has been reported. A clear correlation between the values of T_c and the dressed density of states $N_\gamma(E_F)$ has been established. With the exception of the $Hf_{75}Fe_{25}$ alloy, higher $N_\gamma(E_F)$ corresponds to higher T_c. More rapid suppression of T_c with x in $Hf_{100-x}Fe_x$ alloys than in $Hf_{100-x}Cu_x$ is probably caused by magnetic effects. In general, the variations of T_c and $N_\gamma(E_F)$ in Hf–Fe, Cu metallic glasses with Fe, Cu content are qualitatively the same as those in the corresponding Zr–Fe, Cu glassy alloys which is consistent with the very similar electronic structures of these alloys. Considerably lower values of T_c in Hf-based metallic glasses than those in the corresponding Zr-based alloys are probably due to the lower Debye temperatures Θ_D, and electronic densities of states $N(E_F)$ in the former system. For a more detailed insight into the superconductivity of Hf-based metallic glasses the additional measurements of the low temperature specific heat (yielding Θ_D) and perhaps tunnelling experiments (giving more directly electron–phonon coupling) are required.

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