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Electronic structure and superconductivity of the metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$

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Abstract. The x-ray photoelectron spectrum (XPS) and the superconducting critical temperature T_c have been measured for the metallic glass $Zr_{76}(Fe_xCu_{1-x})$ with $x = 0.1, 0.2, 0.4, 0.6, 0.8$ and 1.0. The results show that the density of electron states at the Fermi level increases while T_c decreases as the amount of Fe increases. This implies the spin fluctuation role depresses T_c effectively. The McMillan equation including the spin fluctuation effect has been used to estimate the T_c behaviour. The doping effects of elemental Fe in this system are discussed.

1. Introduction

The physical properties, such as superconductivity and magnetism, of the Zr-based metallic glasses have been studied extensively [1]. The discussion of superconducting transition temperature T_c has been mainly based on the Varma–Dynes theory for transition metals and alloys [2], namely, T_c is determined by the density of states (DOS) at the Fermi energy ($N(E_F)$). This idea has been confirmed by many experimental results, especially by those for the metallic glass Zr–Cu [1], but it cannot be used in the case of the existence of localized magnetic momentum and spin fluctuations [3] and the hybridization of the d band has a non-negligible effect [4]. Altounian *et al* [5, 6] have measured the susceptibility of the metallic glass Zr–M (M is a late 3d transition metal element) system. Their results showed that no measurable local magnetic moment can be detected in this system and there is hardly any spin fluctuation in the Zr–Cu system. The results indicated that spin fluctuations are increased as Cu is replaced by Ni, Co, and Fe successively. Therefore, elemental Fe should be an effective probe to study magnetism effects on superconductivity. In addition, the amount of substitutional element is not limited by solid solubility of alloys and there is less complexity due to the different degrees of disorder. Thus the influence of the degree of disorder on superconductivity can be excluded. In this work the metallic glasses $Zr_{76}(Fe_xCu_{1-x})_{24}$ ($x = 0.1$, 0.2, 0.4, 0.6, 0.8 and 1) are chosen to investigate the relationship between T_c and $N(E_F)$ and spin fluctuations by using x-ray photoelectron spectroscopy (XPS) and T_c measurements. The experimental results are presented and discussed.

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2. Experimental details

The samples were prepared by the melt-spinning method. Their amorphous structure was checked by x-ray diffraction. The temperature dependence of the resistivity showed a weak negative temperature coefficient, which is usually considered as a mark of amorphous metals and alloys.

XPS measurements were carried out using an Escalab mark II electron-spectrometer. An Al Kα x-ray source (1486.6 eV) was used to measure valence band (VB) spectra as well as core level scans. Ar^+ sputtering was used to clean the sample surface. We did not take the spectrum measurements until all contamination of C or O had been removed.

The T_c was determined resistively by means of a standard four-point probe down to 2.17 K. The samples were placed in a liquid helium vessel. The temperature of the vessel was controlled through the vapour pressure with a home-made device [7]. The temperature fluctuation was less than 1 mK during the experiments.

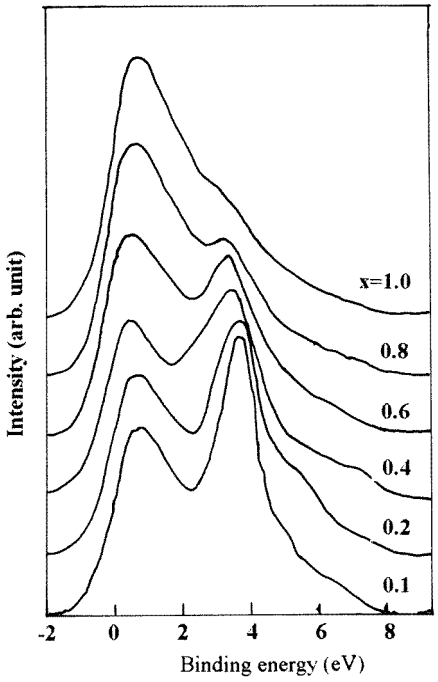

Figure 1. VB spectra of the metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$.

3. Results and discussion

3.1. XPS

The XPS VB spectra for the metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$ series are shown in figure 1. The presented curves were normalized after substrating the background non-linearly from the original curves. As we can see, only one peak can be observed in the binary metallic glass $Zr_{76}Fe_{24}$, like other Zr-based binary metallic glasses [8], but two peaks in each ternary amorphous alloy. As the Fe concentration increases, the intensity of the first peak near to

Table 1. $N(E_F)$ and λ_{ep} of metallic glasses Zr–Fe and Zr–Cu.

	$N(E_F)$	λ_{ep}
$Zr_{70}Cu_{30}$	0.58[a], 5.5[b]	
$Zr_{70}Fe_{30}$	1.07[a], 9.6[b]	
$Zr_{75}Cu_{25}$	1.31[c]	0.64[c]
$Zr_{75}Fe_{25}$	1.33[c]	0.56[c]
$Zr_{76}Cu_{24}$	5.6[b], ≈5.3[d]	
$Zr_{76}Fe_{24}$	9.4[b], ≈9.1[d]	

[a] Unit: states eV^{-1} $atom^{-1}$ $spin^{-1}$; the renormalized atom method [3].
[b] Unit: states Ryd^{-1} $atom^{-1}$ $spin^{-1}$; the virtual bound state method [11].
[c] Arbitrary unit; from figure 1.

E_F increases monotonically, showing a deviation from the spectra of metallic glass Zr–M series. The band position of the first peak moves towards E_F with respect to $Zr_{76}Fe_{24}$.

The VB spectra in figure 1 also indicate that each curve of ternary metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$ can be roughly decomposed into two independent contributions from the state of binary metallic glass Zr–Fe and Zr–Cu. This means that the addition of the third element causes hardly any obvious change in the 3d band position of the second element. It suggests that the bonding force between Zr and Cu or Fe is strong while the interaction between Fe and Cu is weak. Inoue *et al* [9] have measured the differential specific heat ΔC_p for the metallic glasses $Zr_{70}(Fe_{0.5}Cu_{0.5})_{30}$ and $Zr_{70}(Fe_{0.25}Cu_{0.75})_{30}$ before and after annealing treatment. They found an additional step in the plot of ΔC_p^{max} versus the annealing temperature. This was well explained by a model of the two-stage enthalpy relaxation during crystallization. This model was based on the assumption that there is a much stronger bonding force between Zr and Cu or Fe than between Fe and Cu. Our analysis supports the model of the two-stage enthalpy relaxation.

The surface characteristics of XPS makes the quantitative comparison of the experimental results with the theoretical values difficult, but the qualitative analysis can still give us some useful information. There are two theoretical methods used to compute the DOS of a $Zr_{1-x}M_x$ glassy alloy: one is the renormalized atom method [3]; the other is the virtual bound state method [10]. Some theoretical and observed values for the Zr-based binary amorphous alloys with almost the same compositions are listed in table 1. From table 1, we can see the present experiment data are coincident with the theoretical calculation, namely, $N(E_F)$ of the Zr–Fe glass is obviously higher than that of the Zr–Cu glass. In [6] Batalla *et al* measured susceptibility and obtained the same DOS for $Zr_{75}Fe_{25}$ and $Zr_{75}Cu_{25}$. The Varma–Dynes relationship between the coupling constant λ_{ep} and $N(E_F)$ [2], $\lambda_{ep} = N(E_F)\delta$, where δ should be approximately a constant for a given transition metal series, has been confirmed experimentally and could be used to estimate λ_{ep} variation from $N(E_F)$ in metallic glasses. λ_{ep} is 0.64 and 0.56 for the metallic glasses $Zr_{75}Fe_{25}$ and $Zr_{75}Cu_{25}$, respectively. So the $N(E_F)$ should be higher in the metallic glass $Zr_{75}Fe_{25}$ than in $Zr_{75}Cu_{25}$.

The binding energy (BE) shift of core levels in the metallic glass $Zr_{76}(Fe_xCu_{1-x})$ are listed in table 2. No obvious shift can be detected in Fe $2p_{3/2}$ and Zr $3d_{5/2}$. There is a large shift in Cu $2p_{3/2}$ and the shift become smaller with reduction of Cu content. This disagrees with the shift in the Zr–Cu series, where the shift becomes larger with decrease of Cu content [8]. Hence the factors of influence on the shift of core levels maybe include other contributions as well as the chemical environment around atoms in the ternary metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$.

Table 2. The core level shift ΔE_b (eV) for the metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$. Note the core level position of the polycrystalline metals: Zr $3d_{5/2}$, 178.7 eV; Fe $2p_{3/2}$, 706.7 eV; cu $2p_{3/2}$, 932.4 eV.

	$x = 0.1$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
Zr $3d_{5/2}$	0.1	0.2	0.0	0.0	0.0	0.1
Fe $2p_{3/2}$	0.1	0.1	0.0	0.0	0.0	0.1
Cu $2p_{3/2}$	0.8	0.7	0.6	0.6	0.6	0.5

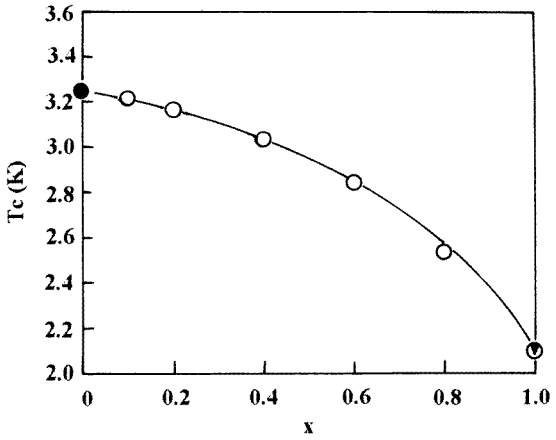

Figure 2. T_c as a function of x of the metallic glass $Zr_{76}(FE_xCu_{1-x})_{24}$. ○, this work; ●, the extrapolation results from [3]; ▼, from [1]; ——, the calculated results.

3.2. The superconducting critical temperature T_c

Figure 2 shows the relationship between superconducting critical temperature T_c and FE content x. T_c decreases smoothly until $x = 0.4$ (9.6 at.%), then drops rapidly. T_c of the metallic glass $Zr_{76}Cu_{24}$ was obtained by extrapolating from the relation of T_c and Cu content in the metallic glass Zr–Cu series [3]. Nevertheless, T_c decreases monotonically with x, similar to the $T_c(x)$ behaviour in the metallic glass $Zr_{1-x}Pd_x$ [4].

Combining $N(E_F)$ with T_c as a function of Fe content, we can see the spin fluctuation plays an important role in T_c determination of $Zr_{76}(Fe_xCu_{1-x})_{24}$. As is well known, the effects of magnetic impurities on T_c in amorphous alloys are very different from those in crystalline materials [11]. The addition of Fe yields two different effects on T_c simultaneously in the metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$: one is the pair breaking, reducing T_c due to magnetism; the other is the increase of $N(E_F)$, enhancing T_c. The McMillan equation [12] has taken the two effects into account:

$$T_c = (\Theta/1.45)\exp[-(1 + \lambda_{ep} + \lambda_{sf})/(\lambda_{ep} - \lambda_{sf} - \mu^*)] \tag{1}$$

where Θ, λ_{ep} and μ^* are the Debye temperature, the electron–phonon coupling constant and the effective Coulomb coupling constant for electron repulsion, respectively. λ_{sf} is the spin fluctuation mass enhancement constant described as follows:

$$\lambda_{sf} = \tfrac{9}{2}\overline{I}\ln[1 + (P_1^2/12)(1 - I)] \tag{2}$$

where $\overline{I}$ is the Stoner enhancement factor and P_1 is the momentum cut-off for spin fluctuations. A linear dependence of the Stoner enhancement factor on x was shown

experimentally in [6] for binary Zr–Fe and Zr–Co metallic glasses. In Zr–Cu metallic glasses, I is basically independent of the composition, so we can assume reasonably a linear variation of the Stoner enhancement factor in the ternary $Zr_{76}(Fe_xCu_{1-x})_{24}$ with the elemental Fe composition. The linear slope is the same as that in the binary Zr–Fe [6]. Furthermore, if we suppose $\lambda_{ep} = a + bx$, Θ remains constant, take $P_1^2 = \frac{1}{6}$ and $\mu^* = 0.13$, the relation of $T_c(x)$ could be fitted using (1) and (2). The fitting curve $T_c(x)$ is plotted in figure 2 (the solid line). From fitting we obtain $\lambda_{ep} = 0.55(\pm 0.02) + 0.07(\pm 0.02)x$.

4. Concluding remarks

The variations of the VB obtained by XPS and T_c with the Fe composition have been measured for the ternary metallic glass $Zr_{76}(Fe_xCu_{1-x})_{24}$. Although the addition of Fe causes an increase of $N(E_F)$ and λ_{ep}, T_c still decreases monotonically. This implies that the spin fluctuation has depressed effectively the superconductivity. The bonding force between Zr and Fe or Cu is much stronger than that between Fe and Cu. The Cu $2p_{3/2}$ core level shift displays abnormal behaviour.

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