The effect of $\alpha$-Fe crystallites on the magnetic structures of $\text{Fe}_{100-x}\text{Zr}_x$ glasses

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Abstract. Neutron scattering experiments with polarization analysis have established that $\text{Fe}_{100-x}\text{Zr}_x$ glasses have non-collinear ferromagnetic structures. The magnitudes of the non-collinear components are enhanced by small fractions of $\alpha$-Fe precipitated in these glasses. Mössbauer spectroscopy has therefore been used to measure the fractions of $\alpha$-Fe in two samples each of $\text{Fe}_{90}\text{Zr}_{10}$ and $\text{Fe}_{92}\text{Zr}_8$ metallic glasses, which are confirmed to contain up to 6 atomic % $\alpha$-Fe. The measured fractions and their influence on the magnetic structures are discussed in the context of the existing literature on nanocrystalline FeZr.

1. Introduction
$\text{Fe}_{100-x}\text{Zr}_x$, metallic glasses with $7 \leq x \leq 12$, have been extensively studied since their discovery more than 20 years ago [1, 2]. They are compositionally close to amorphous iron and have a rich magnetic phase diagram with ferromagnetic, spin glass and re-entrant spin-glass structures [3]. The majority of the studies conclude that the ferromagnetic states are non-collinear [4, 5, 6, 7, 8, 9, 10, 11].

Neutron polarization analysis experiments [11] confirm that Fe-Zr glasses exhibit non-collinear ferromagnetism, since their measured neutron spin flip cross sections are non-zero. The spin flip cross sections have a peak at $Q \approx 3 \text{ Å}^{-1}$, showing that the non-collinear components of the magnetic moments are also spatially correlated. Such correlations occur in a wandering-axis [6] or a clustered ferromagnet [5, 8], both of which have been proposed for FeZr metallic glasses.

The neutron measurements show that the non-collinear ferromagnetism is sample dependent. Two samples each of $\text{Fe}_{90}\text{Zr}_{10}$ and $\text{Fe}_{92}\text{Zr}_8$ were measured in the neutron experiments, one pair from the University of Sheffield, and the other from the Research Institute for Solid State Physics, Budapest. The transition temperatures of the samples were measured using SQUID magnetometry and are given in Table 1. They are similar, showing that the compositions of the corresponding samples match to $\leq 0.1$ at.%. The spin flip cross-sections were fitted with a Gaussian peak, to model a spatially correlated component, on a sloping background, to model
a diffuse contribution due to randomly oriented non-collinear moments. The magnitudes of the non-collinear moments in each phase were calculated and are listed in Table 1. The Sheffield samples have considerably larger non-collinear moments than the Budapest samples.

This difference was attributed to (different) trace amounts of crystalline \( \alpha \)-iron in the glasses, first identified by the presence of a small remanent magnetization above the Curie temperature, \( T_C \), and later by tiny Bragg peaks in the measured structure factors of the ribbons. Quantitative comparison of crystalline and amorphous phases from diffraction measurements is intrinsically difficult. Magnetization measurements above \( T_C \) were initially used to estimate the crystalline fraction of the different ribbons. The values obtained are small, as shown in Table 1. The Sheffield samples have the larger \( \alpha \)-Fe fraction, however it is surprising that such small fractions have such a marked effect on the overall magnetic structures of these samples.

Mössbauer spectroscopy is a more sensitive technique to determine accurately the fraction of the \( \alpha \)-Fe in these samples. The measurements are discussed in the context of the literature.

2. Experimental methods and data analysis

Sub-samples of the two pairs of the \( \text{Fe}_{92}\text{Zr}_{8} \) and \( \text{Fe}_{90}\text{Zr}_{10} \) metallic glasses were prepared for the Mössbauer measurements. Spectra were collected at 300K from \( \sim 50 \text{ mg} \) (\( \sim 0.3 \text{ m} \)) of ribbon mounted in a conventional constant acceleration spectrometer with a 50mCi \( ^{57}\text{Co-Rh} \) source. The surfaces of the ribbons were perpendicular to the \( \gamma \)-ray beam direction.

The Mössbauer spectra are shown in Figure 1. Each spectrum shows a paramagnetic, quadrupole-split doublet. However, an additional six-line spectrum is clearly visible in both Sheffield samples and there is the suggestion of a sextet in the \( \text{Fe}_{92}\text{Zr}_{8} \) Budapest sample. The sextet is indicative of crystalline \( \alpha \)-Fe, which is ferromagnetic at 300K. No sextet was observed in the spectrum from the \( \text{Fe}_{90}\text{Zr}_{10} \) Budapest ribbon.

The data were analysed using the software package Recoil [12], and fits are shown in Figure 1 as solid lines. The fitted parameters are listed in Table 2. The best fit for the paramagnetic component was obtained using two Lorentzian quadrupole split doublets. The ferromagnetic component was fitted using a Lorentzian sextet with relative line intensities of 3:2:1:1:2:3.

The areas of the two doublet sub-spectra were combined to obtain the glassy, paramagnetic fractions, which were compared to the areas of the sextet to obtain the crystalline, ferromagnetic fractions. The values, listed in Table 1, show that three of the samples contain measurable amounts of \( \alpha \)-Fe and that the atomic fractions obtained from Mössbauer spectroscopy are larger than those from magnetometry. They also agree qualitatively with the magnitudes of the Bragg peaks in the measured \( S(Q) \) [11], i.e. \( \text{Fe}_{92}\text{Zr}_{8} \) (Sheffield) > \( \text{Fe}_{90}\text{Zr}_{10} \) (Sheffield) > \( \text{Fe}_{92}\text{Zr}_{8} \) (Budapest) > \( \text{Fe}_{90}\text{Zr}_{10} \) (Budapest). The values derived from the Mössbauer spectroscopy data should now be adopted as representative of the samples.

This method slightly underestimates the crystalline fraction. The samples have a finite thickness which causes the ratios to decrease. The area of the innermost pair in the sextet, which are in the doublets, will be larger than calculated. At worst, however, the fraction will be under-estimated by \( <10 \% \), which is of the same order as the error in the fits.

3. Discussion

The discovery of small fractions of \( \alpha \)-Fe in these Fe-Zr glasses is not surprising since the constitutional phase diagram shows that glasses must be quenched through a shallow eutectic at a very high temperature (1337°C) [13]. An estimate for the critical cooling rate give \( \partial T / \partial t \approx 10^8 \text{ Ks}^{-1} \), which is \( \sim 100 \) times greater than that for an easy glass former such as \( \text{Fe}_{83}\text{B}_{17} \).

The formation of \( \alpha \)-Fe crystallites causes the samples to become more non-collinear. They will also cause a direct change in local stress, stoichiometry, density and magnetostatic properties.

It is unlikely that stress causes more non-collinearity. Small increases in the \( T_C \) of Fe-Zr have been observed on isothermal annealing at 400 K [8] and on partial crystallization [14]. The
This would make the sample more collinear, not less, which contradicts the neutron data. Stress, increases the ferromagnetic exchange and decreases the size of the non-collinear clusters.

-Fe contamination from SQUID magnetometry [11] and Mössbauer spectroscopy (this work). α

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magnetically isolated. The study concluded that heating relaxes these effects will be small as the crystalline volume [18]. These changes were described using the distance between the crystallites, d, and an exchange-correlation length, L_{ex}. In regions where L_{ex} > d the crystallites are magnetically coupled, whereas for d ≪ L_{ex} the crystallites are magnetically isolated. The study concluded that L_{ex} ~ 100 Å in Fe_{87}Zr_{6}B_{6}Cu_{1}, corresponding to a crystalline volume of ~ 5% of the sample, which is similar to the values in Table 1. The values of d and L_{ex} are not known in the glassy FeZr system [18], however the dipole fields caused by an α-Fe minority phase with a magnetization 40% greater and a T_{C} 600% greater than the glassy matrix is the best explanation for the enhancement to the non-collinearity.

4. Conclusions
The estimates for the crystalline fraction of four metallic glass FeZr samples has been revised based on the results of Mössbauer spectroscopy. The presence of α-Fe appears to influence the magnitude of the non-collinear magnetism. The size of the fractions is similar to those observed in a study on the first stages of crystallization in the compositionally similar Fe_{87}Zr_{6}B_{6}Cu_{1} glass, thus suggesting that this system bears some strong similarities to iron-rich FeZr metallic glasses.

4.1. Acknowledgments
The authors would like to thank Prof. T Kemény and Dr L Kiss for their continued support and interest in this programme.

Table 1. Characteristic data for the four samples. Shown are the Curie (T_{C}) and freezing (T_{f}) temperatures [11]; the magnitudes of the non-collinear moments for the random (⟨μ_{2}^{α}⟩_{Rand.}) and correlated (⟨μ_{2}^{α}⟩_{Corr.}) parts of the magnetic structures [11]; and estimates for the fractions of α-Fe contamination from SQUID magnetometry [11] and Mössbauer spectroscopy (this work).

| Sample       | Laboratory | T_{C} (K) | T_{f} (K) | ⟨μ_{2}^{α}⟩_{Rand.} (μ_{B}^{2}) | ⟨μ_{2}^{α}⟩_{Corr.} (μ_{B}^{2}) | α-Fe at.% (SQUID) | α-Fe at.% (Mössbauer) |
|--------------|------------|-----------|-----------|-------------------------------|-------------------------------|-------------------|------------------------|
| Fe_{90}Zr_{10} | Sheffield | 232±2     | 10±0.5    | 1.94±0.05                     | 1.8±0.1                       | ≤ 0.5             | 3.2 ± 0.2              |
| Fe_{90}Zr_{10} | Budapest  | 228±1     | 12.8±0.5  | 1.25±0.05                     | 1.5±0.1                       | ≤ 0.05            | 0                      |
| Fe_{92}Zr_{8}  | Sheffield | 180±2     | 61±2      | 1.48±0.05                     | 2.0±0.2                       | ≤ 0.2             | 5.9 ± 0.2              |
| Fe_{92}Zr_{8}  | Budapest  | 173±2     | 67±2      | 0.73±0.06                     | 1.4±0.2                       | ≤ 0.05            | 2.5 ± 0.3              |

Changes have been interpreted using a magnetic cluster model [8], reasoning that heating relieves stress, increases the ferromagnetic exchange and decreases the size of the non-collinear clusters. This would make the sample more collinear, not less, which contradicts the neutron data.

Stoichiometry may have a small effect. Increasing the Zr fraction causes an increase in T_{C} and a decrease in T_{f} [3], and increases the non-collinear angle [4]. The data in Table 1 are consistent with these reports. Precipitation of α-Fe will increase the local concentration of Zr. The Fe_{90}Zr_{10} samples are more non-collinear than Fe_{92}Zr_{8}, and the Sheffield samples, with more α-Fe, are more non-collinear than the Budapest. Density may also have a small effect. Ab-initio band structure calculations show that non-collinear ferromagnetic structures can become stable at higher densities [10, 15, 16], and glassy Fe_{90}Zr_{10} is less dense than α-Fe [17]. However, both these effects will be small as the α-Fe crystallites are < 5 at.%, while the differences between the (⟨μ_{2}^{α}⟩) listed in Table 1 are as much as 50%.

Magnetostatic effects, however, will strongly influence the magnetic structure. A study of the Fe_{87}Zr_{6}B_{6}Cu_{1} glass at the first stages of crystallization shows changes to the magnetization and the field history with increasing crystalline volume [18]. These changes were described using the distance between the crystallites, d, and an exchange-correlation length, L_{ex}. In regions where L_{ex} > d the crystallites are magnetically coupled, whereas for d ≪ L_{ex} the crystallites are magnetically isolated. The study concluded that L_{ex} ~ 100 Å in Fe_{87}Zr_{6}B_{6}Cu_{1}, corresponding to a crystalline volume of ~ 5% of the sample, which is similar to the values in Table 1. The values of d and L_{ex} are not known in the glassy FeZr system [18], however the dipole fields caused by an α-Fe minority phase with a magnetization 40% greater and a T_{C} 600% greater than the glassy matrix is the best explanation for the enhancement to the non-collinearity.
Table 2. The parameters determined from the fits to the data in Figure 1.

|                     | Doublet 1                  | Doublet 2                  | Sextet         |
|---------------------|---------------------------|---------------------------|----------------|
| Isomer shift (mm/s) | $-0.085 \pm 0.001$        | $-0.047 \pm 0.001$        | $0.00 \pm 0.01$|
| Quadrupole split (mm/s) | $0.21 \pm 0.02$        | $0.57 \pm 0.03$        | $0.00 \pm 0.01$|
| Hyperfine field (T) | $-$                      | $-$                      | $33.05 \pm 0.05$|

Figure 1. The Mössbauer spectra collected at 300K. The solid lines show the fits to the data.

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