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MAGNETIC PROPERTIES OF Zr-3d GLASSY ALLOYS

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Systematic analysis of the magnetic susceptibilities for a number of Zr-M glassy alloys (M = Cu, Ni, Co and Fe) and for ternary $Zr_2(Ni_{1-x}M_x)_1$ glassy alloys with M = Ti, V, Cr, Mn, Fe, Co and Cu has been performed. By combining our data for the magnetic susceptibility and superconducting transition temperature with the literature data for low-temperature specific heat, we have extracted the Pauli susceptibilities (χ_p) and the Stoner enhancement factors (S) for these alloys. The binary Zr-Cu and Zr-Ni alloys have practically the same S, whereas Zr-Co and Zr-Fe alloys show larger S which increases in going from Co to Fe. In ternary alloys, χ_p and S show pronounced maxima centred around M = Mn. For these alloys we also estimated S from the low-temperature magnetoresistivity.

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1. Introduction

This paper is devoted to the magnetic properties of Zr-3d glassy alloys. Previously, we have measured the magnetic susceptibility of binary amorphous Zr-3d alloy systems $Zr_{1-x}Cu_x$ ($0.26 \leq x \leq 0.71$), $Zr_{1-x}Ni_x$ ($0.22 \leq x \leq 0.67$), $Zr_{1-x}Co_x$ ($0.19 \leq x \leq 0.35$) and Zr_{76} Fe_{24} [1]. Since bulk glassy alloys of Zr with 3d elements appearing before Fe cannot be made, we have extended our research to amorphous ternary $Zr_2(Ni_{1-x}M_x)_1$ alloys (M = Ti, V, Cr, Mn, Fe, Co and Cu), and measured their magnetic susceptibilities [2]. In order to get better insight into the electronic structure of ternary alloys, we have also measured their magnetoresistivity in low fields [3]. Here we report the results for the Pauli susceptibilities and the Stoner enhancement factors of all investigated alloys. Our results can be explained by the

combination of the changes in the electronic band structure on alloying and the appearance of localized magnetic moments for M around Mn.

2. Experimental procedures

The amorphous binary and ternary Zr-3d glassy alloys were prepared by melt-spinning of master alloys with the predetermined concentration. The resulting ribbons were about 2 mm wide and 20–30 μm thick [1,2]. The magnetic susceptibility was measured on samples weighting few miligrams with the Faraday method [1]. The absolute values of the magnetic susceptibility were accurate to about one percent while the relative accuracy was about 0.1%. Magnetoresistance and electrical resistivity measured out using an AC four-probe method on 3 – 5 cm long samples to which were attached Pt voltage and current leads. Magnetic field up to 1.2 T was provided by a superconducting magnet [3]. The samples were mounted on a copper holder situated in an evacuated cryostat. The resolution of the magnetoresistance measurements was 1:10^6. The temperature range 3 – 10 K was obtained using liquid helium cooling. For all alloys, we also measured the superconducting transition temperatures [2,4] and the electrical resistivity from 3 K up to room temperature. Some data relevant to our alloys are given in Tables 1 and 2. While most of the data used in the analysis presented below are from our previous publications [1–5] we also used some new results for the magnetoresistance of ternary alloys in order to illustrate an alternative method for the determination of the Stoner enhancement factor.

TABLE 1. Data relevant to binary $Zr_{1-x}M_x$ (M = Cu, Ni, Co *and* Fe) *glassy alloys:* T_c *is the superconducting transition temperature,* $N_0(E_F)$ *is the bare density of states at* E_F, χ_{exp} *is the magnetic susceptibility at room temperature,* χ_p *is* χ_{exp} *with* χ_{ion} *and* χ_{orb} *subtracted,* χ_p^0 *is the Pauli susceptibility calculated from* $N_0(E_F)$ *and* S *is the Stoner factor.*

Zr_{1-x} M_x	T_c (K)	$N_0(E_F)$ $\left(\frac{\text{eV}}{\text{atom spin}}\right)$	$\chi_{exp}10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	χ_p10^3 $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	$\chi_p^0 10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	S
$Zr_{0.74}Cu_{0.26}$	3.13	0.66	1.08	0.64	0.43	1.50
$Zr_{0.70}Cu_{0.30}$	2.68	0.63	1.07	0.66	0.41	1.63
$Zr_{0.60}Cu_{0.40}$	1.60	0.57	0.93	0.61	0.37	1.65
$Zr_{0.50}Cu_{0.50}$	0.7	0.5	0.78	0.54	0.32	1.68
$Zr_{0.42}Cu_{0.58}$	0.3	0.44	0.66	0.42	0.29	1.47
$Zr_{0.33}Cu_{0.67}$	0.3	0.4	0.51	0.42	0.26	1.64
$Zr_{0.78}Ni_{0.22}$	3.36	0.71	1.30	0.72	0.46	1.56
$Zr_{0.76}Ni_{0.24}$	3.20	0.69	1.29	0.71	0.44	1.59
$Zr_{0.72}Ni_{0.28}$	3.06	0.67	1.26	0.69	0.43	1.59

(Table 1 continued)

Zr_{1-x} M_x	T_c (K)	$N_0(E_F)$ $\left(\frac{\text{eV}}{\text{atom spin}}\right)$	$\chi_{exp}10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	χ_p10^3 $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	$\chi_p^0 10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	S
$Zr_{0.67}Ni_{0.33}$	2.68	0.63	1.19	0.64	0.41	1.58
$Zr_{0.62}Ni_{0.38}$	2.36	0.6	1.14	0.61	0.39	1.56
$Zr_{0.33}Ni_{0.67}$	< 1.2	0.41	0.83	0.40	0.27	1.48
$Zr_{0.81}Co_{0.19}$	3.9		1.54	0.86		
$Zr_{0.78}Co_{0.22}$	4.3		1.53	0.84		
$Zr_{0.75}Co_{0.25}$	3.63		1.55	0.85		
$Zr_{0.67}Co_{0.33}$	2.8		1.55	0.84		
$Zr_{0.65}Co_{0.35}$	2.7	0.56	1.57	0.86	0.36	2.39
$Zr_{0.76}Fe_{0.24}$	~ 1.7	0.74	2.18	1.37	0.48	2.86

TABLE 2. Data relevant to ternary $Zr_2(Ni_{1-x}M_x)_1$ *glassy alloys:* T_c *is the superconducting transition temperature,* $N_0(E_F)$ *is the bare density of states at* E_F, χ_{exp} *is the magnetic susceptibility at room temperature,* χ_p *is* χ_{exp} *with* χ_{ion} *and* χ_{orb} *subtracted,* χ_p^0 *is the Pauli susceptibility calculated from* $N_0(E_F)$, S *is the Stoner factor, and* $\Delta\rho/\rho^2$ *is the measured magnetoresistance at 4.2* K *and* $B = 1$ T.

M_x	T_c (K)	$N_0(E_F)$ $\left(\frac{\text{eV}}{\text{atom spin}}\right)$	$\chi_{exp}10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	χ_p10^3 $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	$\chi_p^0 10^3$ $\left(\frac{\text{J}}{\text{T}^2\,\text{mol}}\right)$	S	$\Delta\rho/\rho^2$ $\left(\frac{1}{\Omega\,\text{m}}\right)$
$Ti_{0.1}$	2.99	0.67	1.24	0.68	0.43	1.57	515.4
$V_{0.1}$	2.48	0.62	1.27	0.69	0.40	1.72	636.8
$Mn_{0.1}$	< 1.3	0.65	1.53	0.86	0.42	2.05	
$Fe_{0.1}$	2.55	0.62	1.27	0.70	0.40	1.74	
$Co_{0.1}$	2.76	0.63	1.21	0.65	0.41	1.58	421.1
Ni	2.68	0.63	1.19	0.64	0.41	1.58	415.5
$Cu_{0.1}$	2.65	0.64	1.17	0.65	0.41	1.58	282.6

3. Results and discussion

The magnetic susceptibility of nonmagnetic transition metal is given as

$$\chi_{exp} = \chi_p + \chi_{ion} + \chi_{orb}, \tag{1}$$

where $\chi_{\rm ion}$ and $\chi_{\rm orb}$ are the ionic-core diamagnetism and the orbital paramagnetism with the Landau contribution included, respectively. The Pauli paramagnetism of the d-band $\chi_{\rm p}$ is enhanced over the free-electron value $\chi_{\rm p}^0 = 2\mu_{\rm B}^2 N_0(E_{\rm F})$ due to the Stoner exchange interaction and is given by

$$\chi_{\rm p} = \frac{2\mu_{\rm B}^2 N_0(E_{\rm F})}{1 - I_{\rm eff} N_0(E_{\rm F})}, \tag{2}$$

where $I_{\rm eff}$ is the effective exchange integral within the d-band, $N_0(E_{\rm F})$ is the bare density of states of d-electrons at the Fermi level and $(1-I_{\rm eff}N_0(E_{\rm F}))^{-1}$ is the Stoner enhancement factor S. The magnetic susceptibilities at room temperature of all our alloys are given in Tables 1 and 2 as measured ($\chi_{\rm exp}$) and with ionic diamagnetic contribution and orbital susceptibility subtracted ($\chi_{\rm p}$). Our results [1,4,5] for $\chi_{\rm exp}$ of Zr-3d alloys (3d = Cu, Ni, Co and Fe) agree quite well with later results for the same alloy systems [6,7]. Since with the exception of $Zr_2(Ni_{0.9}Mn_{0.1})_1$ alloy [2], $\chi_{\rm exp}$ for all other alloys showed very weak temperature dependence ($< 10^{-5}$ $\rm JT^{-2}mol^{-1}$ from 4.2 K to 293 K) the values of $\chi_{\rm exp}$ in Tables 1 and 2 adequately represent those for T going to 0 K. The ionic diamagnetic susceptibilities are small:

$$\begin{aligned}
\chi_{\rm ion} = {} & -35.8 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Zr,}\\
& -19.4 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Cu,}\\
& -19.3 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Ni,}\\
& -19.4 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Co,}\\
& -23.1 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Ti,}\\
& -21.6 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for V,}\\
& -20.3 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Mn}\\
\text{and } & -19.8 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Fe [8].}
\end{aligned}$$

The orbital paramagnetic susceptibilities are

$$\begin{aligned}
\chi_{\rm orb} = {} & 102 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Zr,}\\
& 119 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Ti [9],}\\
& 51 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Ni,}\\
& 98 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Co,}\\
& 183 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for V,}\\
& 149 \times 10^{-5}\ \rm JT^{-2}mol^{-1} && \text{for Fe [10] and Mn,}
\end{aligned}$$

whereas $\chi_{\rm orb}$ in Cu we assumed to be zero [9]. We scaled the values for $\chi_{\rm ion}$ and $\chi_{\rm orb}$ of particular element to their atomic fraction in our alloys. From the specific heat results for Zr-Cu [11], Zr-Ni [12], Zr-Fe [13] and Zr-Co [14] binary alloys and those for ternary $Zr_2(Ni_{1-x}M_x)_1$ [15,16] the dressed electronic densities of states $N^* = (1+\lambda)N_0(E_{\rm F})$ (with λ the electron-phonon coupling parameter) and the corresponding Debye temperatures ($\Theta_{\rm D}$) are known. From the experimental $T_{\rm c}$ values, using the McMillan's expression [17]

$$T_{\rm c} = \frac{\Theta_{\rm D}}{1.45} \exp\left(-\frac{1.04\,(1+\lambda)}{\lambda - \mu^*\,(1+0.62\lambda)}\right) \tag{3}$$

with the effective Coulomb potential $\mu^* = 0.13$, we determined λ and hence $N_0(E_F)$ for our alloys. From $N_0(E_F)$, we calculated χ_p^0 and then from (2) the Stoner enhancement factor S. The calculated values of χ_p^0 and S are also given in Tables 1 and 2.

The superconducting transition temperatures T_c decrease approximately linearly with decreasing Zr content in amorphous Zr-3d alloys [4,6,18]. In particular, the decrease of the Zr content lowers the electronic density of states at the Fermi level $N_0(E_F)$ and is associated with the decrease of the effective electron-phonon coupling [18]. Accordingly, χ_p^0 for these alloys should decrease with increasing x (Table 1). However, strong decrease of χ_{exp} with x for Zr-Cu and Zr-Ni alloys (Fig. 1) is mainly due to the decrease of the overall χ_{orb} with x [5] and not due to the strong spin-fluctuations and associated Stoner enhancement, as erroneously assumed in Ref. [6]. Simultaneously, the Stoner factor $S = \chi_p/\chi_p^0$ is nearly the same both for Zr-Cu and Zr-Ni alloys and does not depend on x (Fig. 2). Both these features indicate that the alloying of Zr with Ni and Cu can be regarded as a dilution of Zr. A similar conclusion has been reached from detailed analysis of the superconductivity and low-temperature specific heat of (Ti,Zr,Hf)-(Cu,Ni) amorphous alloys [18]. In Zr-Co and Zr-Fe alloys χ_{exp} is larger than that in corresponding alloys with Cu and Ni (Fig. 1) and seems to increase with x at higher x [7]. Simultaneously, their S is enhanced in respect to that of Zr-Cu and Zr-Ni

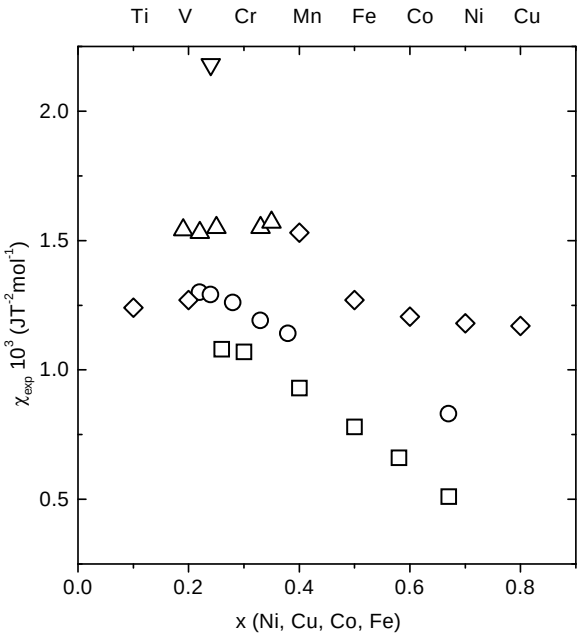

Fig. 1. Magnetic susceptibility χ_{exp} *of* $Zr_{1-x}Cu_x$ *(□),* $Zr_{1-x}Ni_x$ *(○),* $Zr_{1-x}Co_x$ *(△),* $Zr_{1-x}Fe_x$ *(▽) alloys versus x (bottom scale), and* Zr_2 $(Ni_{0.9}\ M_{0.1})_1$ *(◇) alloys versus M (top scale).*

alloys (Fig. 2). The enhancement of S in Zr-Co and Zr-Fe alloys is consistent with the onset of ferromagnetism observed at higher x in these alloys [7]. Our results for S of Zr-Co and Zr-Fe alloys are consistent with $I_{\rm eff}$ and $N_0(E_{\rm F})$ values for similar alloys in Ref. [7].

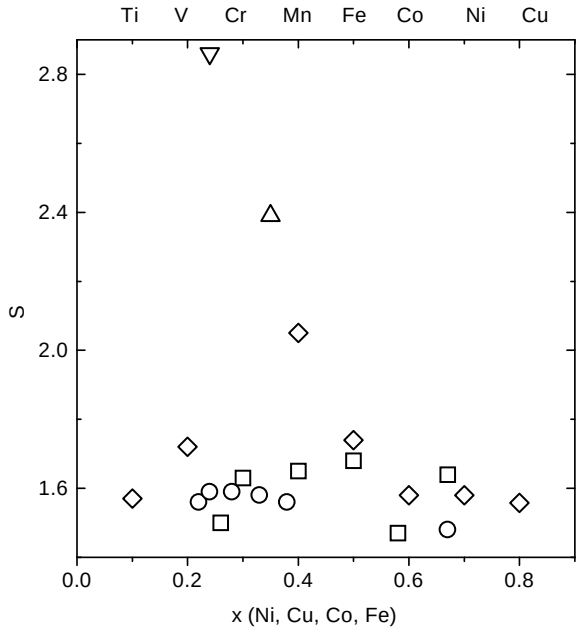

Fig. 2. The Stoner factor of $Zr_{1-x}Cu_x$ (□), $Zr_{1-x}Ni_x$ (○), $Zr_{1-x}Co_x$ (△), $Zr_{1-x}Fe_x$ (▽) *alloys versus* x *(bottom scale), and* $Zr_2(Ni_{0.9}M_{0.1})_1$ (◇) *alloys versus* M *(top scale).*

The magnetic susceptibility $\chi_{\rm exp}$ of ternary $Zr_2(Ni_{0.9}M_{0.1})_1$ alloys tends to increase when going from M = Cu towards Ti (Fig. 1). This tendency is somewhat obscured by the pronounced maximum for M = Mn. The electronic specific heat coefficient γ of a linear term in similar alloys $(Zr_{67}Ni_{33})_{85}M_{15}$ [15,16] shows almost identical variation as $\chi_{\rm exp}$. Similar behavior shows the Stoner enhancement factor S too (Fig. 2). In particular, S for ternary alloys with M = Cu, Co and Ti is the same as that of Zr_2Ni matrix. This is plausible since small amount of M has little influence on the overall electronic band structure. Accordingly, a modest (M = Fe, V) and sizeable (M = Mn) enhancement of S (hence $\chi_{\rm p}$) for M around the middle of 3d series also cannot be the band structure effect. Indeed, our study of $\chi_{\rm exp}(T)$ for $Zr_2(Ni_{1-x}M_x)_1$ alloys with M = Fe, Cr and Mn has shown the presence of localized magnetic moments in these systems [2]. Therefore, the enhancement of $\chi_{\rm p}$ for M = Fe, Mn and V is probably due to the Kondo effect. In principle, the low-temperature magnetoresistivity can be used to deduce S. From our magnetorestivity measurements for ternary alloys (Table 2), we calculated inelastic relaxation times $\tau_{\rm in}$ and spin-orbit relaxation times $\tau_{\rm so}$ [19], and using the theory of Refs. [20–22] we calculated S. For $\tau_{\rm so}$ we obtained values of $\sim 10^{-12}$ s, which

are lower than the corresponding $\tau_{\rm in}$. Although the uncertainties in $\tau_{\rm so}$ determined from magnetoresistivity are large (because the contribution to the magnetorestivity from the superconducting fluctuations is larger than the contribution due to electron localization), we obtained reasonable values for S. In particular, we got S = 2.3, 4.1 and 5.1 for $M_x = Ti_{0.1}$, $Co_{0.1}$ and $Fe_{0.5}$, respectively. (We note that S is very sensitive to $I_{\rm eff}N_0(E_{\rm F})$, hence a small change in $I_{\rm eff}$ produces sizeable change in S).

4. Conclusion

In binary Zr-Cu and Zr-Ni alloys, $\chi_{\rm p}$ increases with Zr content, while in Zr-Co and Zr-Fe alloys, $\chi_{\rm p}$ increases with the concentration of Co and Fe [7]. The Stoner enhancement factor S is larger in Zr-Fe and Zr-Co alloys than in Zr-Cu and Zr-Ni alloys. Therefore, our analysis of $\chi_{\rm exp}$ for Zr-Cu and Zr-Ni alloys is consistent with dilution of amorphous Zr (with probably fcc-like local atomic structure [18]), whereas that for Zr-Co and Zr-Fe alloys indicates the onset of magnetic correlations occuring at higher x in these systems [7]. The addition of the third transition element M (Ti, V, Cr, Mn, Fe, Co or Cu) to the amorphous Zr_2Ni alloy causes, for fixed M content, a systematic decrease of $T_{\rm c}$ in going from M = Ti towards M = Cu. These findings are also consistent with the results of UPS (ultraviolet photoemission spectroscopy) studies performed on similar alloys and showing a decrease in $N_0(E_{\rm F})$ on going from Ti towards Cu. The pronounced minimum in $T_{\rm c}$ and $\Delta\rho/\rho^2$ as a function of M for M = Cr and Mn can be associated with the appearance of magnetic correlations in the alloys containing these impurities and is consistent with the observed enhancement of the electronic specific heat in similar alloys. The magnetic susceptibility increases when going from Cu to Ti, having a maximum at Mn. Similar behaviour shows also the Stoner enhancement factor S. Although in our alloys $\chi_{\rm p}$ is smaller than $\chi_{\rm exp}$, we got very reasonable values of S and the expected dependence of S on M.

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MAGNETSKA SVOJSTVA Zr-3d STAKLASTIH SLITINA

Napravili smo sustavnu analizu magnetske susceptibilnosti za niz Zr-M staklastih slitina (M = Cu, Ni, Co i Fe) i za ternarne $Zr_2(Ni_{1-x}M_x)_1$ staklaste slitine gdje je M = Ti, V, Cr, Mn, Fe, Co odnosno Cu. Kombinirajući naše podatke za magnetsku susceptibilnost i temperaturu supravodljivog prijelaza s podacima iz literature za specifični toplinski kapacitet na niskim temperaturama, izračunali smo Paulijevu susceptibilnost (χ_p) i Stonerov faktor (S) za naše slitine. Binarne Zr-Cu i Zr-Ni slitine imaju gotovo jednak S, dok Zr-Co i Zr-Fe slitine pokazuju veći S koji raste od Co prema Fe. U ternarnim slitinama, χ_p i S pokazuju izrazit maksimum centriran oko M = Mn. Za ove slitine izračunali smo S iz magnetootpora na niskim temperaturama.