Effect of composition on Curie temperature, magnetic moment, and high-field susceptibility of amorphous $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Mn, Co, Ni, Cu, Si, and B) alloys

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Magnetization measurements for amorphous $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Mn, Co, Ni, Cu, Si, and B) alloys prepared by single-roller spin quenching have been made by an extracting sample magnetometer in magnetic fields up to 65 kOe and at temperatures ranging from 1.5 to 300 K. Preliminary results show that the magnetic properties of these amorphous alloys strongly depend upon the M concentration and display a similarity to those of the parent Fe-Zr base; compared with amorphous Fe-M-B alloys with the same concentration, all the samples are characterized by a large high-field susceptibility, a small magnetic moment, and a low Curie temperature, which, for low M concentration, are particularly sensitive to applied fields. The noncollinear spin structures that characterize Fe-rich Fe-Zr–based amorphous alloys have been proposed to explain the observed results.

I. INTRODUCTION

Amorphous Fe-Zr–based alloys in the Fe-rich region with compositions near 10 at. % Zr have been studied systematically. Many of the unusual properties, such as the low value of Fe atomic moment and Curie temperature,[1–6] the large high-field susceptibility even at low temperature,[4–6] and the broad distribution of hyperfine fields extending down to $H_{eff}=0$[7], were found in these amorphous alloys. In addition, these alloys exhibit various interesting behaviors such as spin-glass-like behavior,[8] Invar effect,[9] resistivity anomalies,[10] and so on, which, all together, seem to suggest that Fe-rich Fe-Zr amorphous alloys (10 at. % Zr) are characterized by a noncollinear spin structure.[11–12] However, the replacement of Fe with 3d transition-metal or metalloid elements in amorphous Fe-rich Fe-Zr–based alloys brings a marked decrease of the number of the Fe atom clusters with noncollinear structure, giving rise to a significant effect on their magnetic properties. In order to obtain more information about the magnetic behavior of Fe-rich Fe-Zr alloys, we prepared the amorphous $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Mn, Co, Ni, Cu, B, and Si) alloys. Some investigations on the magnetic and electrical properties of these amorphous alloys have been carried out.[2–5,13,14] In this paper we report the effect of concentration and transition metals or metalloid elements on the Curie temperature, magnetic moment, and high-field susceptibility of amorphous $Fe_{90-x}M_xZr_{10}$ alloys.

II. EXPERIMENT

Amorphous alloys $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Mn, Co, Ni, Cu, B, and Si) about 1.5 mm wide and 20–30 μm thick were prepared by the melt-spinning technique in an argon atmosphere. Amorphousness of the ribbons was checked by x-ray diffraction. The magnetization curves of the samples at 1.5 K and thermomagnetization curves were measured with an extracting sample magnetometer. The measurement accuracy of the magnetic moment is 3×10^{-4} emu. The Curie temperatures were determined from the magnetization versus temperature in a field of about 45 Oe or the temperature dependence of ac susceptibility in a weak field of about 1 Oe.

III. RESULTS AND DISCUSSIONS

A. Curie temperature

Figure 1 shows an example of the thermomagnetization curves for amorphous $Fe_{90-x}M_xZr_{10}$ alloys. Our investigation results show that the thermomagnetization curves of amorphous $Fe_{90-x}M_xZr_{10}$ alloys, particularly at low M concentration, are strongly affected by applying a magnetic field as those of other amorphous Fe-based alloys,[15] and the Curie temperature determined from the σ^2-versus-T curves is higher than the real Curie temperature as shown in Fig. 1. Therefore, the T_C of the amorphous $Fe_{90-x}M_xZr_{10}$ alloys was determined from the thermomagnetization curves in an external field of about 45 Oe or the temperature dependence of ac susceptibility measured at about 1 Oe. The present data of T_C measured by a small field are reasonable; the value of T_C for $x=0$ is in agreement with that determined by Arrott plots.[16]

The Curie temperatures of amorphous $Fe_{90-x}M_xZr_{10}$ alloys are shown in Fig. 2 as a function of M concentration. As can be seen from Fig. 2, the concentration dependence of T_C varies in behavior when different M atoms are added; the T_C increases markedly with increasing Co, Ni, Si, and B, but decreases linearly with increasing Mn; interesting to note that, for V, Cr, and Cu, the T_C-x curves even form a clear maximum with the initially increasing T_C followed by a drop around $x=4$. The T_C is found to be below room temperature for all compositions containing V, Cr, Mn, or Cu and low Co, Ni, Si, or B concentration, 100–300 K lower than those of the amorphous Fe-M-B alloys[17–19] with the same M concentration.

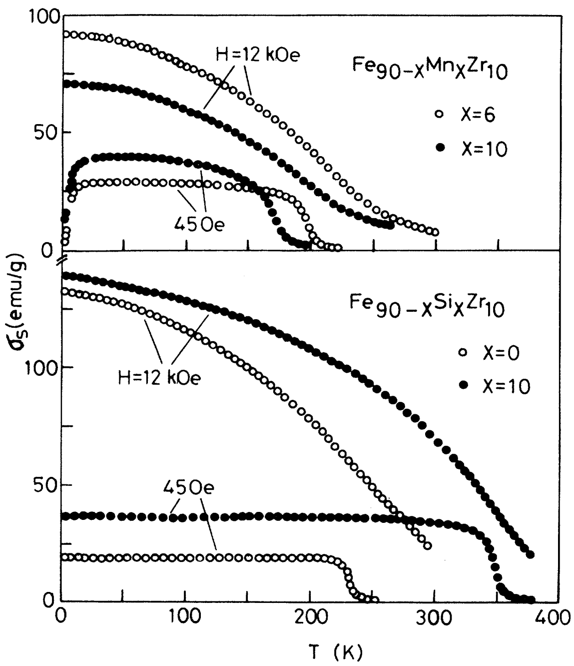

FIG. 1. Thermomagnetization curves at external fields of about 45 Oe and 12 kOe for amorphous $Fe_{90-x}M_xZr_{10}$ (M=Mn and Si) alloys.

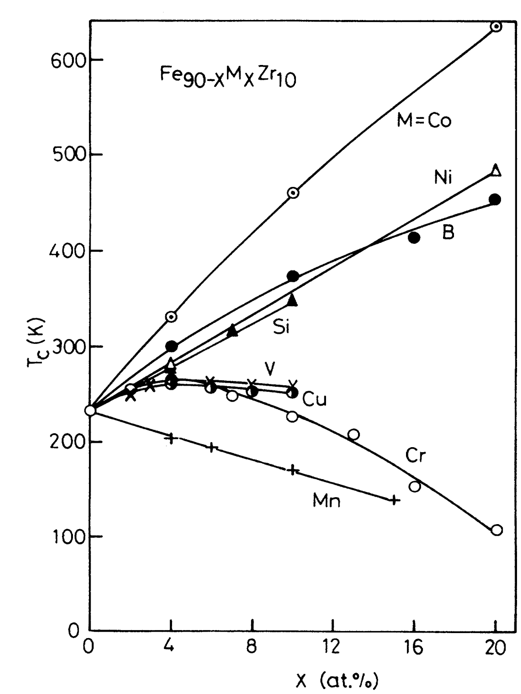

FIG. 2. Curie temperatures T_C of amorphous $Fe_{90-x}M_xZr_{10}$ alloys as a function of M concentration x.

Composition effects on Curie temperature, in many cases, are discussed according to the average molecular-field models. But in these models the attention is usually focused on the pure ferromagnetic or pure antiferromagnetic materials. This is obviously not the case we currently are faced with.

Indeed, the amorphous Fe-M-Zr alloys we currently are discussing displayed a T_C behavior similar to the amorphous Fe-Zr alloys.[20] This indicates that the unusual concentration behavior of T_C in amorphous Fe-M-Zr shares the same mechanism as in the Fe-Zr alloys; it is closely related to the noncollinear spin structures that characterize Fe-rich amorphous Fe-Zr alloys. In Fe-based amorphous alloys the distance between nearest-neighbor Fe-Fe atoms has a distribution which results in a variation of direct exchange interactions between Fe-Fe atoms. The sensitivity of the Fe-Fe exchange interaction to distance can be found in the coordination number, which is 8 for ferromagnetic bcc Fe and 12 for antiferromagnetic fcc Fe. Amorphous $Fe_{84}Zr_{16}$ alloys[21] have an average coordination number of 11.6, which supports the assumption of the presence of the antiferromagnetic exchange interactions. These antiferromagnetic couples would lead to noncollinear spin structures, as is indicated in the Mössbauer study[22] and the neutron measurement[11] performed on amorphous $Fe_{91}Zr_9$ and further discussed by Ryan *et al.*[12] for the Fe_xZr_{1-x} with $88<x<93$. In terms of this model, the concentration behavior of the T_C in amorphous Fe-M-Zr alloys would be attributed to the variation in spin structure and its correlation length resulting from the concentration effect on the number of antiferromagnetic couples existing in the Fe-Zr base. This explanation can be further detailed by discussing three typical cases involved in our Fe-M-Zr system.

(1) When Co is added to the parent Fe-Zr base, the T_C increases with increasing Co content within the whole concentration range measured. This effect might be explained by assuming that the Fe-Co exchange interaction is larger than the Fe-Fe couples as discussed in other (Fe-Co, Fe-Ni) based amorphous alloys.[23] However, adding the Co atom also destroys the reentrant behavior of the initial susceptibility that is expected in the undoped Fe-Zr alloys. This reflects the fact that the noncollinear spin structures in the parent Fe-Zr base have been changed. In other words, by adding the Co atoms into the Fe-Zr base, we are preparing a more stable "ferromagnetic" alloy with its spin structure approaching the parallel alignment. So, in addition to the contribution of the Fe-Co interaction (which is thought to be larger than the Fe-Fe interaction according to the average molecular model), the stabilization of the spin structure should also be responsible for the enhancement of T_C.

(2) When Cr is added, the T_C-x curve forms a maximum, and there is no reentrant behavior observed for the investigated Cr concentration. This is a situation which can be described just as the first case, with the only exception being that the Fe-Cr interaction should be assumed to be less than the Fe-Fe interaction.

(3) Fe-Mn-Zr alloys differ from the first two cases; the T_C decreases monotonically with increasing Mn content and the reentrant behavior of the initial susceptibility is

observed at up to $x=10$ (as shown in Fig. 1). This indicates that Mn atoms have less effect on the stabilization of the spin structures in its parent Fe-Zr base and, hence, on the enhancement of T_C related to the spin-correlation length. Therefore, by assuming a smaller Fe-Mn interaction, a monotonically decreasing T_C should be expected for the Fe-Mn-Zr alloys.

It follows from the above discussion that the M atoms have a significant effect on the spin structure of the Fe-Zr base, which, in return, influences the T_C behavior. Such an effect is also reflected in our measurements of the magnetic moment and high-field susceptibility, as will be seen in the following discussion.

B. Magnetic moment

Figure 3 shows an example of the magnetization curves of amorphous $Fe_{90-x}M_xZr_{10}$ alloys at 1.5 K. By a linear extrapolation of the magnetization curves at higher magnetic field to zero magnetic field, the spontaneous magnetizations $\sigma_s(1.5)$ at 1.5 K are obtained. Here the average moment per atom of amorphous $Fe_{90-x}M_xZr_{10}$ alloys has been calculated using the values of $\sigma_s(1.5)$.

The average magnetic moments $\bar{\mu}$ per Fe atom or Fe+M atom are shown in Fig. 4 as a function of M concentration. It can be seen from the figure that the $\bar{\mu}$ of amorphous $Fe_{90-x}M_xZr_{10}$ alloys is significantly small, especially at low M concentration, compared with amorphous (Fe-M-B) alloys.[17–19] The $\bar{\mu}_{Fe}$ of amorphous Fe-Si-Zr and amorphous Fe-B-Zr increases monotonically with increasing M concentration, in contrast with the variance of $\bar{\mu}_{Fe}$ with x for amorphous Fe-B (Ref. 18) and Fe-Si-B (Ref. 19) alloys. When Co, Ni, or Cu was added

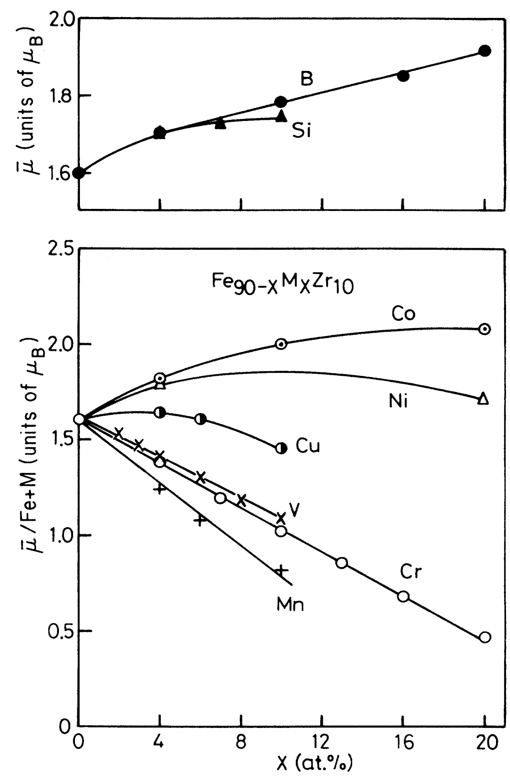

FIG. 4. Average magnetic moment per Fe or Fe+M atoms for amorphous $Fe_{90-x}M_xZr_{10}$ alloys as a function of M concentration x.

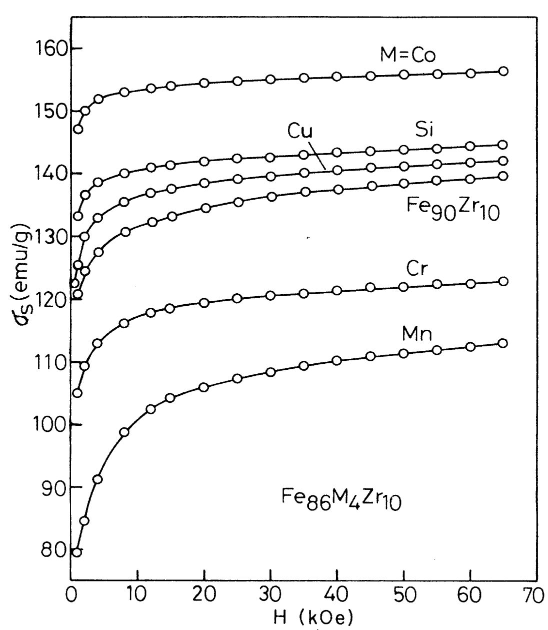

FIG. 3. Magnetization curves of some amorphous $Fe_{86}M_4Zr_{10}$ alloys at 1.5 K.

to Fe-Ze–based amorphous alloys, the $\bar{\mu}$-x curve forms a maximum. When V, Cr, or Mn was added, the $\bar{\mu}$ decreases linearly with increasing M content, with no indication of a maximum. However, a maximum in $\bar{\mu}$ in amorphous Fe-M-Zr (M=V, Cr, and Mn) alloys has been obtained from magnetization measurements in a magnetic field up to 10 kOe.[24] A similar result has also been found in amorphous Fe-Zr alloys,[20] in which the deduced Fe atomic moment from saturation magnetization measurements under an external field of 110 kOe indicates a monotonical increase of Fe moment, a complete reversal of the low-field measurements.

In summary, the amorphous Fe-M-Zr at low M concentration has unusually small magnetic moments which are sensitive to the applied field and can be enhanced by adding a M element. These results show that amorphous Fe-M-Zr alloys have a large high-field susceptibility, and their magnetization curves are not easily saturated even in higher external fields, and the magnetic moment of Fe can be, in general, undervalued. The phenomena listed above support the existence of the noncollinear spin structures in the amorphous Fe-M-Zr alloys and the effect of the spin-structure variation on the magnetic properties.

More details concerning the magnetic moment and its relevance to the noncollinear spin alignment are demonstrated in the following discussion carried out on amorphous $Fe_{90-x}Co_xZr_{10}$. As shown in Fig. 5, the magnetic

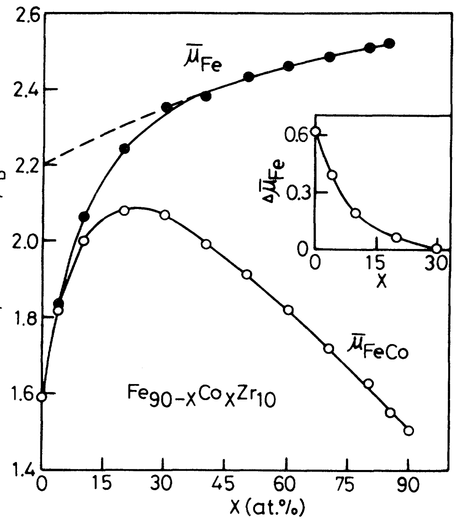

FIG. 5. Co-content dependence of the average atomic moment for amorphous $Fe_{90-x}Co_xZr_{10}$ alloys.

moment in Fe-rich amorphous $Fe_{90-x}Co_xZr_{10}$ ($x<30$) decreases drastically in comparison with that of other (Fe-Co) based amorphous alloys containing metalloid. Collins and Forsyth[25] reported that the results obtained by polarized neutron diffraction showed that the average magnetic moment per iron atom $\bar{\mu}_{Fe}$ of the crystalline $Fe_{100-x}Co_x$ alloys rose from $2.2\mu_B$ for pure iron to just over $3\mu_B$ for alloys of 50 at. % or more Co; and the average magnetic moment per Co atom, $\bar{\mu}_{Co}$, remained essentially constant ($1.8\mu_B$). The similar result was observed for amorphous $(Fe_{1-x}Co_x)_{78}Si_{9.5}B_{12.5}$ alloys,[26] in which $\bar{\mu}_{Fe}$ increases from $2.1\mu_B$ for $x=0$ to $2.6\mu_B$ for $x=0.9$, and $\bar{\mu}_{Co}$ remained constant at $1.2\mu_B$. By assuming that the $\bar{\mu}_{Co}$ of amorphous $Fe_{90-x}Co_xZr_{10}$ alloys keeps a value of $1.5\mu_B$ (the value at $x=90$) over the whole concentration, we obtained the calculated $\bar{\mu}_{Fe}$, which increases markedly with increasing Co content as shown by the solid circles in Fig. 5. This result is in agreement with the Mössbauer study of amorphous $Fe_{90-x}Co_xZr_{10}$ alloys measured by Hosoma and Nanso,[27] in which it was found that the average hyperfine field increases with x content. As can be seen from Fig. 5, when extrapolating $\bar{\mu}_{Fe}$ versus ($x<30$) plots to $x=0$, $\bar{\mu}_{Fe}$ increases from $2.2\mu_B$ for $x=0$ to $2.36\mu_B$ for $x=30$. This may be partially attributed to the increase of the magnetic moment of iron atoms like that of the (Fe-Co) based amorphous alloys containing metalloid. But the difference $\Delta\bar{\mu}_{Fe}$ between the extrapolated magnetic moment $\bar{\mu}_{Fe}^{ext}$ and $\bar{\mu}_{Fe}$ implies an effect of the noncollinear spin alignment on the magnetic moment. The inset in Fig. 5 shows $\Delta\bar{\mu}_{Fe}$ versus x. The decrease of $\Delta\bar{\mu}_{Fe}$ with x implies the change of the noncollinear spin alignment into a less dispersed spin alignment. At $x=30$ a nearly pure ferromagnetic state is established, which corresponds to the maximum of the magnetic moment $\bar{\mu}_{Fe\text{-}Co}$ as shown in Fig. 5. For $x>30$ the decrease of the magnetic moment is similar to those in other (Fe-Co) based amorphous alloys.

C. High-field susceptibility

The high-field susceptibilities χ_h obtained from the slope of the linear portion of magnetization curves at higher magnetic fields for amorphous $Fe_{90-x}M_xZr_{10}$ alloys are shown in Fig. 6 as a function of M concentration. The value of χ_h is found to be extremely large at low M concentration; that is, the magnetization curves of these amorphous alloys are difficult to saturate even with applied fields up to 60 kOe. It is interesting to note that the added M elements have a different effect on χ_h for amorphous $Fe_{90-x}Mn_xZr_{10}$ alloys and other amorphous $Fe_{90-x}M_xZr_{10}$ alloys: χ_h for the Mn-doped sample keeps its high value up to $x=10$ with only little dropping. For amorphous $Fe_{90-x}M_xZr_{10}$ (M=V, Cr, Cu, Co, and Ni) alloys, the χ_h drops sharply until $x=4$ and then decreases in a smaller rate with x. This variation exhibits a clear kink at about $x=4$, which is just the concentration where the maximum of the Curie temperature is located. A large value of χ_h has also been found in the crystalline Fe-Ni Invar alloys[28] and other amorphous Fe-based alloys such as Fe-B Invar alloy.[29] The large high-field susceptibility is one characteristic feature of the Invar effect. Shirakawa *et al.*[9] has indeed observed the Invar characteristic of amorphous $Fe_{90-x}M_xZr_{10}$ (M=Co and Ni) alloys.

The large χ_h has been often discussed using the localized or itinerant-electron model. According to the localized model, the large value of χ_h is caused by the flipping of weakly coupled antiferromagnetic spins under high magnetic field.[30] In the amorphous $Fe_{90}Zr_{10}$ alloy, there are magnetic inhomogeneities, as evidenced in the broad magnetic hyperfine field distribution,[7] suggesting the coexistence of ferromagnetic and antiferromagnetic

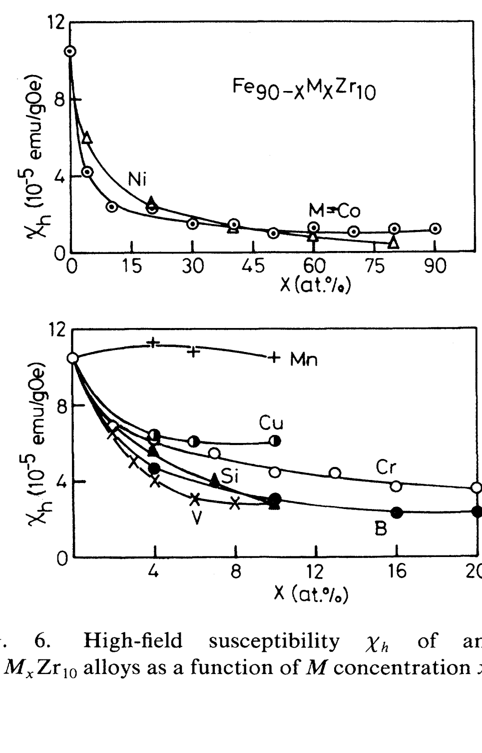

FIG. 6. High-field susceptibility χ_h of amorphous $Fe_{90-x}M_xZr_{10}$ alloys as a function of M concentration x.

states. We feel that the large value of χ_h in amorphous $Fe_{90-x}M_xZr_{10}$ alloys can be most consistently explained in terms of the presence of antiferromagnetic states and the related noncollinear structures. As being particularly indicated in the Mn-doped samples, the large high-field susceptibility (kept for Mn concentration up to $x=10$) and the concomitant reentrant behavior of the initial susceptibility are closely related to each other; the relation between the two could be established only through the noncollinear spin structures, which for the Mn-doped case are not stable and can be frustrated into an asperomagnetic state as generally proposed for the reentrant behavior occurring in the Fe-rich Fe-Zr alloys.

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