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Effects of Exchange Frustration on the Magnetic Properties of Iron-Rich Amorphous Alloys

bу

Hong Ren Department of Physics, McGill University Montréal, Québec June 1993

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Exchange Frustration Effects in Iron-Rich Magnetic Glasses

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Abstract

The magnetic properties of amorphous Fe_xT_{100-x} (T=Zr, Hf, Sc; $89 \le x \le 93$) alloys have been systematically studied mainly by Mössbauer spectroscopy and magnetization measurements. Two magnetic transitions have been observed in Fe92.5Hf7.5 (the only FeHf alloys studied here) and FeZr alloys with Fe content between 90 and 93 at.%. We have ruled out the cluster models, which attribute the second transition either to the ordering of AFM clusters or to the freezing of FM clusters, and confirmed that the second transition is due to the homogeneous freezing of the transverse spin components as a result of exchange frustration. On varying the frustration level, the evolution process from a ferromagnetic to a spin glass ordering has been observed. Fe₈₉Zr₁₁ essentially exhibits conventional ferromagnetic behavior, while Fe₉₀Zr₁₀ shows two magnetic transitions with a noncollinear ground state. As we increase the Fe content further (and thus raise the frustration level), the second transition temperature T_{xy} and the noncollinearity of the ground state increase, whereas the first transition temperature T_c drops. T_{xy} and T_c are expected to meet at x $\simeq 94.5$, suggesting that Fe94.5Zr5.5 (which can not be made by melt-spinning) would be a spin glass. Fe91Sc, is the most frustrated system studied here and it exhibits a single transition to a spin glass. Extrapolation of the magnetic properties of all systems gives a common limit as the Fe concentration approaches 100%, and suggests that amorphous Fe is a spin glass with the spin freezing temperature about 100K and an average iron moment of $\sim 1.6 \mu_B$. Below the second transition, the transverse spin components are strongly correlated on a nearest neighbor scale in Fe₉₂Zr₇Sn, while the correlation length of the longitudinal components shows no detectable change on the local scale. Our experimental results are in quantitative agreement with the Monte Carlo simulations which invoke only the exchange frustration, therefore indicating that the magnetic ordering behavior of the alloys studied here is controlled primarily by the exchange frustration.

Résumé

Les propriétés des alliages amorphes de $\operatorname{Fe}_{x}T_{100-x}$ (T=Zr, Hf, Sc; $89 \leq x \leq 93$) ont été systématiquement étudiées par spectroscopie Mössbauer et par des mesures de magnétisation. Deux transitions magnétiques furent observées dans l'alliage Fe92.5Hf7.5 (le seul alliage de FeHf étudié içi) et l'alliage de FeZr contenant du Fe entre 90 et 93 at.%. Nous avons écarté les modèles de groupes, qui attribue la seconde transition soit à une organisation des groupes antiferromagnétiques ou à un gel des groupes ferromagnétiques, et avons confirmé que la seconde transition est causée par un gel homogène de la composante transverse du spin dû à une frustration d'échange. En variant le niveau de frustration, le processus d'évolution d'un ferroaimant à une organisation de type verre de spins est observée. Le Fe₈₉Zr₁₁ se comporte essentiellement comme un ferroaimant conventionnel pendant que le Fe₉₀Zr₁₀ révèle deux transitions magnétiques avec un état fondamental noncolinéaire. Lorsque nous augmentons la concentration de Fe à nouveau (et donc augmentons le niveau de frustration) la seconde température de transition T_{xy} et la noncolinéarité de l'état fondamental augmentent, alors que la première température de transition T_c diminue. T_{xy} et T_c devraient se croiser à x \simeq 94.5, ce qui suggère que l'alliage Fe_{94.5}Zr_{5.5} (qui ne peut être fabriqué par "melt-spinning") serait un verre de spins. Le Fe₉₁Sc₉ est le système étudié le plus frustré et montre une transition unique à un verre de spins. Une extrapolation des propriétés magnétiques pour tous les systèmes étudiés converge vers une limite commune lorsque la concentration du Fe approche 100%, et ceci suggère que le Fe amorphe est un verre de spins avec une température de gel des spins de 100K et le moment magnétique d'un atome de Fe est de $\sim 1.6 \mu_B$. Sous la seconde transition, la composante transverse des spins est fortement corrélée à l'échelle des plus proches voisins dans l'alliage Fe₉₂Zr₇Sn, alors que la longueur de corrélation de la composante longitudinale ne montre aucun changement détectable à l'échelle locale. Nos résultats expérimentaux sont en accord quantitatif avec des simulations de Monte Carlo qui invoquent seulement les frustrations d'échange, ce qui indique que le comportement d'organisation magnétique des alliages étudiés içi est controlé principalement par les frustrations d'échange.

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Chapter 1

Introduction

The presence of both ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions in magnetic materials leads to a phenomenon known as exchange frustration where the magnetic moments experience conflicting interactions[1,2]. If a system has only FM (or positive) interactions, it is simply a ferromagnet. When a certain amount of AFM interactions are introduced so that the average interaction is zero (this is referred to as complete frustration), the system is a spin glass which is characterized by random orientation of spins (or zero magnetization) and very slow dynamics. However, if FM and AFM interactions are both present but the distribution of exchange integral is biased towards positive values, the system will show rather complicated behavior which is between that of a ferromagnet and a spin glass. These materials are referred to as partially frustrated systems and they have drawn intensive attention in recent years. In the following sections, the theories and the experimental observations about these materials will be described.

1.1 Theory of Frustrated Systems

Before going to the theories about partially frustrated materials, it is useful to describe the theory concerning complete frustration developed by Edwards and Anderson (EA model)[3]. The system they studied consists of an assembly of Ising spins with J_{ij} being the exchange integral between spins \vec{S}_i and \vec{S}_j . Complete frustration is achieved by assuming that the exchange integrals have a Gaussian distribution with both positive and negative values and that the average exchange is zero. The analysis shows the existence of spin glass phase where all spins are frozen in random directions, that is, $\langle \vec{S}_i \rangle = 0$ where $\langle \rangle$ represents the average over all sites. Suppose at time 1, the measured spin at point *i* is $S_i^{(1)}$. If it is studied again a long time later (time 2), since the spin is frozen, there is a non-zero probability that $S_i^{(2)}$ will point in the same direction. Thus, an order parameter defined by Edwards and Anderson

$$q = < S_i^{(1)} \cdot S_i^{(2)} > \tag{1.1}$$

will only reflect the frozen nature and is not affected by the random orientation of the spins in spin glass state.

This model was extended by Sherrington and Kirkpatrick[4,5] (SK model). The average exchange is not constrained to be zero so that partial frustration could be considered. The exchange integrals still have a Gaussian distribution

$$P(J_{ij}) = \frac{1}{\sqrt{2\pi J}} exp \frac{-(J_{ij} - J_0)^2}{2J^2}$$
(1.2)

with the average J_0 and width J scaled according to

$$J_0 = \bar{J}_0 / N \quad J = \tilde{J} / N^{1/2}$$

so that \tilde{J}_0 and \tilde{J} are both intensive. Two order parameters are defined:

$$m = << S_i >>_J q = << S_i >^2>_J$$

where $\langle \rangle$ and $\langle \rangle_J$ denote the thermal average and exchange average over the distribution respectively. In this model, a nonzero q indicates magnetic order. If additionally m=0, it corresponds to spin glass state while for m≠0, the order is ferromagnetic. The magnetic phase diagram (Fig. 1.1) shows rather complicated ordering behavior. For $\bar{J}_0/\bar{J} < 1$ and $\bar{J}_0/\bar{J} > 1.25$ the system exhibits a single transition to spin glass or ferromagnet respectively. However, when \bar{J}_0/\bar{J} is in the middle range, two magnetic



Figure 1.1: The magnetic phase diagram of SK model where the exchanges of Ising spins have a Gaussian distribution with average \bar{J}_0 and width \bar{J} . Two magnetic transitions are expected for $1 \le \bar{J}_0/\bar{J} \le 1.25$. From Ref.[4].

transitions are expected with the ferromagnetic transition followed by a second transition to spin glass. The values of magnetization, m(T) and frozen moment, $q^{1/2}(T)$, are obtained by numerical solution and shown in Fig. 1.2. It should be noted that for $\tilde{J}_0=1.15\tilde{J}$ where two transitions are expected, m remains smaller than $q^{1/2}$ in ferromagnetic state and becomes zero as the system enters spin glass region. The loss of magnetization is caused by the limited freedom of Ising spins. They can not have any other response (such as noncollinearity) to the frustration.

Since for most experimental materials, the spins are vectors, the behavior of real systems may not be well described by Ising models. A mean-field theory for m-component Heisenberg spins (m=3 corresponding to most experimental materials) with infinite range interactions has been developed by Gabay and Toulouse[6]. The phase diagram they obtained is shown in Fig. 1.3. Unlike the SK model which predicts



Figure 1.2: The calculated magnetization, m and ordered moment, $q^{1/2}$ as function of normalized temperature for different values of \bar{J}_0/\tilde{J} . From Ref.[5].

a second transition from ferromagnet to spin glass, two transitions are obtained following the ferromagnetic transition and both M_1 and M_2 phases are not spin glasses. M_1 is characterized by the coexistence of a ferromagnetic ordering of longitudinal spin components and a spin glass ordering of the transverse components. M_2 has the same coexistence of ordering but the replica symmetry is broken which is usually associated with the irreversibility in the system. Two order parameters:

 $q_1 = << S_1 >^2>_J$, the longitudinal EA order parameter,

 $q_T = << S_{\mu} >^2 >_J$, the transverse EA order parameter,

are used to describe the different phases[7]:

paramagnet:
$$q_1 = 0$$
 $q_T = 0$



Figure 1.3: Phase diagram in zero field of Heisenberg spins which have a Gaussian exchange distribution with width of 1 and average of J_0 . F: ferromagnetic; P: paramagnetic; SG: spin glass; M_1 and M_2 are mixed states described in the text. From Ref.[6].

spin glass:
$$q_1 > 0$$
 $q_T > 0$
ferromagnet: $q_1 > 0$ $q_T = 0$
 M_1 and M_2 : $q_1 > 0$ $q_T > 0$

Cragg et al.[8] have argued that the symmetry between replicas is broken as soon as the ordering of transverse components occurs. This suggests that below the ferromagnetic transition, there is only one further transition at which the ordering of transverse spin components is accompanied by irreversibility.

Besides the mean-field theories, computer simulations have also been performed to understand the frustration problem. Two-dimensional XY spins on a square lattice with competing nearest-neighbor interaction have been studied by Saslow and Parker through a local mean-field approach[9,10]. Site frustration is introduced by changing two of the four FM bonds at any randomly selected site with AFM bonds. They have reported two transitions at T_K and T_r below the ferromagnetic transition. As one decreases the temperature below T_K , the frustrated bonds made themselves felt, and the system begins to order in the transverse directions, while at T_r , the frustrated spins finally freeze, which leading to the canting of other spins and thus a decrease of the magnetization (Fig. 1.4).



Figure 1.4: Temperature dependence of the magnetization m, root mean square of spin length S_{rms} , and noncollinearity order parameter Q_{nc} from the simulations of XY spins. From Ref.[9].

1.2 Experimental Results on Frustrated Systems

1.2.1 Iron-rich amorphous binary alloys

Since iron-rich amorphous binary alloys in the form Fe_xT_{100-x} (T=Zr,Hf,Sc) are the materials studied here, the experimental results on these systems will be described

first.

The main characteristic of amorphous materials is the absence of long range structural and chemical order. The techniques to produce the amorphous materials involve the rapid solidification of the constituents from the gas or liquid phase, such as sputtering or melt spinning. As a consequence of structural and chemical disorder, the separations between nearest-neighbor Fe atoms in those iron-rich amorphous alloys have a wide distribution and the average nearest-neighbor separation is expected to be close to 2.6Å, which is obtained from anomalous x-ray scattering of $Fe_{90}Zr_{10}[11,12]$. Kouvel *et al.*[13] have shown that the nearest-neighbor Fe-Fe interaction in fcc Fe (γ -Fe) is AFM, in contrast to the FM interaction in bcc Fe where the nearest-neighbor distance between Fe atoms is larger than that in fcc Fe (Fig. 1.5). It was found later



Figure 1.5: The Bethe-Slater curve applied to exchange interactions between nearest neighbor atoms in metals and alloys. a_0 and $D_{d-shell}$ are the nearest neighbor atomic separation and the diameter of the d electron shell respectively. From Ref.[13].

that two forms of γ -Fe may be prepared [14-18]. γ -Fe precipitates in Cu have a Fe-

Fe separation of 2.54Å[18] and show AFM order below a Néel temperature of about 67K[15,17], while epitaxial γ -Fe films on Cu have a Fe-Fe separation of 2.56Å and order ferromagnetically with T_c above 600K[14,16]. The fact that different nearest-neighbor Fe-Fe separations in the two types of γ -Fe result in different ordering behavior indicates that the exchange interaction is strongly dependent on the nearest-neighbor Fe-Fe separation and it changes from FM to AFM when the nearest-neighbor Fe-Fe separation is around 2.55Å (average of 2.54 and 2.56Å). Therefore, the wide distribution of nearest-neighbor Fe-Fe separations in amorphous iron-rich alloys will lead to a wide distribution of exchange interactions which may include both FM and AFM components. Since the average distance between Fe atoms in Fe₉₀Zr₁₀ (2.6Å) is larger than 2.55Å, the distribution of exchange integral is biased towards FM side. Increasing Fe content will make the nearest-neighbor Fe-Fe separations smaller and shift the exchange integral distribution toward AFM side since the radius of Fe atoms (1.26Å) is smaller than that of Zr atoms (1.60Å).

Among these alloys, Fe-Zr has been studied most extensively. The first evidence that suggests the Fe-Zr alloys are not conventional ferromagnets comes from the low field magnetization measurements [19,20] (Fig. 1.6). When the sample is cooled in a small field (~10 Oe), magnetization shows a rapid increase at T_c , and then remains at a constant value determined by the demagnetization factor down to ~0K. If the measuring field is applied after cooling in zero field, the measured magnetization agrees well with the values obtained in field cooling at high temperatures but becomes smaller below a temperature T_h . The ac susceptibility (χ_{ac}) also shows an unusual decrease at low temperature. If χ_{ac} is measured in a superposed dc field[21], in addition to a peak at T_c , a second peak is observed at a lower temperature T_{peak} (Fig. 1.7). These data suggest a second transition below T_c , and T_h or T_{peak} were considered as transition temperatures. However, these temperatures are strongly dependent on the fields used in measurements and fields about 500 Oe can completely suppress the irreversibility in χ_{dc} . It should be emphasized that these results only indicate that anisotropy has been developed at low temperatures and that the spin



Figure 1.6: Magnetization of $Fe_{92}Zr_8$ in different fields. The magnetization obtained in zero-field cooling (solid line) and field cooling (dashed line) separates below T_h . From Ref.[19].

system becomes stiff. As will be shown later, although these phenomena are associated with the second transition, they are not the characteristic features of the second transition and thus T_h or T_{peak} can not be considered as the transition temperature.

Information about the nature of magnetic ordering at the second transition is mainly provided by Mössbauer spectroscopy combined with magnetization measurements. The six lines observed in a magnetically split Mössbauer spectrum have intensities 3:R:1:1:R:3, where $R = 4sin^2\theta/(1 + cos^2\theta)$, and θ is the angle between the magnetic moment and the direction of γ -beam. Mössbauer spectra of Fe₉₃Zr₇ measured in an external field parallel to the γ -beam are shown in Fig. 1.8[22]. It is clear that lines 2 and 5, which are absent at high temperatures, appear at low temperature. R can be derived from the spectra and is plotted in Fig. 1.9. R is zero at high



Figure 1.7: Temperature dependence of χ_{ac} for Fe_{91.4}Zr_{8.6} in three different dc field showing a second peak. From Ref.[21].

temperatures, indicating a collinear state where full magnetization is achieved ($\theta=0$). Below a certain temperature, T_{xy} (the reason it is called T_{xy} will be explained later), R becomes non-zero, that is, a field of 3T can not align all moments in its direction $(\theta \neq 0)$, thus revealing a non-collinear state. If the system is a spin glass after the second transition, the random orientation of the spins will lead to R of 2. R measured at 5K is only 0.53 ± 0.04 , much smaller than 2. Although R was obtained in a 3T field, which may rotate spins towards the field direction and cause R to be slightly smaller than 2, 0.53 is too smaller than the expected value for a spin glass, indicating that the ground state is not completely random. Moreover, the magnetization measured below the second transition is not zero as expected for a spin glass[22]. Based on the above observations, it is concluded that below the second transition, the long-range ferromagnetic order is not lost, inconsistent with the model proposed by Sherrington



Figure 1.8: Mössbauer spectra of $Fe_{98}Zr_7$ in an external field of 3T at different temperatures. The lines 2 and 5 are indicated by arrows.



Figure 1.9: Temperature dependence of R for Fe93Zr7.

and Kirkpatrick[4,5].

It has been argued that the non-collinear state at low temperature may result from canting of spins from the direction of net magnetization[9,10]. This model predicted that the magnetization would exhibit a sudden drop at the second transition. However, the magnetization measured for $Fe_{93}Zr_7$ increases smoothly on lowering the temperature and does not show a jump either up or down at the second transition[22], inconsistent with a spin canting model. In addition to the observed increase of R below the second transition, it was also found that below the second transition, the average iron moment obtained from Mössbauer spectra is larger than the magnetization, which actually reflects the component of iron moment along the field direction[22]. These observations can be explained in terms of transverse spin freezing[1,22-24], which is similar to the model by Gabay and Toulouse[6]. Below T_e , the longitudinal spin components order ferromagnetically, and there are substantial transverse spin components present above T_{xy} but they precess rapidly so that their time average is zero. Below T_{xy} , the transverse components freeze in random directions without affecting the collinear order of the longitudinal components. The freezing of the transverse components causes the system to enter a noncollinear state. Furthermore, the transverse components contribute to the total moments and make the average total moment to be larger than its longitudinal component measured by magnetization. Since the transverse components are usually referred to as xy components, the transition temperature is labelled as T_{xy} . The freezing of the transverse spin components makes the spin system more resistant to rotation of the magnetization, and the rapid increase in anisotropy and coercivity leads to a number of secondary effects being observed at T_{xy} , including reduction of the ac susceptibility and irreversibility in the dc susceptibility described above. The ground state of the system is characterized by non-collinearity and non-zero magnetization and is usually referred to as asperomagnetic[2].

In spite of the evidence of homogeneous transverse spin freezing in Fe-Zr alloys, inhomogeneous models have also been proposed. Read *et al.* have argued[25] that there may be some regions in the samples where iron atoms have all iron nearest neighbors and that the exchange interactions within these regions (clusters) are antiferromagnetic (AFM). The AFM clusters are distributed throughout the alloy matrix which orders ferromagnetically. It has been suggested that the transition at T_c corresponds to the ordering of the FM matrix whereas the ordering of the AFM clusters at lower temperature leads to the second transition at T_{xy} . In contrast to the model of AFM clusters plus FM matrix, another approach[26] suggests a FM clusters plus FM matrix picture where the density fluctuations lead to some low density regions in the alloys. The FM coupling in these regions (clusters) are stronger than that in the remaining bulk (matrix) due to the larger average nearest-neighbor distance between Fe atoms in the clusters, but the local magnetization in these clusters is smaller. According to this model, the observed second transition corresponds to the freezing of the FM clusters. It is also claimed that the freezing process does not start abruptly but proceeds gradually over a wide temperature range extending from 130K down to 4.2K for $Fe_{90}Zr_{10}$. The main evidence supporting the inhomogeneous models is that the hyperfine field distribution, $P(B_{hf})$, derived from Mössbauer spectra can be decomposed into two Gaussian components[25-27]. While both cluster models consider the high-field component being due to the FM matrix, the low-field component is supposed to correspond to the AFM clusters or FM clusters in the two different models respectively.



Figure 1.10: Mössbauer spectra of $Fe_{92}Hf_8$ in different external fields at 4.2K. Note the appearance of lines 2 and 5 in both cases. From Ref. [28].

Experimental data for Fe-Hf alloys are limited. Mössbauer spectra in different external fields parallel to γ -ray direction have been measured for Fe₉₂Hf₈ at 4.2K (Fig. 1.10)[28]. The appearance of lines 2 and 5 indicate a non-collinear state at low

temperatures. For Fe_xHf_{100-x} with x=90, 91 and 92, magnetization measured at 4.2K does not saturate in fields up to 19T, which confirms that these alloys can not be collinear ferromagnets[28]. It appears that Fe-Hf alloys exhibit similar behavior to Fe-Zr alloys, consistent with the strong chemical and physical similarity between Zr and Hf.

The magnetic behavior of Fe-Sc alloys seems very similar to that described by mean-field theory[6] for highly frustrated materials. Melt-spun amorphous $Fe_{90}Sc_{10}$ was first prepared and studied by Day *et al.*[29]. A sharp cusp at 99K in ac susceptibility (χ_{ac}) was observed (Fig. 1.11), suggesting a spin glass state at low temperatures.



Figure 1.11: Temperature dependence of χ_{ac} for Fe₉₀Sc₁₀. The cusp in χ_{ac} is usually referred as one of the characteristic feature of spin glass. From Ref.[29].

Ryan et al. [30] have shown that all of the samples they studied (Fe_xSc_{100-x} , x=89,90 and 91) exhibited non-zero hyperfine fields in their Mössbauer spectra at almost the same temperature that the irreversibility in thermomagnetic measurements appeared, suggesting a single sharp transition to an asperomagnetic state (see Fig. 1.12). In recent studies of $Fe_{90}Sc_{10}$ using Mössbauer spectroscopy in external fields, Ghafari et



Figure 1.12: Thermomagnetic curve for $Fe_{90}Sc_{10}$ in afield of 10mT. The solid square is for field-cooled and the open circle for zero-field cooled. From Ref. [30].

al. [31,32] found evidence for superparamagnetic clusters above T_c , and attributed the onset of non-collinear order at T_c to a blocking of these clusters in random orientations.

1.2.2 Other Materials

Crystalline Au-Fe alloys with Fe concentration around 15 at.% exhibit magnetic properties similar to those observed in iron-rich amorphous binary alloys. Au_{100-x}Fe_x alloys with $x \le 10$ are spin glasses as a result of the oscillating RKKY interactions. The RKKY interactions originate from the polarization of the conduction electrons. The magnetic spin S_i induces an oscillating polarization in the conduction band, and the polarized conduction electrons interact in turn with another spin S_j. The interaction between two spins can be expressed as a $1/r_{ij}^3$ term modulated by $\cos(ar_{ij}+b)$, where r_{ij} is the distance between the two spins and a and b are coefficients independent of r_{ij} . Due to the chemical disorder in the alloys, the distances between Fe atoms are more or less random, which leads to essentially random interactions with the average interaction close to zero. For low Fe content $(x \le 10)$, direct interactions are not important and the dominant RKKY interactions lead to the spin glass behavior. As the Fe content increases, the positive direct interactions between Fe atoms become more significant. In the concentration range of $15 \le x \le 20$, the direct interactions become dominant while the oscillating RKKY interactions are still present, which makes these alloys partially frustrated materials. Similar to iron-rich Fe-Zr alloys, ac susceptibility (χ_{ac}) measured in zero dc field on Au₈₅Fe₁₅ exhibits a steep increase at T_c and then a steady decrease at a lower temperature [33]. χ_{ac} obtained in a small dc field shows two peaks, one at T_c and another at a lower temperature [34,35]. A magnetic phase diagram of the Au-Fe system was constructed by Sarkissian[34] and is shown in Fig. 1.13. The data used for the phase diagram are from various measurements, and the second transition temperatures may not be accurate, but this does not affect the main features of magnetic ordering behavior as a function of composition. All of the characteristic signatures of transverse spin freezing have been observed[36-38]. Mössbauer spectra in external field parallel to the γ -beam are shown in Fig. 1.14, where the development of intensities of lines 2 and 5 at low temperature can be seen. The intensity ratio of line 2 to 3 and the average hyperfine field are plotted in Fig. 1.15. It is clear that R increases from zero at a temperature below T_c, indicating the freezing of the transverse components. The average hyperfine field, which is proportional to the average Fe moment, exhibits a rapid increase at the same temperature due to the contribution of the additional frozen transverse component to the total moment.

One of the problems associated with the Au-Fe system is the chemical short range order (CSRO). It has been shown that annealing the alloys at different temperature results in different CSRO, which in turn leads to different magnetic ordering behavior[39]. Actually, the magnetic phase diagram as a function of the reciprocal of annealing temperature for a specific composition is very similar to that as a function



Figure 1.13: The magnetic phase diagram of $Au_{100-c}Fe_c$ alloys based on data from Mössbauer spectroscopy (•), susceptibility (\Box and •) and magnetic resonance measurements (\triangle and •). p: paramagnetic; sg: spin glass; cg: cluster glass; f^{*}: quasi-critical region; f: ferromagnetic. From Ref.[34].



Figure 1.14: Mössbauer spectra of $Au_{33,2}Fe_{16,8}$ in an external field of 2T at different temperatures and in zero field at 4.2K (bottom). The solid lines are fitted curves. From Ref.[36].



Figure 1.15: Temperature dependence of average hyperfine field derived from zero field Mössbauer spectra (top) and ratio of line 2 to 3 from spectra in a 2T field (bottom) for Au_{83.2}Fe_{16.8}. From Ref.[36].

of composition (see Fig. 1.16). Both X-ray diffraction[40] and neutron scattering[41] suggest the existence of $\langle 420 \rangle$ platelets in the alloys. Violet and Borg[42] reported that the Mössbauer spectra measured for Au-Fe alloys at 4.2K can be described by two superposed six-line spectra which are supposed to correspond to the two different chemical environments *i.e.* (420) platelets and solid solution phase. They argued[43] that the observed double transitions can be explained by the ordering of the ferromagnetic Fe-rich regions ($\langle 420 \rangle$ platelets) and the Fe-poor spin glass matrix (solid solution phase). This picture was questioned [44,45] since the platelets are so small



Figure 1.16: The magnetic phase diagram of $Au_{85}Fe_{15}$ and $Au_{86}Fe_{14}$ as a function of reciprocal of annealing temperature. Note the similarity between this phase diagram and that as a function of composition. From Ref.[39].

and are strongly correlated, which makes it doubtful if the distinction of two types of regions is meaningful. Furthermore, there is no direct evidence that the two types of regions exist. Brand *et al.* [46] have used two independent hyperfine field distributions to fit the zero field Mössbauer spectra. The two distributions (high field part and low field part) would correspond to the clusters and matrix if they exist. They found that the transition at T_{xy} is the homogeneous ordering of the whole sample, inconsistent with the picture of ferromagnetic precipitates plus spin glass matrix. It should be emphasized that the Au-Fe alloys exhibit characteristic behavior in common with that observed for iron-rich amorphous alloys, which are free from all but nearest neighbor SRO.

Another problem for Au-Fe alloys is that the concentration region where two magnetic transitions are observed lies close to the percolation threshold. Thus, no matter
if there is exchange frustration, the ferromagnetic order must be lost. Moreover, in this concentration region, the magnetic behavior will be modified by percolation.

Transverse spin freezing is also observed in amorphous alloys of the form $(Fe_xT_{1-x})_yG_{100-y}$ with T=Ni, Mn and glass formers G being one or more of B, C, P, Si, Al. Since Ni atoms carry much smaller moments compared to Fe atoms, the T=Ni system appears like there is only one magnetic species, Fe. Thus the distribution of exchange interactions in this system is quite similar to that in Au-Fe alloys with the same Fe concentration, and two magnetic transitions were observed when the Fe content is above arount 17%. For T=Mn, the Fe moments and Mn moments are comparable, and the direct interactions between the Mn-Mn and Mn-Fe pairs are AFM while those between Fe-Fe pairs are FM. When the Fe content is small, the AFM interactions dominate, making the alloys spin glasses since it is not possible to construct an amorphous antiferromagnet. Partial frustration occous when the Fe concentration is larger than 0.6 where FM interactions between Fe-Fe pairs become dominant. Double transitions have been reported for both Ni and Mn systems [47-49](see Fig. 1.17). The composition range where double transitions are observed is slightly dependent on the glass formers and their precise concentrations. The magnetic phase diagrams were established mainly from the susceptibility measurements and the second transition was initially interpreted as being from a ferromagnet to a spin glass. Neutron scattering studies on $(Fe_xMn_{1-x})_{75}P_{16}B_6Al_3[50]$ show that for strongly frustrated alloy with x=0.68, the spin correlation length decreases at low temperature, suggesting the breakdown of ferromagnetic order. It was also found that for both Ni and Mn systems, the stiffness constant of spin wave exhibits a reduction at low temperature [51-53]. However, ferromagnetic domains of several hundred μm have been observed directly in weakly frustrated (Fe78Mn22)75P16B6Al3 by Transmission Electron Microscopy[54]. The domain structure shows no substantial change as the sample is cooled through the second transition temperature (\sim 35K), demonstrating that the ferromagnetic order is not lost after the second transition. Recent neutron depolarization measurements on $(Fe_xMn_{100-x})_{75}P_{16}B_6Al_3$ [55] indicate that do-



Figure 1.17: The magnetic phase diagram $(Fe_xT_{1-x})_{75}P_{16}B_6Al_3$ with (a) T=Ni and (b) T=Mn. PM: paramagnetic; FM: ferromagnetic; SG: spin glass. From Ref.[47].

mains persist down to the lowest measuring temperature (~10K) for both weakly and strongly frustrated samples ($70 \le x < 78$), although domain sizes decrease from 1µm to about 2000Å for strongly frustrated alloy (x=70), which is inconsistent with the loss of ferromagnetic order. Similar results were reported for (Fe_xNi_{100-x})₇₅P₁₆B₆Al₃[56]. Characteristic behavior of transverse spin freezing has been observed in the two systems. For (Fe_{0.064}Ni_{0.936})₇₈Si₉B₁₃, Mössbauer spectra in an external field parallel to the γ -ray[57] show development of lines 2 & 5 at T_{xy} . At the same temperature, the average hyperfine field changes slope and exhibits a faster increase. Comparison of magnetization and average hyperfine fields for (Fe_{0.765}Mn_{0.235})₇₅P₁₆B₆Al₃[58] indicates the total Fe moment and its component in field direction begin to separate below 80K, signaling transverse spin freezing (Fig. 1.18). A kink in the temperature dependence of the average hyperfine field at T_{xy} has been also reported for



Figure 1.18: The temperature dependence of average hyperfine field and magnetization for (Fe_{0.765}Mn_{0.235})₇₅P₁₆B₆Al₃. Transverse spin freezing is identified by the separation of the two curves. From Ref.[58].

$(Fe_{1-x}Mn_x)_{77}Si_{10}B_{13}[48].$

 $\operatorname{Eu}_{x}\operatorname{Sr}_{100-x}\operatorname{S}$ serves as a typical example of insulating frustrated materials. EuS is a insulator with the first neighbor interactions (J_1) being FM and the second neighbor interactions (J_2) AFM with a ratio of $J_1/J_2 \simeq -2$. Since the first neighbor FM interactions are dominant, it is a ferromagnet despite of the presence of AFM interactions. Upon dilution with the non-magnetic impurity Sr, the exchange integrals remain unchanged but the relative number of magnetic second neighbors increases, thus the distribution of exchange integrals will include more AFM components and eventually makes $\operatorname{Eu}_{x}\operatorname{Sr}_{1-x}\operatorname{S}$ frustrated materials (see Fig. 1.19). Between the percolation concentration $x_p=0.13$ and the critical concentration $x_c=0.51$, the system undergoes a single transition from paramagnet to spin glass. In the composition range $0.51 \leq x \leq 0.65$, the system shows two magnetic transitions, but the second transition has been considered as being from ferromagnet to spin glass. Detailed information concerning the magnetic ordering in the double transition region is limited



Figure 1.19: Magnetic phase diagram of $Eu_xSr_{1-x}S$. PM: paramagnetic; FM: ferromagnetic; SG: spin glass. From Ref.[59].

as most of studies about this system are mainly focused on ac susceptibility (χ_{ac}) and neutron scattering[59-62]. The temperature dependence of χ_{ac} for several samples with $x \ge 0.53$ are shown in Fig. 1.20[62]. χ_{ac} shows a sharp increase at T_c and falls off at a lower temperature, similar to what observed in amorphous Fe-Zr and crystalline Au-Fe alloys. For x=0.52, spin correlation length was reported to decrease near the second transition temperature $T_{sg}[60]$, while in neutron depolarization measurements on the x=0.54 sample, the neutron beam was found to be less depolarized at low temperature[63], both suggesting that the ferromagnetic order established at T_c begins to disappears at T_{sg} . On the other hand, spin waves were observed for all the samples with $x\ge 0.50[61]$. The observed behavior of $Eu_xSr_{1-x}S$ is usually interpreted in terms of random field effect[62]. This model assumes that the system consists of two



Figure 1.20: χ_{ac} of $Ev_x Sr_{1-x}S$ with different x. From Ref.[62].

distinct spin-glass-like and ferromagnetic networks. At low temperatures, the spinglass-like network orders and imposes a random field on the ferromagnetic network, thus destroying the ferromagnetic order. Definitely, this model is totally invalid for all other systems described above since there is clear evidence that the ferromagnetic order is not lost below the second transition. Even for $Eu_xSr_{1-x}S$, the similarity in χ_{ac} 's behavior and phase diagrams between $Eu_xSr_{1-x}S$ and other systems leads us to suggest that more work concerning the low temperature state is needed. Furthermore, it was shown[64] that the dipolar interactions in this system have comparable strengths as the exchange interactions and the reported loss of ferromagnetic order at low temperature may be due to the strong dipolar interactions.

1.3 Motivation for This Work

As mentioned above, partially frustrated materials have drawn great interest in recent years and exhibit a universal behavior: double transitions. In contrast to most studies which focused on investigations of magnetic properties as a function of temperature for one specific sample, we will emphasize on the evolution of a system in composition space. By changing composition, the degree of frustration can be adjusted. Therefore, we are able to study how a system evolves from a ferromagnet to a spin glass as we increase the frustration level, and to understand the effects of exchange frustration on the magnetic properties of the system. The iron-rich binary amorphous alloys of the form Fe_xT_{100-x} (T=Zr,Hf,Sc) have been chosen in this work for several reasons. Firstly, amorphous materials can be made over a wide composition range without the problem of phase separation or segregation of constitutants. Secondly, the iron contents are so high ($x \ge 89$) that the magnetic properties will not be influenced by percolation effects. Thirdly, the alloys contain only one kind of magnetic element Fe, so it is a simple system. Finally, high transition temperatures due to the high Fe contents make the study easier.

The main issues we will address in this thesis are as following:

- Clarifying the nature of the second transition in iron-rich binary amorphous alloys. As mentioned earlier, the nature of the second transition remains controversial and the models divide broadly into homogeneous freezing of the transverse spin components and inhomogeneous ordering of AFM clusters (or freezing of FM clusters), which are embedded in FM matrix.
- Studying the effects of exchange frustration on the magnetic properties of these materials. We will investigate the ordering behavior of alloys with different degree of frustration and try to understand the effects of exchange frustration. This forms the main part of the thesis.
- Detecting spin correlations. It has been suggested that the asperomagnetic state below the second transition is characterized by collinear order of longitudinal

spin components and random order of transverse components. In order to obtain detailed information about the magnetic order below the second transition, spin correlations on a local scale will be investigated.

The main experimental techniques we used are Mössbauer spectroscopy and magnetization measurements. It is clear that in order to clarify the nature of the second transition, Mössbauer spectroscopy has to be used, but the more important reason is that it offers the clearest method to observe the freezing of transverse spin components. Finally, it is a local probe, thus spin correlations on a local scale can be detected. On the other hand, magnetization measurements provide global properties of the samples, which can then be compared with those obtained by the local probe.

Chapter 2

Experimental Methods

2.1 Sample Preparation

The samples studied in this work are amorphous alloys of the form $\text{Fe}_{x}M_{100-x}$ (M=Zr, Hf, Sc; $89 \le x \le 93$) and amorphous $\text{Fe}_{92}\text{Zr}_7\text{Sn}$. All samples were prepared by melt-spinning.

Ingots for melt-spinning were prepared by arc-melting appropriate quantities of constituents (Fe, Zr, Hf etc.) under titanium gettered argon. The purities of the metals used are listed in Table 1.1. For binary alloys Fe_xM_{100-x} (M=Zr, Hf, Sc), small pieces of metals weighed according to the desired stoichiometric ratio were melted three or four times to ensure homogeneity. In the case of $Fe_{92}Zr_7Sn$, the melting point of Sn is only 232°C, far below that of Fe and Zr (1536 and 1850°C respectively). In order to minimize the evaporation of Sn, the Fe and Zr were first

Table 2.1: Purities of the metals used for preparing the samples.

metal	Fe	Zr	Hf	Sc	Sn
purity	99.98%	99.8%	99.99%	99.9%	99.9%

melted two or three times, then the appropriate amount of Sn was added and remelted with the Fe-Zr ingot three times. The weight loss of materials in the process of alloying was checked by weighing the materials before and after alloying and the uncertainty of composition introduced is estimated to be usually less than 0.3 at.%.

Amorphous ribbons were produced by a single roller melt-spinner. Several pieces (typically three) of the ingot with total weight of around 300mg were placed in a quartz crucible with a small orifice (typically 0.3-0.5mm in diameter) at one end. The ingots were heated by r.f. induction. Once melted, the alloy was expelled out of the crucible under argon pressure released by a manually operated solenoid valve, onto the rim of a copper wheel, which was rotating with a tangential speed of ~ 50 m/s. The resulting ribbons are 1 to 2mm wide and about 20 μ m thick.

2.2 Characterization

For the iron-rich alloys studied here, all of the amorphous phases have their ordering temperatures below room temperature, while all of the crystalline phases e.g. α -Fe, Fe₂Zr, etc., are ferromagnetic at room temperature. Therefore, any crystalline contaminants (principally α -Fe here) will strongly affect the magnetic properties of samples. Moreover, they also change the composition of the amorphous phase.

Conventional x-ray diffraction was used to check if the samples are amorphous. The x-ray diffractometer used in this study is Nicolet-stöe L11 powder diffractometer. All x-ray diffraction measurements were made in the reflection mode with Cu K_{α} radiation ($\lambda = 1.5418$ Å). The ribbon samples were stuck to a glass slide by a piece of double sided adhesive tape. Both faces of the samples need to be checked, mainly for reflections around 45° and 65° (due to the (110) and (200) planes of α -Fe), since a crystalline layer may be present on either face and be oriented so as to exhibit only the (200) reflection. In Fig. 2.1, diffraction patterns for two Fe₉₂Zr₇Sn samples are presented. The top one exhibits a broad peak around 45° and no peak near 65°, demonstrating the amorphous nature of the sample, while the bottom plot shows a



Figure 2.1: X-ray diffraction patterns for amorphous (top) and partially crystalline (bottom) Fe92Zr₇Sn. The samples were scanned in two separate regions $(350 \le 2\theta \le 50^{\circ} \text{ and } 610 \le 2\theta \le 67^{\circ})$. Since the peak around 65° (if it is present) is much sharper, that scan region is very narrow.

more narrow peak with a sharp spike near 45° and indicates that the alloy is partially crystallized. X-ray diffraction can detect crystalline contaminants down to a few percent.

Differential scanning calorimetry (DSC) was also used to test the sample quality. Thermal scans were performed in the temperature range of 300 to 900K with a heating rate of 40K/min. The position and area of the crystallization peak provide information on sample quality. A partially crystalline sample will show a crystallization peak that is broadened and shifted to lower temperature as the microcrystals present in the sample act as nucleation sites and facilitate re-crystallization.

Mössbauer spectroscopy provides a more sensitive measure of crystalline contam-

inants in samples. Because all contaminant phases are magnetic at room temperature, their contributions to the room temperature Mössbauer spectra can be easily distinguished from those of the amorphous phases, which are not magnetic at room temperature. Detection limits less than 1% can be achieved.

The compositions of samples were checked by electron micro-probe. For most samples, the compositions were found to be within 0.4 at.% of the nominal values. The results for Fe-Hf alloys are about 1 at.% different from the nominal values. This mainly reflects the uncertainty in the micro-probe measurements as the reference sample used contained only 0.9% Hf.

2.3 Mössbauer Spectroscopy

2.3.1 Principles

The Mössbauer effect

The Mössbauer effect is based on the recoil-free resonant emission and absorption of γ -rays by a nucleus. Resonant processes are very common phenomena, but the unique feature of the Mössbauer effect is that it eliminates the destructive effect of recoil energy which is critical for nuclear resonant processes.

Let us consider the ⁵⁷Fe isotope, which is the most commonly used source in Mössbauer spectroscopy. For the 14.4keV transition, the width of the transition energy (Γ) is only 4.67 x 10⁻⁹eV, which leads to a very high energy resolution of ~3x10¹². However, the energy resolution actually obtained is far below 10¹² in the presence of recoil, in some cases, the resonant process can not even be observed. This can be illustrated clearly by considering a free atom. When the atom emits a γ -photon, it will recoil since the total momentum is conserved. The energy of the emitted γ -photon can be written as

$$E_{\gamma} = E_0 - E_R - E_T \tag{2.1}$$

where E_0 is the transition energy and E_R and E_T are recoil energy and thermal energy

respectively. The recoil energy

$$E_R = \frac{E_\gamma^2}{2Mc^2} \tag{2.2}$$

is proportional to square of γ -ray energy (c is velocity of light and M the mass of the atom). The thermal energy E_T is dependent on the thermal motion of the nucleus, and will have a distribution with a average value $\overline{E_T}$, which is temperature dependent. Thus the energy of the emitted γ -photon is less than the nuclear transition energy by E_R and is broadened with a full width of $2\overline{E_T}$. Similarly, when a γ -photon is absorbed by a nucleus, we have

$$E_{\gamma} = E_0 + E_R - E_T \tag{2.3}$$

That is, the energy of γ -photon to be absorbed should be greater than E_0 by E_R and may also has a distribution. Therefore, the energies of the emitted and absorbed γ -rays by the same nucleus are shifted away by $2E_R$. In fact, the principles outlined above can be applied to any kind of resonant processes, such as the resonant emission and absorption of ultraviolet radiation by atoms. However, the transition energy and hence the photon energy for ultraviolet radiation is much smaller than that of γ -photon in nuclear resonant processes. Since E_R is proportional to the square of the photon energy, the recoil energy in atomic resonant processes is much smaller than that in nuclear resonant processes. The typical energy value of a ultraviolet photon is 6.2eV, which yields E_R of 2.1 x 10^{-10} eV and E_T of 3 x 10^{-6} eV if the the mass of the atom is 100amu[65]. Since E_T is much larger than E_R , the emission and absorption profiles are strongly overlapped in spite of the recoil effect. Furthermore, both E_R and E_T are smaller than the width of the transition energy, so the energy resolution is not reduced. On the other hand, for the 14.4keV transition of 57 Fe, E_R is around 2 x 10^{-3} eV and $\overline{E_T} \sim 1$ x 10^{-2} eV at 300K. E_R is much larger than the width of the transition energy (~10⁻⁹ eV). Thus the shift of $2E_R$ for energies of emitted and absorbed γ -rays will lead to no overlap of the emission and absorption profiles and destroy the resonant processes completely. With the thermal broadening $\overline{E_T}$, which is larger than E_R , the emission and absorption profiles can still overlap but the energy resolution is dropped by a factor of $\sim 10^7$.

The recoil can also be compensated by moving source with a velocity v relative to the absorber, thus adding the Doppler energy E_d to E_{γ}

$$E'_{\gamma} = E_{\gamma} + E_d = E_{\gamma} + E_{\gamma}(v/c) \tag{2.4}$$

where c is the velocity of light. To make the emission and absorption profiles overlap completely, E_d should equal to $2E_R$, which requires a huge velocity about 10^5 mm/s.

When the atom is bound to a solid matrix, the situation is quite different. The recoil energy in this case is transferred to the lattice through the creation of phonons. Since the phonon energies are quantized, a minimum energy is required to create a phonon. For a simple Einstein model, the energies of phonons can take the values $\pm h\nu$, $\pm 2h\nu$, \cdots . If $E_R < h\nu$, a certain number of γ -photons will be emitted without energy transfer to the lattice (zero phonon events). Similarly, the nuclei in a solid can absorb γ -photons in a recoil-free process. That is, recoil-free nuclear resonant processes can be achieved in some solid materials. This forms the basis of Mössbauer effect. Since the thermal broadening is also eliminated when the atom is bound to the solid matrix, the extremely small natural full-width of the transition energy, for example, of ⁵⁷Fe leads to a energy resolution of about 1 part in 10¹² in practice.

The Mössbauer effect can be measured in a transmission configuration schematically shown in Fig. 2.2. A solid matrix containing the excited nuclei of a suitable



Figure 2.2: A schematic representation of a experimental setup to measure a transmission Mössbauer spectrum

isotope is used as the source of γ -rays. A second matrix containing the same isotope in its ground state is placed in front of the source and serves as an absorber (it is the sample in transmission configuration). The intensity of the γ -rays transmitted through the sample is measured. Tiny difference between the transition energy in the source and that in the sample can be measured as a result of very high energy resolution. By moving the source relative to the sample with a velocity v, the energy of a γ -photon "seen" by the sample can be varied by a Doppler energy E_d (see equation 2.4). If the source and absorber are identical as shown in Fig. 2.2, the emission and absorption profiles completely overlap at v=0 and the absorption is at a maximum. Any increase or decrease in velocity can only decrease the overlap and therefore reduce the absorption. It then follows that a record of absorption as a function of the velocity v will show an absorption spectrum. In Fig. 2.3, a measured spectrum with a single absorption line is shown. Usually, velocity v scans in a range of a few mm/s, in contrast to 10^5 mm/s needed to compensate for the recoil energy.

Hyperfine Interactions

There are several factors which affect the nuclear transition energy through the hyperfine interactions between a nucleus and its environments. If the nuclei of the source and absorber have different local environment, the nuclear transition energies of source and absorber will be different, which can then be measured by Mössbauer spectroscopy. Static and time-dependent hyperfine interactions will be considered below.

Static Interactions

A. Isomer Shift, δ

The isomer shift is due to the Coulomb interaction between the nuclear charge distribution over a finite nuclear radius R and the s-electron charge density at the nucleus. The s-electron density at the nucleus can be varied by the chemical environment. When the nuclei in the source and absorber have different chemical environments, the shift of the energy levels due to the Coulomb interaction in the source



Figure 2.3: Mössbauer spectrum of a stainless steel foil at room temperature

and absorber will be different. Thus the absorption peak will be shifted by δ (see Fig. 2.4(a)).

$$\delta = C \frac{\delta R}{R} (|\psi_A(0)|^2 - |\psi_S(0)|^2)$$
(2.5)

where C is a constant for a given isotope and $\delta R/R$ is the relative change of nuclear radius between excited and ground states, and the term in parenthesis represents the difference of s-electron density at a nucleus between the absorber and source.

B. Quadrupole Splitting, Δ

The quadrupole splitting is due to the interaction between the nuclear electric quadrupole moment, $e\vec{Q}$, with the electric field gradient (EFG), $\nabla \vec{E}$, at the nucleus. The interaction can be expressed by the Hamiltonian

$$\mathcal{H} = -\frac{1}{6}e\vec{Q}\cdot\nabla\vec{E} \tag{2.6}$$



Figure 2.4: The energy-level schemes for an $I_g=1/2-I_e=3/2$ nuclear transition with (a) isomer shift, and (b) quadrupole splitting. The Mössbauer absorption transition and the resulting spectra are also shown. From ref.[66]

The nuclear quadrupole moment is a measure of deviation of the nuclear charge distribution from spherical symmetry, while the EFG is a tensor and can be written as

$$\nabla_i E_j = -\frac{\partial^2 V}{\partial x_i \partial x_j} = -V_{ij} \tag{2.7}$$

where V is the electrostatic potential and $x_i, x_j = x, y, z$. A principal axis system may always be defined such that all the V_{ij} terms with $i \neq j$ are zero, leaving the three finite principal values of V_{xx}, V_{yy}, V_{zz} . Furthermore, $\nabla \vec{E}$ is a traceless tensor. That is

$$V_{xx} + V_{yy} + V_{zz} = 0 (2.8)$$

As a result, only two parameters are required to describe the $\nabla \vec{E}$ and usually they are $V_{xx} = eq$, the largest value of $|V_{ii}|$, and the asymmetry parameter η , which is defined by

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$
(2.9)

such that $|V_{zz}| > |V_{yy}| \ge |V_{xx}|$ and $0 \le \eta \le 1$. For both ⁵⁷Fe and ¹¹⁹Sn, the quadrupole

moments of ground states with I=1/2 are zero, while for excited states with I=3/2, the energy of quadrupole interaction is

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1)](1+\eta^2/3)^{1/2}$$
(2.10)

Therefore, the excited state is split into two sublevels while the ground state remains unchanged. This is shown in Fig. 2.4(b). If $\eta=0$, we have

$$E_{Q} = \begin{cases} \frac{e^{2}qQ}{4} & I_{z} = \pm \frac{3}{2} \\ -\frac{e^{2}qQ}{4} & I_{z} = \pm \frac{1}{2} \end{cases}$$
(2.11)

and the quadrupole splitting is

$$\Delta = E_Q(I_z = \pm \frac{3}{2}) - E_Q(I_z = \pm \frac{1}{2}) = \frac{e^2 q Q}{2}$$
(2.12)

C. Magnetic Hyperfine Interaction

The interaction of a nuclear magnetic moment $\vec{\mu}$ with a magnetic field \vec{B} at the nucleus splits nuclear states with spin quantum numbers I (I>0) into (2I+1) sublevels. The Hamiltonian describing the interaction is expressed as:

$$\mathcal{H} = -\vec{\mu} \cdot \vec{B} = -g\mu_N \vec{I} \cdot \vec{B} \tag{2.13}$$

where g is the nuclear g-factor and μ_N is the nuclear magneton. The energies of the sublevels are determined by

$$\Delta E_M = -g\mu_N B I_z \tag{2.14}$$

where I_z is the z component of the nuclear spin quantum number I.

For both ⁵⁷Fe and ¹¹⁹Sn, the excited state with I=3/2 will split into four sublevels and the ground state with I=1/2 into two. Transitions between different sublevels can take place if $\Delta I_z=0$ or ± 1 , and consequently six-line spectra are observed (see Fig. 2.5). The measured Mössbauer spectrum of α -Fe (bcc Fe) at room temperature in Fig. 2.6(a) is an example of the magnetically split spectra and it shows six well resolved absorption lines. It is known that the magnetic hyperfine field in α -Fe at room temperature is 33T. From the well established hyperfine parameters of α -Fe, the



Figure 2.5: The energy-level schemes for an $I_g=1/2-I_e=3/2$ nuclear transition with magnetic splitting. The Mössbauer absorption transition and the resulting spectra are also shown. From ref.[66]

positions of the absorption lines due to magnetic splitting for α -Fe can be calculated. The separation of the 1-6 lines, 2-5 lines, and 3-4 lines at room temperature are 10.625mm/s, 6.15mm/s, and 1.68mm/s respectively. The Mössbauer spectrum of α -Fe at room temperature is usually used for velocity calibration. Since in experiments a Mössbauer spectrum is recorded as γ -ray counts versus channel number, the velocity calibration transforms the channel number to Doppler velocity.

The intensity ratio of the six lines in a spectrum can be written as 3:R:1:1:R:3, where $R = 4sin^2\theta/(1 + cos^2\theta)$, and θ is the angle between the magnetic moment and the direction of γ -beam. When the magnetization is parallel to the γ -beam, θ is zero, leading to zero R and thus a four-line spectrum. If the magnetization is perpendicular to the γ -beam, R will take its maximum value of 4. For a pc der sample, as the directions of the magnetization are random, R should be averaged over a sphere and the result is 2. The measured spectra of α -Fe in different configurations are shown in Fig. 2.6.

The magnetic field at a nucleus can originate in several ways. A general expression would be

$$B = B_0 - DM + LM + B_S + B_M \tag{2.15}$$

where B_0 is the field at the nucleus generated by an external magnet and the next two terms are the demagnetizing field and the Lorentz field. B_S arises from an imbalance in the s-electron spin density at a nucleus. It may be due to the intrinsic unpaired selectrons, or indirectly as a result of polarization of s-electrons by unpaired d-electrons or f-electrons from the parent atom or near neighbor atoms. B_M is the effective field due to the orbital and spin moment of the parent atom. The total field at the nucleus is referred to as the hyperfine field, B_{hf} . B_{hf} is found to be proportional to the atomic moment, and in the case of α -Fe and crystalline Fe-Y alloys[68], the conversion factor is $15T/\mu_B$. This factor will be used throughout the thesis.

In the absence of an external field, the hyperfine field can be approximated as

$$\vec{B_{hf}} = a\vec{S_0} + b\sum_{i=1}^{n} \vec{S_i}$$
(2.16)

where \vec{S}_0 and \vec{S}_i are the magnetic moments of the parent and neighbor atoms respectively and the sum runs over the *n* nearest-neighbors. The coefficients *a* and *b* relate the transferred field at the probe nucleus to the atomic moments causing it. In the case of a Mössbauer measurement with a magnetic probe atom, such as ⁵⁷Fe, B_{hf} is dominated by the contribution from the moment of the probe atom itself (*i.e.* the first term of equation (2.16)), and the effect of the neighbors amounts to only a few percent of the total field. However, with a non-magnetic atom such as ¹¹⁹Sn, the local contribution is zero and B_{hf} measured at the probe nucleus is due solely to the magnetic nearest-neighbors (*i.e.* the second term of equation (2.16)).

In summary, from a measured spectrum, the magnitude of the B_{hf} can be determined from the positions of the absorption peaks, and the information about the spin



Figure 2.6: Mössbauer spectra of α -Fe at room temperature (a) $B_{ext} = 0$, (b) $B_{ext} = 5$ T, $\theta = 0^{\circ}$, (c) $B_{ext} = 0.35$ T, $\theta = 90^{\circ}$. B_{ext} indicates the external magnetic field. From ref.[67]

structure can also be obtained from the intensity ratio of the six lines.

D. Combined magnetic and quadrupole interactions

Since both the magnetic and quadrupole hyperfine interactions are direction dependent, when both are present, the resultant behavior can be much more complex. The formal Hamiltonian is the sum of equations 2.13 and 2.6 and has no general solution. The spectra can be obtained by calculating the eigenvalues and eigenfunctions of the Hamiltonian. In general, additional "forbidden" transitions ($\Delta I_x = \pm 2$) occur and ⁵⁷Fe and and ¹¹⁹Sn spectra will consist of eight absorption lines. However, if the quadrupole interaction is much smaller than the magnetic interaction (*i.e.* $e^2qQ \ll \mu B$) and can be treated as a first-order perturbation to the latter, there is a relatively simple solution giving eigenvalues as

$$E = -q\mu_N BI_z + (-1)^{|I_z| + 1/2} \frac{\Delta}{2} \left(\frac{3\cos^2\theta - 1}{2}\right)$$
(2.17)

where θ is the angle between magnetic field and EFG's principal axis (assuming EFG tensor is axially symmetric *i.e.* $\eta=0$). In this case, the excited state splits into four sublevels and the ground state into two, similar to the case of magnetic interaction. However, the positions of the sublevels are shifted due to the quadrupole interaction. The energy levels are illustrated in Fig. 2.7 and a six-line spectrum is expected.

Time-Dependent Interactions

The Mössbauer process (recoil-free emission and absorption of γ -rays) and the hyperfine interactions have characteristic times. Thus, in principle, they are both time-dependent. Time-dependent changes in the nuclear environment, often referred to as relaxation processes, can relate to structural changes in systems as well as to changes involving the electronic configuration. When the time dependence involves the orientation of the electronic spin and hence affects the magnetic hyperfine interaction, the process is often known as magnetic relaxation and can be considered in terms of a time dependence of the magnitude and direction of the magnetic hyperfine field experienced by the nucleus. The characteristic time of the magnetic relaxation,



Figure 2.7: The energy-level schemes for an $I_g=1/2-I_e=3/2$ nuclear transition with combined magnetic and quadrupole splitting. The Mössbauer transition and the resulting spectra are also shown. From ref.[65]

 τ_R , can be defined as a period of time over which the magnitude and direction of the magnetic hyperfine field remains essentially unchanged. The reciprocal of the τ_R is called relaxation frequency.

The effect of magnetic relaxation on a measured spectrum is dependent on the relative magnitudes of the relaxation frequency f_R and the nuclear Lamor precession frequency f_L . If $f_R \gg f_L$, the relaxation frequency of the hyperfine field is so high that its time-average over a nuclear Lamor precession period $1/f_L$ is zero, thus the nucleus will experience no hyperfine field and the measured spectrum shows no magnetic

splitting. This is the paramagnetic case. If $f_R \ll f_L$, the relaxation frequency of the hyperfine field is very low and the nucleus can not feel the relaxation of the hyperfine field. This corresponds to the static case. When $f_R \sim f_L$, the calculation of the spectra becomes much more complicated. One approach to this problem is referred to as the stochastic model[69] where the hyperfine field is assumed to flip between two values +h and -h (*i.e.* up and down) with flipping frequencies f_{R1} $(+h\rightarrow-h)$ and f_{R2} $(-h\rightarrow+h)$. This model was initially applied to superparamagnets where the net magnetization is zero and hence the two flipping frequencies were equal. The method was extended later to calculate the spectra of crystalline magnetic alloys[70,71] where the two flipping frequencies were assumed to be unequal since the magnetization in π ferromagnet is not zero.

2.3.2 Mössbauer spectrometer

The Mössbauer spectrometer we used is shown schematically in Fig. 2.8. The source was attached to a velocity transducer and its velocity was controlled by a digital function generator and a Mössbauer driving unit. In our measurements, the velocity is set in a triangle (constant acceleration) or sinusoidal mode. γ -rays transmitted through the sample were detected by a proportional counter. The signal is amplified and fed to a single channel analyzer (SCA), which rejects all but the signals produced by γ -photons around 14.4keV. The output of the SCA is sent to the ACE-MCS system (EG&G ORTEC), which was installed in a personal computer (PC) and performs multichannel scaling. The recording of γ -ray count in each channel and the controlling of the velocity transducer are synchronized by the function generator so that every channel number corresponds to a particular velocity. The detailed description is presented below.

Sources

The Mössbauer sources we have used are ⁵⁷CoRh and Ca^{119m}SnO₃ for ⁵⁷Fe and ¹¹⁹Sn Mössbauer measurements respectively. They are unsplit single line sources because



Figure 2.8: A schematic arrangement for our Mössbauer spectrometer

a multi-line source will make the measured spectra much more complicated. The nuclear decay schemes of ⁵⁷Co and ^{119m}Sn are shown in Fig. 2.9. The excited state of ⁵⁷Fe at 136.3keV is populated by electron capture of ⁵⁷Co with a half-life of 270 days. 91% of the decays from 136.3keV state result in a 121.9keV γ -ray and therefore the first excited state at 14.4keV is efficiently populated. The 14.4keV transition occurs between the excited state of nuclear spin quantum number 3/2 and the ground state of spin 1/2. While most of the 14.4keV transitions lead to internally converted electrons, about 10% result in 14.4keV γ -rays, which are used in Mössbauer measurements. The half-life of the excited state is 97.7ns, which yields a natural full-width of 0.192mm/s according to the Heisenberg uncertainty principle. For ¹¹⁹Sn, the γ -transition used for Mössbauer measurements is the 23.87keV decay from the first excited state. The precursor is metastable ^{119m}Sn which has a half-life of 250 days and can be prepared by adequate activity by neutron capture in isotopically enriched ¹¹⁸Sn. The 23.87keV





Figure 2.9: The nuclear decay schemes of ⁵⁷Co and ^{119m}Sn

transition is a $3/2 \rightarrow 1/2$ magnetic dipole transition similar to ⁵⁷Fe. The excited-state has a lifetime of 18.3ns corresponding to a natural full-width of 0.626mm/s, which is much larger than that of ⁵⁷Fe.

Detectors

Detectors used in this study were proportional counters filled with Xe plus $3\% CO_2$ gases. CO_2 is added as quench gas and it suppresses the photon-induced effects, which can leads to a loss of proportionality. The gas pressure of the detectors used for ⁵⁷Fe Mössbauer measurements is 1 atm. For ¹¹⁹Sn Mössbauer spectroscopy, although the energy of γ -rays used for Mössbauer work (23.87keV) is quite close to that of the K_{α} X-ray of Sn (25keV), the Xe- CO_2 proportional detector can still resolve the useful γ -ray from the X-ray. By using a palladium foil of 0.1mm thick, the 25keV X-ray can be preferentially absorbed as palladium has a K-edge for photoelectric absorption of 24.35keV, just between the unwanted X-rays and the required 23.88keV γ -rays. The detector with gas pressure of 2 atm was used for ¹¹⁹Sn measurements since it produce count rates about twice that obtained by 1 atm detectors.

Cryostat

Since the ordering temperatures of all our samples are below room temperature, most measurements were made at lower temperatures. For these measurements, the sample was placed in a cryostat and its temperature was controlled by a home-made temperature controller with the precision better than 0.1K. Cooling is provided by helium gas. Liquid helium was drawn from the helium reservoir through the capillary tube and vaporized by the vaporizer heater (see Fig. 2.10). Normally, the helium gas was heated to a temperature slightly lower than the set point of the sample, and a small current (typically about 100mA) is used to maintain the sample at its set temperature. In this case, the sample's temperature can be quite stable in spite of the large variation in the helium flow rate. The cryostat has two windows which allow the γ -ray to pass through. The window material is aluminized mylar, which is





transparent to the γ -rays used.

Mössbauer spectra in high magnetic fields (>100mT) were recorded using a cryostat with a superconducting magnet which can produce magnetic fields up to 7 Tesla. For the measurements with magnetic field parallel to the γ -beam, the source was located inside the cryostat at the null point of the magnet (Fig. 2.11). Since the transducer had a larger load in this case, it was operated in sinusoidal mode so that error signal was reduced due to the smoother change of velocity. In the case of magnetic field being perpendicular to the γ -beam or without magnetic field, the sources were outside the cryostat and the transducer was set to constant-acceleration mode. The sample's temperature was controlled in a similar way.

2.3.3 Analysis Techniques

The materials we have studied are amorphous alloys in which various local environments exist. Therefore, the hyperfine parameters, such as quadrupole splitting and magnetic hyperfine field, will have continuous distributions rather than some small number of discrete values as for crystalline materials. Different fitting procedures have been used to obtain these distributions and they will be described below.

Qgauss

This fitting routine is used to fit the spectra with a distribution of quadrupole splittings. Since the Curie temperatures of all our samples are below room temperature, the spectra of these alloys at room temperature were fitted by Qgauss, which assumes a Gaussian distribution of quadrupole splittings. A linear correlation between the isomer shift and the quadrupole splitting has been introduced to account for the asymmetries in the spectra. A measured quadrupole split spectrum is shown in Fig. 2.12 with the fitted quadrupole splitting distribution. By fitting the room temperature spectra, the average quadrupole splitting, Δ_{av} , can be obtained. It was shown in Section 1.3.1. that for combined magnetic and quadrupole interactions, the effect of quadrupole interaction (if it is much smaller than the magnetic interaction)



Figure 2.11: A schematic drawing of the Mössbauer cryostate with a superconducting magnet.



Figure 2.12: (a) Mössbauer spectrum of a-Fe₉₂Zr₇Sn at room temperature is shown with fits. (b) the derived quadrupole splitting distribution.

is to shift the magnetically split lines by

$$\varepsilon = (-1)^{|I_s|+1/2} \frac{\Delta}{2} \left(\frac{3\cos^2\theta - 1}{2}\right)$$

For our amorphous alloys, θ may take any value between 0 and 2π and thus ε can be positive or negative for a given I_z . The result is that the magnetically split lines are not shifted, but broadened. The broadening can be estimated by replacing Δ with Δ_{av} and calculating the root mean square of ε . When fitting all spectra measured below the Curie temperature, the full linewidth was set to the natural full-width Γ plus the broadening $2\overline{\varepsilon}$ ($\overline{\varepsilon}$ is the root mean square of ε) due to the quadrupole splitting.

Window's method

Window's method[72] is the most commonly used procedure to fit the magnetically split spectra for amorphous samples. The technique is based on a series expansion of the probability function of hyperfine field $P(B_{hf})$

$$P(B_{hf}) = \sum_{n=1}^{N} a_n f_n(B_{hf})$$
(2.18)

where $f_n(B_{hf}) = \cos(n\pi B/B_{hf}^{max}) - (-1)^n$ satisfying the boundary conditions $P(B_{hf}^{max}) = 0$ and $dP/dB_{hf} = 0$ for $B_{hf} = 0$ and $B_{hf} = B_{hf}^{max}$. Except for the boundary conditions, this routine makes no assumptions about the shape of the $p(B_{hf})$. Similar to Qgauss, we have assumed a linear correlation between the isomer shift and the hyperfine field. Since only a finite number of terms of the series are used, oscillatory components in $P(B_{hf})$ are necessarily obtained, and this requires careful interpretation as described later. Another problem is that this method sometimes gives unphysical negative probability $P(B_{hf})$. These problems are illustrated in Fig. 2.13.

Asymmetric Gaussian model

Like Window's method, this procedure is used to fit the magnetically split spectra of amorphous systems. It differs from Window's method in that it assumes that



Figure 2.13: (a) Mössbauer spectrum of a-Fe₉₀Zr₁₀ at 65K is fitted by Window's method. (b) the derived hyperfine field distribution.

 $P(B_{hf})$ is an asymmetric Gaussian function with two different widths to higher and lower fields. This assumption is based on the fact that the $P(B_{hf})$ obtained from Window's method resembles an asymmetric Gaussian function. Again, a linear correlation between the isomer shift and the hyperfine field is assumed. Usually, the fitting quality of this procedure is not as good as that of the Window's method. However, in some cases, this simple procedure can fit the spectra as well as Window's method. This procedure show several advantages over Window's method. First, it eliminates the artifact oscillatory results in $P(B_{hf})$. Second, it can not yield negative values of $P(B_{hf})$, and is stable even in the presence of relatively large noise and line overlap. In Fig. 2.14, a measured spectrum is shown with fit obtained by using this fitting routine. The obtained $P(B_{hf})$ is also shown.

Subtraction Procedure

Besides the oscillatory components in $P(B_{hf})$, there are other problems associated with the deconvolution of $P(B_{hf})$ from a measured spectrum for an amorphous sample. Usually, the absorption lines in a spectrum are very broad due to the various local environments in amorphous materials. The overlap among the six lines of a magnetically split spectrum makes all conventional deconvolution routines unstable. Moreover, the presence of magnetic texture affects the intendities of the $\Delta m_I = 0$ transitions (lines 2 and 5) and can substantially modify the derived $P(B_{hf})$. Standard solutions to the magnetic texture problem are either to ignore it, *i.e.*, to argue that the spin directions will be essentially random and set the intensity ratio R equal to 2, or else to allow R to be a variable parameter in the fit. Neither procedure is satisfactory. The first is simply wrong as R=2 is rarely observed for ribbon samples, while the second, allowing R to vary, exacerbates the problems, since the shape of $P(B_{hf})$ and R are highly conclused fitting parameters.

Kaptás et al. have proposed a special procedure to obtain unambiguous $P(B_{hf})[73]$. It is known that for a ribbon sample, R is usually smaller than 2 due to the magnetic texture (see Fig. 2.15(a)). If a small external field is applied parallel to the



Figure 2.14: (a) Mössbauer spectrum of a-Fe₉₃Zr₇ at 5K is fitted by the asymmetric Gaussian model. (b) the derived hyperfine field distribution.

plane of ribbons and perpendicular to the γ -ray in Mössbauer measurements, spins in the ferromagnetic phase will be polarized along the field direction. Since $R = 4sin^2\theta/(1 + cos^2\theta)$ (θ is the angle between the spin and the γ -beam), it will be increased for a spectrum recorded in the small field (see Fig. 2.15(b)). If the field is small enough, it will not affect the hyperfine magnetic fields experienced by the nuclei, and hence the hyperfine field distribution $P(B_{hf})$. Therefore, except for the increase of R, the spectrum with a polarizing field (will be referred to as polarized spectrum) is the same as the spectrum without the polarizing field (unpolarized spectrum). By subtracting the unpolarized spectrum from the polarized spectrum, a two-line pattern is obtained (see Fig. 2.15(c)) and $P(B_{hf})$ can be derived from the two-line spectrum. This procedure has the following advantages: First, it minimize the line overlap by subtracting off the other four lines. Second, it eliminates the magnetic texture problem as we do not need to know the intensity ratio to fit the two-line pattern. Therefore, more reliable $P(B_{hf})$ can be obtained by using this procedure.

Usually, the polarization effect is enhanced if the sample is cooled from above the ordering temperature in the polarizing field (in our case, it is produced by a permanent magnet). It should be noted that this subtraction procedure only works when the system responds homogeneously. If some of the spins in the system do not respond to a small polarizing field for some reason, their contribution to the polarized and unpolarized spectra are the same, and thus will be cancelled in the subtraction process. In this case, the obtained two-line pattern contains no information about these spins and the derived $P(B_{hf})$ can not represent the whole sample. This procedure is also not suitable for strongly frustrated systems. Since the large anisotropy in strongly frustrated systems makes it hard to rotate the magnetization, therefore the effect of spin polarization for these materials by a small field is not significant.

Relaxation models

In the stochastic approach [69] described before, the magnetic relaxation was modeled by assuming the hyperfine field being flipping between two values +h and -h



Figure 2.15: Mössbauer spectra of a-Fe₉₀Zr₁₀ at 5K (a) polarized in a 50mT field, (b) unpolarized, (c) difference of polarised and unpolarized spectra.
(i.e. up and down) with flipping frequencies f_{R1} $(+h\rightarrow -h)$ and f_{R2} $(-h\rightarrow +h)$. The model, referred to as a single-site relaxation model, has been applied to crystalline magnetic systems [70,71] but the presence of substantial static disorder reduces its applicability to amorphous materials as shown in Fig. 2.16. At T=5K, the amorphous alloys we have studied exhibit very broad distributions of hyperfine field, indicating strong static disorder. Moreover, this static disorder remains significant even when the temperature is close to the ordering temperature. Therefore, to tackle the relaxation problem in amorphous systems, both relaxation and static disorder need to be considered. As a result of static disorder, e wide distribution of cluster moments is expected. However, both the shape and the temperature dependence of this distribution are unknown. In our models, this distribution has been assumed to be equivalent to that of the static hyperfine fields, and the temperature dependence has been neglected. Thus, the cluster moment distribution for a given alloy was determined from Mössbauer spectrum at 5K in zero field and remained unchanged for all temperature. The asymmetric Gaussian model was used to obtain the hyperfine field distribution. This model fits the 5K spectra quite well and simplifies subsequent analysis by ensuring a smooth hyperfine field distribution and minimizing the number of fitting parameters used. Relaxation effects were added in two ways. In 'Relax-1' all of the components in the hyperfine field distribution are assumed to relax at the same rates: f_{R1} and f_{R2} , and they are varied in order to obtain the best fit. The two flipping frequencies are assumed to be correlated with the magnitude of the hyperfine field in 'Relax-2' where high field components relax more slowly than those at lower fields. An exponential dependence of the frequency on field was used to model an (assumed) activated flipping process.

2.4 Magnetization

Magnetization was measured using a SQUID magnetometer in the Physics Department at McMaster University. Magnetic fields of up to 5.5T were produced by a

٠.



Figure 2.16: Mössbauer spectra of a-Fe₉₂Zr₈ at 125T. A single field relaxation model (without considering the static disorder) can not fit the spectrum.



Figure 2.17: A schematic representation of the second-derivative detection coil configuration

superconducting solenoid. Samples were obtained by cutting the original ribbons about 1mm wide and 20μ m thick into pieces of ~3mm long. Samples of this size or smaller are effectively point sources. The specimen is mounted on the surface of a long quartz tube by using insulating glue. When it is in the middle of the tube so that the tube always extends completely through the pick up coils, the resulting signal in the SQUID detector will represent only the sample. In this case, the tube presents a uniform background to the closely spaced pick up coils, and only the signal from the sample remains. The SQUID pick up coils are wound in a second-derivative configuration in which the upper and lower single turn are counterwound with respect to the two-turn center coils (see Fig. 2.17). This configuration strongly rejects interference from nearby magnetic sources, particularly the uniform field from the superconducting magnet, making the SQUID detector relatively insensitive to drifts in the magnet following even very large field changes. This enables the system to function without the need for a superconducting shield around the SQUID sensing loop. Samples were cooled by cold gas drawn into the cooling annulus outside the sample chamber from the liquid helium bath and were heated by applying power to either the sample chamber or gas heater (Fig. 2.18). Longitudinal copper wires along the length of the sample chamber maintain thermal uniformity, and a few torr of helium gas in the sample chamber provides thermal contact with the sample. The system uses two thermometers to cover the entire temperature range of 1.9 to 400K. A germanium resistance thermometer is used from 1.9 to 40K, and a platinum resistance thermometer is used above 40K. The normal measurement process is to position the sample far below the detection coils first, and then to raise the sample through the coils while measuring the output of the SQUID detector. Therefore, the raw data from a measurement are a set of voltage readings taken as a function of position as the sample is moved upward through the detection coils. The magnetic moment is calculated as the root-mean-square of the voltage readings, normalized by the calibration factor. The magnetic moment calibration for the system is determined by measuring a palladium standard sample, which is a right circular cylinder approximately 3 mm diameter x 3 mm high. Once a sample is mounted, measurements including field and temperature changes can be programmed, and thus performed automatically.



Figure 2.18: The schematic configuration of the sample chamber and the temperature control system of the SQUID magnetometer.

Chapter 3

Experimental Results

3.1 Sample Characterization

All of the samples studied here are paramagnetic at room temperature. A typical Mössbauer spectrum measured at room temperature is shown in Fig 3.1(a). The two absorption lines due to quadrupole splitting are broadened so much as a result of the distribution of local iron environments that they can hardly be resolved. The Qgauss fitting program was used to fit the room temperature spectra and the obtained distribution of the quadrupole splitting is plotted in Fig 3.1(b). A linear correlation between isomer shift, δ , and quadrupole splitting, Δ , was assumed to account for the asymmetry of the observed spectra. Some fitted parameters, including average isomer shift relative to α -Fe ($\langle \delta \rangle$), average quadrupole splitting ($\langle \Delta \rangle$) and width (standard deviation) of the distribution of quadrupole splittings (σ_{Δ}) are summarized in 'Table 3.1.

3.2 Magnetic Properties of a-FeZr alloys

3.2.1 Magnetic Relaxation Around T_c

Determination of Ordering Temperature T_c



Figure 3.1: (a) Room temperature Mössbauer spectra of $Fe_{02}Zr_8$ fitted with Qgauss model. (b) The distribution of the quadrupole splitting.

Typical zero field Mössbauer spectra at different temperature for one of our Fe-Zr samples, Fe₉₃Zr₇, are plotted in Fig 3.2. The spectra were fitted by using Window's method (described in Chapter 2) and the temperature dependence of average hyperfine field, $\langle B_{hf} \rangle$), is shown in Fig 3.3 (a). The ordering temperature, T_c, is defined as the temperature at which the average hyperfine field become non-zero. T_c can also be obtained from the plot of absorption vs. temperature. Above T_c, the doublet spectra due to quadrupole splitting yield high absorptions. After the magnetic order sets in, the spectra begin to show six lines and the absorption starts to drop. Therefore, it is expected that the temperature dependence of the absorption changes slope at the ordering temperature (see Fig. 3.3 (b)).

Mignetization of all Fe-Zr samples was measured by a SQUID magnetometer in fields of up to 5.5T. From the modified Arrott plots, *i.e.*, $M^{1/\beta}$ as a function of $(B/M)^{1/\gamma}$ where β and γ are critical exponents, the ordering temperature can be determined since the critical plot at $T=T_c$ is a straight line through the origin. It has been shown that the critical exponents obtained from magnetization measurements for iron-rich Fe-Zr alloys[74,75] agree well with the theoretical predictions for the homogeneous three-dimensional Heisenberg model[76] where $\beta=0.365$ and $\gamma=1.387$. Thus, these values have been used for all of the samples studied here. The magnetization curves and the modified Arrott plots around T_c for Fe₉₀Zr₁₀ are shown in Fig. 3.4. The ordering temperature obtained from the modified Arrott plots is denoted as T_c^m and is $230\pm6K$ for Fe₉₀Zr₁₀. T_c^m for all Fe-Zr samples in this study are listed in Table 3.2 and they are in good agreement with the values of T_c determined from Mössbauer measurements.

Evidence of Magnetic Relaxation Around T_c

The early evidence of magnetic cluster relaxation above T_c in iron-rich amorphous Fe-Zr alloys was reported several years ago[77,78]. While the zero field Mössbauer spectra at room temperature were typical for amorphous paramagnetic materials, room temperature spectra measured with an external field were quite different from those expected in the case of mixed static quadrupole and magnetic hyperfine inter-

Samples	$\delta_0 \ (mm/s)$	$<\Delta>(mm/s)$	$\sigma_{\Delta} \ ({ m mm}/{ m s})$	
Fe ₈₉ Zr ₁₁	-0.101±0.006	$0.369 {\pm} 0.001$	0.283 ± 0.005	
Fe ₉₀ Zr ₁₀	-0.100	0.377	0.300	
Fe ₉₂ Zr ₈	-0.082	0.368	0.284	
Fe ₉₂ Zr ₇ Sn	-0.075	0.379	0.287	
Fe93Zr7	-0.084	0.354	0.297	
Fe _{92.5} Hf _{7.5}	-0.051	0.352	0.280	
Fe ₉₁ Sc ₉	-0.076	0.368	0.271	

Table 3.1: Mössbauer parameters of all the samples at room temperature

Table 3.2: Ordering temperature of ~FeZr alloys

Samples	Fe ₈₉ Zr ₁₁	Fe ₉₀ Zr ₁₀	Fe ₉₂ Zr ₈	Fe ₉₂ Zr ₇ Sn	Fe ₉₃ Zr ₇
T_{c} (K) (from $ < B_{hf}(T) >)$	260	230	178	180	134 ± 5
T_{c} (K) (from absorption)		-	176		149 ± 5
T_{c}^{m} (K) (from Arrott plots)	252	230		190	150 ± 6



Figure 3.2: Mössbauer spectra of Fe93Zr7 at different temperatures fitted with Window's model.



Figure 3.3: The temperature dependence of (a) average hyperfine field obtained by using Window's method and (b) Mössbauer absorption for $Fe_{98}Zr_7$.



Figure 3.4: (a) Magnetization curves and (b) modified Arrott plots at temperatures around T_c for $Fe_{90}Zr_{10}$.

actions. Yamamoto *et al.* also reported that the superparamagnetic behavior was observed in Fe₉₂Zr₈ above T_c [79].

Evidence of magnetic relaxation below T_c has also been reported. The average hyperfine fields derived from Mössbauer spectra recorded in a 3T field are about 10T larger than those obtained from zero field spectra at temperatures close to but below $T_c[22]$. The significant enhancement of the average hyperfine fields must be due to the slowing down of relaxation rates by an external field.

Fitting of Mössbauer spectra with Relaxation Models

Fitting routines considering both the static and time-dependent hyperfine interactions were developed. The two routines are called Relax-1 and Relax-2 as described in Chapter 2.

Zero field Mössbauer spectra of $Fe_{90}Zr_{10}$, $Fe_{92}Zr_8$ and $Fe_{93}Zr_7$ were fitted by the two relaxation models as well as Window's method. In fig. 3.5, Mössbauer spectra of $Fe_{92}Zr_8$ measured at different temperatures are shown with fits obtained by different methods. The simple relaxation model where all clusters are assumed to relax with the same rate (Relax-1) can not fit most of the spectra. In Relax-2, a correlation between the cluster moments and their relaxation rates is introduced, and much better fitting is achieved. However, the fitting quality is not as good as that obtained by Window's method. The reduced χ^2 values obtained from the fitting programs are indications of the fitting quality and are plotted in Fig. 3.6 for the three fitting routines.

The same analysis was performed on $Fe_{93}Zr_7$ and $Fe_{90}Zr_{10}$. The reduced χ^2 vs. reduced temperature are shown in Fig. 3.7 for the two samples. Similar behavior is observed for all three alloys. Relax-1 was proved to be the worst fitting routine among the three models, and although Relax-2 does not work as well as Window's model, it does yield reasonable fits. For $Fe_{92}Zr_8$, a single site relaxation model was also used where the static disorders were not considered. It works only in a very narrow temperature range $(0.91T_c \leq T \leq 0.97T_c$ or about 10K) as expected, since in amorphous materials, the wide distribution of local environment leads to wide distributions of quadrupole splittings as well as hyperfine fields (static disorders). If



Figure 3.5: Mössbauer spectra of Fe92Zr8 fitted with (a) Window's method and (b) Relax-2.



Figure 3.6: Reduced χ^2 vs reduced temperature for Fe₉₂Zr₈. Results for three different models are compared.

we include the quadrupole distribution determined from room temperature ($\sim 1.7 T_c$) spectrum, the model can fit spectra above T_c , but still fails below 0.91 T_c as the effect of static magnetic disorder starts to dominate.

Although Relax-2 can give reasonable fits to the spectra of all three samples, little new insight into the magnetic properties of the materials is obtained due to some artificial assumptions (as will be discussed in Chapter 4). In principle, some information about the clusters may be obtained from the simple single-site fits above T_c . For Invar (Fe₆₅Ni₃₅), plots of the temperature dependences of magnetisation



Figure 3.7: Reduced χ^2 vs reduced temperature for Fe₉₃Zr₇ and Fe₉₀Zr₁₀. Results for three different models are compared.

 $(< M > = (f_1 - f_2)/(f_1 + f_2))$ and average relaxation frequency $(\nu = (f_1 + f_2)/(f_1 \cdot f_2))$ allowed a clearer definition of the characteristic temperature than was possible on the basis of zero velocity thermal scans or average hyperfine fields [70,71]. These parameters are plotted in Figs. 3.8(a)-(d) for Fe₉₂Zr₈. It is found that the relaxation model tends to underestimate T_c. Finally, $d \ln(\nu)/d(1/T)$ above T_c may be used to derive the size of the relaxing clusters. The slope of the solid line in Fig. 3.8(b) is about 6000K, following the analysis of Rancourt[71] and using a T_c of 176K, we obtain an average cluster size of ~ 10Å, much smaller than the value (~100Å) obtained from neutron scattering[80].

3.2.2 Second Transition

For the Fe-Zr system at the iron-rich end, only the alloys with Fe content between 89 at.% and 93 at.% can be made amorphous by the melt-spinning technique and they are the materials studied here.

$\mathrm{Fe}_{89}\mathrm{Zr}_{11}$

For a-Fe₈₉Zr₁₁, the Mössbauer spectra measured in a 3.5T field parallel to the γ -beam are shown in Fig. 3.9. The six lines observed in a magnetically split spectrum have intensities 3:R:1:1:R:3, where $R = 4sin^2\theta/(1 + cos^2\theta)$, and θ is the angle between the magnetic moment and the direction of γ -beam. There is no evidence of the presence of lines 2 and 5 at low temperature, which is the characteristic feature of the second transition previously observed in Fe₉₃Zr₇[22]. Since Fe₈₉Zr₁₁ is the least frustrated sample among the Fe-Zr group, it is possible that it does not show two magnetic transitions. In order to verify our speculation, R at different temperature need to be derived. However, conventional fitting routines (like Window's method) can not yield an accurate R value due to the correlation between R and the hyperfine field distribution, P(B_{hf}). Therefore, we need to derive P(B_{hf}) independently by a subtraction procedure. Polarizing the sample with a 100mT field has strong effects: the intensities of lines 2 and 5 increase easily and R of around 3.7 is achieved. Then the P(B_{hf}) derived from the difference of polarized and unpolarized spectra



Figure 3.8: Comparison of T_c determinations from single site relaxation fits (a) & (b) and static distribution fits (Window's method) (c) & (d) for $Fe_{92}Zr_8$.



Figure 3.9: Mössbauer spectra of $Fe_{89}Zr_{11}$ measured with a 3.5T field parallel to the γ -beam. The 5K spectrum is shown with two fits: one with R=0 and another with R=0.04 obtained by using the $P(B_{hf})$ derived from the subtraction procedure.

at a certain temperature was checked by using it to fit the original polarized and unpolarized spectra. Most $P(B_{hf})$ obtained in this way can give reasonable fits to the original spectra, but the fitting quality is not very good. This does not mean that the subtraction procedure has some problems. It will be seen later that for $Fe_{90}Zr_{10}$, $P(B_{hf})$ obtained from the subtraction procedure can fit original spectra quite well at all temperature. The fact that the subtraction procedure does not work well for Fe89Zr11 is probably due to the strong anisotropy present in the sample. For ribbon samples, the demagnetization effect tend to align the spins in the plane of the ribbons, which will cause R to be greater than 2 (the value expected for random spin orientations). However, the measured R for most ribbon samples is less than 2 due to the quenched-in stresses in the ribbons. For Fe₈₉Zr₁₁, R is only about 1.0, in contrast to the values of ~ 1.5 obtained for Fe₉₀Zr₁₀. The very small values of R for $Fe_{89}Zr_{11}$ indicate the presence of very strong anisotropy due to the stresses. The strong anisotropy can prevent some spins from responding to the small polarizing field and therefore yields $P(B_{hf})$ that are not representative of the whole sample (the validity of the subtraction procedure is discussed in Chapter 2). $P(B_{hf})$ obtained at 5K has been used to fit the spectrum with the 3.5T field at the same temperature. Since the shape of the $P(B_{hf})$ is fixed, the fitting program has only R and a field shift as adjustable parameters. The latter takes account of the applied field, which reduces the hyperfine field at the iron nucleus. R of 0.04 ± 0.01 was obtained from this procedure. However, no improvement in fitting quality can be seen for the fit with R=0.04 compared to that with R=0 (see Fig. 3.9).

Fe₈₉Zr₁₁ shows typical magnetization behavior of conventional ferromagnets (Fig. 3.10). Magnetization has reached 92% of the saturation value (extrapolation of M vs. 1/B plot to 1/B=0) in a small field of 0.1T. M_z is a measure of the component of the iron moment in the field direction, and is obtained by extrapolating the high field part ($2T \le B \le 5.5T$) of the magnetization curves to B=0 T. The average total iron moment (μ_{av}) can be obtained from average hyperfine field, $\langle B_{hf} \rangle$, derived from Mössbauer spectra. If the Mössbauer spectra are measured in an external field, the



Figure 3.10: Magnetization curves at different temperatures for $Fe_{89}Zr_{11}$.

derived $\langle B_{hf} \rangle$ includes the contributions from the external field and the demagnetizing field. We have corrected these effects by adding the external field and subtracting off the demagnetizing field, and the obtained μ_{av} are plotted in Fig. 3.11, where it is compared with M_z. μ_{av} and M_z are in good agreement at all temperatures, indicating



Figure 3.11: Comparison of component of iron moment in the field direction, M_x , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 3.5T field for Fe₈₉Zr₁₁.

a collinear state down to 5K.

These Mössbauer and magnetization measurements indicate that a-Fe₈₉Zr₁₁ exhibits conventional ferromagnetic behavior down to 5K and no evidence of a second transition is observed.

$Fe_{90}Zr_{10}$

Similar measurements have been performed on $Fe_{90}Zr_{10}$. Although small differences between low-temperature and high-temperature spectra can be seen in Fig. 3.12, R obtained by fitting the spectra with Window's method is zero at all temperatures



Figure 3.12: Mössbauer spectra of $Fe_{90}Zr_{10}$ measured with a 3T field parallel to the γ -beam. The 5K spectrum is shown with two fits: the upper one where R is forced to be zero, the lower one where R is allowed to take its optimum value.

between 5 and 86K. Fortunately, for this weakly frustrated alloy, the subtraction procedure can be applied to obtain the more reliable $P(B_{hf})$ independently. The $P(B_{hf})$ obtained from the subtraction procedure fit the original spectra quite well. Since R obtained from zero field spectra of $Fe_{90}Zr_{10}$ is about 1.5, much closer to 2 compared to the values of ~1 for $Fe_{89}Zr_{11}$, a smaller anisotropy in $Fe_{90}Zr_{10}$ ribbons due to stresses is expected. This is the reason that the subtraction procedure works better in $Fe_{90}Zr_{10}$ than in $Fe_{89}Zr_{11}$. The field spectra were fitted using the $P(B_{hf})$ obtained from the subtraction procedure and the fitted R values as a function of temperature are shown in Fig. 3.13. R is zero at high temperatures when the sample is fully



Figure 3.13: Temperature dependence of R obtained from Mössbauer spectra with a 3.5T field for $Fe_{90}Zr_{10}$

magnetized parallel to the γ beam. As the sample is cooled below a certain temperature (labelled as T_{xy} in Fig. 3.13), R begins to increase, indicating that the system enters a noncollinear state. A similar transition has been observed in Fe₉₃Zr₇ and been explained in terms of transverse spin freezing. Above T_{xy} , the longitudinal spin components order ferromagnetically while the transverse components precess rapidly with time-average of zero. Below T_{xy} , the transverse components freeze in random directions without affecting the collinear order of the longitudinal components, and causes the system to enter a noncollinear state.

Although R at 5K is small, the highly constrained fitting procedure allows reliable determination of R. In Fig. 3.12, the 5K spectrum is shown with two fitted lines: one where R is forced to be zero, the other one where R is allowed to take its optimum value. The fits clearly show the presence of lines 2 and 5 at 5K. Fitting the non-zero R at low temperatures (in this case only two points) with a linear function gives the freezing temperature, T_{xy} , of 28±3K. To get a quantitative measure of the deviation of the spin orientations from the field direction, we consider a simple asperomagnetic model where the iron moments are distributed randomly within a cone of half-angle ψ [81]. From R=0.14±0.01, ψ is estimated to be 22±1° at 5K.

Magnetization in fields of up to 5.5T was measured. All magnetization curves shown in Fig. 3.14 exhibit small slopes at high field $(2T \le B \le 5.5T)$. In Fig. 3.15, M_z is compared with the average iron moment (μ_{av}) obtained from Mössbauer spectra measured in a 3T field. μ_{av} and M_z are consistent above about T_{xy} , but begin to separate below this temperature: another characteristic feature of transverse spin freezing. In the high temperature collinear state, μ_{av} and M_z are the same. After the transverse spin components are frozen, they do not affect M_z since they are perpendicular to the field direction, however, they do contribute to the total moment, and therefore cause the separation of μ_{av} and M_z . Using the same cone model described above, ψ is estimated to be $17\pm4^\circ$ from the ratio of M_z to μ_{av} , consistent with the value obtained from fitted R.

$Fe_{92}Zr_7Sn$

The initial motivation to prepare $Fe_{92}Zr_7Sn$ is to study the spin correlation in Fe-Zr system by ¹¹⁹Sn Mössbauer spectroscopy with Sn as probe atoms. It is expected that 1 at.% of Sn will not cause significant changes of structural and magnetic properties. In



Figure 3.14: Magnetization curves at different temperatures for Fe90Zr10.



Figure 3.15: Comparison of component of iron moment in the field direction, M_x , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 3T field for Fe₉₀Zr₁₀.

fact, the temperature dependence of the average hyperfine field and the magnetization for $Fe_{92}Zr_7Sn$ and $Fe_{92}Zr_8$ (Fig. 3.16) show almost identical behavior. T_c obtained from Fig. 3.16(a) for the two samples are very close (185K and 178K for $Fe_{92}Zr_7Sn$ and $Fe_{92}Zr_8$ respectively). Therefore, we expect $Fe_{92}Zr_7Sn$ to exhibit very similar magnetic behavior to $Fe_{92}Zr_8$.

Mössbauer spectra of $Fe_{92}Zr_7Sn$ measured in a 3.5T field applied parallel to the γ -beam are shown in Fig. 3.1.. From Fig. 3.17, we can see that the lines 2 and 5, which are absent at high temperature, appear at low temperature. As it is not easy to



Figure 3.16: Temperature dependence of (a) average hyperfine field and (b) magnetization (linear extrapolation of high field magnetization curves to B=0T) for $Fe_{92}Zr_7Sn$ and $Fe_{92}Zr_8$.

2



Figure 3.17: Mössbauer spectra of Fe₉₂Zr₇Sn measured with a 3.5T field parallel to the γ -beam.

polarize the spins in this system by a small field, we were not able to use the subtraction procedure to obtain the $P(B_{hf})$. The spectra were fitted by Window's method. Since the intensities of lines 2 and 5 for low temperature spectra are relatively high, non-zero values of R were obtained for these spectra in spite of the large uncertainty of R due to the correlation of R and $P(B_{hf})$. The temperature dependence of the fitted R (Fig. 3.18) shows typical behavior of the transverse spin freezing: the increase of



Figure 3.18: Temperature dependence of R obtained from Mössbauer spectra with a 3.5T field for Fe92Zr₇Sn

R from zero at T_{xy} . From Fig. 3.18, T_{xy} is determined to be $46\pm8K$. R is 0.35 ± 0.05 at 5K, which gives a half-angle of $34\pm3^{\circ}$ for the cone model.

The magnetization curves in Fig. 3.19 show bigger high field slopes compared to those of $Fe_{90}Zr_{10}$, indicating a higher degree of noncollinearity. Due to the larger high field slopes in magnetization curves, M_z obtained by linear extrapolation of high field part has bigger uncertainty. In Fig. 3.20, M_z and μ_{av} at different temperature



Figure 3.19: Magnetization curves at different temperatures for Fe90Zr7Sn.



are shown. As the temperature is reduced, both of them increase but μ_{av} increases

Figure 3.20: Comparison of component of iron moment in the field direction, M_z , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 3.5T field for Fe₉₂Zr₇Sn.

faster than M_x . The rapid increase of μ_{av} at low temperature can be understood as a result of the freezing of transverse spin components, which contribute an extra component to μ_{av} . What is different from the case of Fe₉₀Zr₁₀ is that M_x and μ_{av} are not consistent above T_{xy} . This must be due to the following factors. First, not all of spins in the system are parallel above T_{xy} . While most spins are parallel to each other, some of the spins may point in the opposite direction. This kind of spin configuration (similar to a ferrimagnet) is possible in the case of strong exchange frustration. Indeed, this has been predicted by Monte Carlo simulations for system with high levels of frustration[82]. Moreover, magnetization curves above T_{xy} , which show large high field slopes (see Fig. 3.19), provide supporting evidence. Mössbauer spectra measured in a 3.5T field parallel to the γ -beam clearly indicate a collinear state above T_{xy} . After taking account of the demagnetizing field, a internal field of 2T is expected. If spins in the system are all parallel, we would expect that the magnetization measured in internal fields with similar magnitude should saturate. However, even in a external field of 5.5T (demagnetizing field is less than 0.1T in this case), which gives a internal field of almost 3 times bigger than that in Mössbauer measurements, the magnetization at 100K $(>2T_{xy})$ clearly has not saturated. For this kind of spin structure, M_z is smaller than the total moment, since when averaging over the sample to obtain M_z , the contributions from the anti-parallel spins cancel each other. Another possible reason is that Mössbauer spectroscopy is sensitive in the time scale longer than 10^{-9} s, whereas magnetization is an average over a few seconds. Therefore, if slow relaxation (with frequencies smaller than $\sim 10^9$ Hz but larger than ~ 10 Hz) occurs in the system, they will only contribute to the Mössbauer measurements and yield a μ_{av} larger than M_x .

When all spins are not parallel but pointing in opposite directions above T_{xy} , after the transverse components are frozen below T_{zy} , the spins are expected to lie within two cones with axes parallel or anti-parallel to the net magnetization respectively (see Fig. 3.21). Therefore, the single cone model will no longer be valid. However, if the population of the spins with the preferred direction anti-parallel to the net magnetization is small, the single cone model may be a reasonable approximation. By applying the single cone model here, a half-angle of $46\pm4^{\circ}$ was estimated from the ratio of M_x to μ_{av} , which is much larger than that obtained from R. Since R is derived from Mössbauer spectra in a 3.5T external field (the internal field is about 2T), it is possible that the field has suppressed the cone. If we use the magnetization in a external field of 2T (demagnetizing field is less than 0.1T), ψ is estimated to be $38\pm4^{\circ}$, in agreement with the $34\pm3^{\circ}$ obtained from R.



Figure 3.21: A schematic drawing of spin configuration below T_{xy} .

$Fe_{93}Zr_7$

The second transition has been observed in Fe₉₃Zr₇ before. Mössbauer spectra in field parallel to γ -rays indicate clearly that the system enters a non-collinear state below T_{xy}=78K[22]. Here, we will present our magnetization measurements on this system and compare them with the earlier Mössbauer results.

Comparison of M_z and μ_{av} is shown in Fig. 3.22. Similar behavior to Fe₉₂Zr₇Sn is



Figure 3.22: Comparison of component of iron moment in the field direction, M_z , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 3T field for Fe₉₃Zr₇. The dashed line is a guide to eyes.

observed. The difference between μ_{av} and M_z starts to increase below T_{xy} , revealing the freezing of the transverse components. The bigger slopes of the magnetization curves (Fig. 3.23), the smaller M_z at 5K and the higher T_{xy} compared with those of Fe₉₂Zr₇Sn indicate that it is more frustrated. The difference between μ_{av} and M_z above T_{xy} is also bigger than that of Fe₉₂Zr₇Sn, suggesting that more spins point in the direction opposite to the net magnetization due to a higher level of exchange frustration and/or more spins have low relaxation rates. The half-angle of the cone estimated from the ratio of M_z to μ_{av} is $64\pm4^\circ$, much larger than $42\pm3^\circ$, which is the value obtained from R. Even the ratio of the magnetization in an internal field of 2T (which is about the value of the internal field in Mössbauer measurements) to μ_{av} still gives a quite bigger ψ (55±4°), demonstrating the limitations of the single cone model.

Our main results on amorphous Fe-Zr alloys are summarized in Table 3.3.

Table 3.3: Summary of our main results on a-FeZr alloys: the average iron moment μ_{av} , ferromagnetic transition temperature T_c , transverse spin freezing temperature T_{xy} , R derived from Mössbauer spectra in parallel fileds, cone half-angle from R ψ_R , ratio of magnetization M_z to μ_{av} as well as cone half-angle ψ_M estimated from M_z/μ_{av} . ψ_M (B=2T) is obtained from the ratio of the magnetization in a field of 2T to μ_{av} .

Samples	μαν	T _c	T _{xy}	R	ψ_R	M_z/μ_{av}	ψм	ψM
	$(\mu_B/{ m Fe})$	(K)	(K)				(B=0T)	(B=2T)
Fe ₈₉ Zr ₁₁	1.56	260	0	_	-	-		_
Fe ₉₀ Zr ₁₀	$1.53 {\pm} 0.04$	230±5	28±3	0.14±0.01	22±1°	0.98	17	-
Fe ₉₂ Zr ₇ Sn	1.58	180	46±8	0.35±0.04	34±3°	0.85 ± 0.03	46±4°	38±4°
Fe93Zr7	1.55	135	78:::8	0.53±0.04	42±3°	0.72	64	55

The second transition temperature T_{xy} obtained from different measurements is plotted in Fig. 3.24. It can be seen that our results are in good agreement with those of other peoples.


Figure 3.23: Magnetisation curves at different temperatures for $Fe_{93}Zr_7$.



Figure 3.24: Comparison of T_{zy} determined from different measurements: • — Mössbauer spectroscopy (our data); \triangle — ac susceptibility[83]; + — ac susceptibility measured in a superposed dc field[21]; • — ac susceptibility[84]. The dashed line is a linear fit to our data.

3.2.3 Shape of the Hyperfine Field Distribution

Two magnetic transitions have clearly been observed in the Fe-Zr alloys with Fe content in the range of 90% to 93%. However, the nature of the second transition remains controversial. While the experimental results can be explained in terms of homogeneous transverse spin freezing, two inhomogeneous models have been proposed. Read *et al.*[25] have suggested that there are some iron-rich regions (or clusters) in the samples, and the spins in these clusters are coupled antiferromagnetically and these clusters are embedded in the iron-poor FM matrix. Another cluster model developed by Kaul et al. [26,85] assumes the existence of FM clusters in a FM matrix, where density fluctuations are supposed to be responsible for the formation of the FM clusters. The second transition has been attributed either to the ordering of the AFM clusters or the freezing of the FM clusters. The main evidence for the cluster models is that the $P(B_{hf})$ derived from Mössbauer spectra can be decomposed into two Gaussian distributions, which are supposed to correspond to the AFM (or FM) clusters and FM matrix. However, unambiguous $P(B_{hf})$ can not be obtained from conventional fitting routines due to the problems that we discussed in Chapter 2. Here, the subtraction procedure is used to derive $P(B_{hf})$, and the more reliable $P(B_{hf})$ will help us to clarify the nature of the second transition.

Mössbauer spectra recorded in zero field, in a small polarizing field, and the difference of the polarized and unpolarized spectra at 5 and 45K are shown in Fig. 3.25 and Fig. 3.26. Window's method was used to fit the two-line patterns and to obtain the hyperfine field distributions. The $P(B_{hf})$ obtained in this way can fit the original spectra with and without the polarizing field (as shown in Fig. 3.25 to Fig. 3.26), demonstrating that the subtraction procedure works well for this sample.

The fitted R values are plotted in Fig. 3.27. For unpolarized spectra, R is smaller than 2 at all temperature and lies in the range of 1.4 to 1.7. This indicates that the assumption of R=2, which is adopted by some people when fitting Mössbauer spectra of ribbon samples, is totally wrong. Therefore, $P(B_{hf})$ obtained under this assumption are not reliable. The fact that R is less than 2 provides evidence of the presence of anisotropy. For ribbon samples, demagnetization effects would tend to align the spins in the plane of the ribbons, which will cause R to be greater than 2. The smaller measured R indicates that most spins are perpendicular to the plane of the ribbons, and the orientation of the spins is mainly determined by anisotropy due to quenched-in stresses. Polarizing the sample increases R significantly. Above 25K, R is around 3.6 and is temperature independent, while at low temperature, K decreases. This decrease of R reflect the system becoming stiff as the transverse spin components freeze, which then reduces the effect of spin polarization.



Figure 3.25: Mössbauer spectra of $Fe_{90}Zr_{10}$ at 5 K with fits. (a) polarized in a 50mT field perpendicular to the γ -rays. (b) unpolarized (in zero field). (c) difference of polarized and unpolarized spectra.



Figure 3.26: Mössbauer spectra of $Fe_{90}Zr_{10}$ at 45 K with fits. (a) polarized in a 50mT field perpendicular to the γ -rays. (b) unpolarized (in zero field). (c) difference of polarized and unpolarized spectra.



Figure 3.27: R as a function of temperature for $Fe_{90}Zr_{10}$ in zero fields and a polarizing field. The dashed line corresponds to the random spin orientation and the dotted line represents the complete polarization of spins.

 $P(B_{hf})$ obtained at different temperatures are shown in Fig. 3.28. There is a low-field tail in the hyperfine field distributions, but it does not show a consistent temperature dependence. As shown earlier, the second transition temperature for $Fe_{90}Zr_{10}$ is 28K. If this transition is due to the ordering of the AFM clusters and the low-field tail reflects the contributions of these clusters, the low-field structure should not appear in the $P(B_{hf})$ above 28K, since the clusters are in the paramagnetic state and are not ordered. However, the low-field tail persists well above 28K, thus inconsistent with the AFM cluster model.



Figure 3.28: Hyperfine field distributions obtained from the difference spectra at various temperatures for $Fe_{90}Zr_{10}$

It should be emphasized that the subtraction procedure only works for magnetically homogeneous systems and that only the polarizable fraction of the spins contributes to the two-line pattern obtained by the subtraction procedure, since the subtraction removes the contribution from the non-polarizable fraction of the spins. If AFM clusters were present, the spins in these clusters would not change direction in response to a 50mT field no matter if the clusters are ordered or not. For the FM cluster model, the clusters are expected to respond to the polarizing field differently from the FM matrix. In fact, when using two Gaussian components to fit the zero field Mössbauer spectra, R obtained for the two components are quite different (about 50%)[26]. Thus, it can not be expected that after polarizing the sample, the change of R would be the same for the FM clusters and the FM matrix, which is a critical condition for applying the subtraction procedure. Therefore, for both cluster models, the obtained distributions could not be expected as the representative of the sample as a whole. However, we are able to use $P(B_{hf})$ derived in this manner to fit spectra both with and without the polarizing field and even the spectra in field of 3T at all temperatures. Furthermore, the residuals (subtracting the fits from the measured spectra) shown in Fig. 3.29 exhibit no change in shape on passing through the second transition temperature, particularly near zero velocity where the paramagnetic absorption line (the clusters in AFM cluster model are expected to be paramagnetic above the ordering temperature) should be located. Thus, our results indicate that $Fe_{90}Zr_{10}$ is a magnetically homogeneous system and that there is no evidence of either AFM or FM clusters.

If we assume that the extra intensity in lines 2 and 5 of the spectrum measured at 5 K in a 3T field parallel to the γ -beam for Fe₉₀Zr₁₀ is actually due to the freezing of AFM clusters, we can estimate the cluster spin fraction from that spectrum to be ~3.8%. Above the second transition, these spins should be in a paramagnetic state and therefore should contribute a central component to any spectrum recorded with or without a field. Let us take the zero-field spectrum at 65 K, it should be fitted by adding the contributions from polarizable spins in FM matrix and the non-polarizable



Figure 3.29: Unpelarized spectra are shown with fits using the hyperfine field distributions obtained from the two-line difference spectra. The solid lines are residuals defined as the difference of the fits and the measured spectra.

paramagnetic spins. The former can be calculated from the $P(B_{hf})$ obtained from the subtraction procedure, and the latter is assumed to be a single line spectrum. A fit composed of the two contributions is shown with the measured spectrum in Fig. 3.30. It does not fit the spectrum at all. Actually, we can set the upper limit of the AFM cluster spin fraction to be 0.5% at 65K. This spin population is too small to account for the change of R at low temperatures.

In summary, our results on $Fe_{90}Zr_{10}$ are completely inconsistent with the two cluster models and strongly favor the view of homogeneous transverse spin freezing



Figure 3.30: Mössbauer spectrum of $Fe_{90}Zr_{10}$ at 65 K shown with fit calculated based on bimodal due to the exchange frustration. Further comments on the two cluster models will be presented in Chapter 4.

We have polarized a-Fe₉₂Zr₈ with the same field, but the intensity of lines 2 and 5 can not be increased significantly. R changes only from 1.7 to 2.4 at 5K. Due to the small change in R, we have not performed the subtraction procedure to obtain $P(B_{hf})$ for Fe-Zr alloys with Fe content equal or larger than 92%. Since the subtraction procedure reduces the signal while increasing the noise, in order to get a subtracted two-line pattern with a reasonable signal-to-noise ratio, the time to collect the original polarized and unpolarized spectra will be very long (more than four days).

3.2.4 Spin Correlations

Although two magnetic transitions have been observed and attributed to the collinear order of longitudinal spin components and the freezing of the transverse components, a detailed description of the magnetic order is still lacking. Both Lorentz microscopy [86-89] and neutron depolarisation measurements[88] confirm that long range ferromagnetic order is established at T_c and domains $\sim 10\mu$ m across are observed. These domains persist through T_{xy} clearly demonstrating that the freezing of the transverse spin components does not lead to a loss of collinear order. However, small angle neutron scattering (SANS) [80] shows that short range (~ 100 Å) spin correlations also develop at T_c and that these appear to coexist with the long range order that leads to the magnetic domains. The short range correlations also persist essentially unchanged through T_{xy} . A complex modulation of the background within domains seen by Lorentz microscopy has also been attributed to fine structure in the magnetic order [86,89]. Both the long and short range correlations are associated with the longitudinal spin components, and the presence of the short range correlations within domains is probably due to the exchange frustration.

In order to probe correlations in the transverse spin components, it is necessary to separate the contribution of the longitudinal components from that of the transverse spin components. One method which permits such a separation, on a nearest neighbor length scale, is the measurement of the transferred hyperfine field at a non-magnetic atom in the alloy. As discussed in Chapter 2 (see eqn.2.16), if the probe atoms are non-magnetic, the transferred hyperfine field, B_{thf} , measured by Mössbauer spectroscopy can be written as:

$$\vec{B_{thf}} = b \sum_{i=1}^{n} \vec{S_i}$$

$$(3.1)$$

where \vec{S}_i are the magnetic moments of the neighbor atoms and the sum runs over the n nearest-neighbors. The coefficient b relates the transferred field at the probe nucleus to the atomic moments causing it. The transferred hyperfine field therefore reflects any local correlation of the neighboring magnetic moments. If the spins remain collinear at all temperatures below T_c , the temperature dependence of the hyperfine fields at magnetic and non-magnetic atom sites will be the same, and the ratio of the two hyperfine fields is temperature independent. However, if the degree of correlation is in any way temperature dependent this simple proportionality is lost. For example, equation (3.1) may be resolved into longitudinal (parallel to the z-axis) and transverse (xy) components:

$$\left|\sum_{i=1}^{n} S_{i}\right| = \sqrt{\left(\sum_{i=1}^{n} S_{z}^{i}\right)^{2} + \left(\sum_{i=1}^{n} S_{zy}^{i}\right)^{2}}$$
(3.2)

When the transverse spin components are fully correlated on the nearest neighbor scale, we will have

$$\left(\sum_{i=1}^{n} S_{z}^{i}\right)^{2} + \left(\sum_{i=1}^{n} S_{xy}^{i}\right)^{2} = m^{2}(S_{z})^{2} + n^{2}(S_{xy})^{2}$$
(3.3)

where $m \le n$ since S_z may be negative in some sites. If the transverse spin components are assumed to have a 2D spin glass ordering below T_{xy} , (*i.e.* $< S_{xy}^{i} \cdot S_{xy}^{j} > = 0$ for $i \ne j$), then

$$\left(\sum_{i=1}^{n} S_{z}^{i}\right) + \left(\sum_{i=1}^{n} S_{xy}^{i}\right)^{2} = m^{2} (S_{z})^{2} + n (S_{xy})^{2}$$
(3.4)

In the latter case, the transverse spin components partially cancel, leading to a reduced transferred hyperfine field below T_{xy} at the non-magnetic atom site. The hyperfine field at the magnetic site is almost entirely due to the local moment and so it will increase at T_{xy} as the extra spin components order. As a result, the ratio $B_{hf}^{non-mag}/B_{hf}^{mag}$ falls at T_{xy} . In disordered alloys, particularly in amorphous alloys, there will be some variation in the local environments and the B_{thf} need to be averaged over different configurations:

$$\langle B_{thf} \rangle = b \sum_{n=1}^{12} P_n |\sum_{i=1}^n \vec{S}_i| = \begin{cases} b \sum_{n=1}^{12} P_n \sqrt{m^2 (S_z)^2 + n^2 (S_{xy})^2} & \text{fully correlated} \\ b \sum_{n=1}^{12} P_n \sqrt{m^2 (S_z)^2 + n (S_{xy})^2} & \text{spin glass order} \end{cases}$$
(3.5)

where P_n is the probability that a non-magnetic atom has n nearest-neighbor Fe atoms. The average hyperfine field $\langle B_{thf} \rangle$ reflects the mean environment and the above argument still holds.

A search for transverse correlations in the AuFe system has been made using ¹⁹⁷Au Mössbauer spectroscopy in Au_{83.2}Fe_{16.8} [90] and ¹¹⁹Sn Mössbauer spectroscopy in Au₇₉Fe₁₉Sn₂ [91,92]. For both alloys, the average hyperfine field derived from ⁵⁷Fe Mössbauer spectra clearly shows a sudden increase at T_{xy} as the extra spin components freeze and contribute to the local hyperfine field. The same behavior of the average hyperfine field is observed in the corresponding ¹⁹⁷Au or ¹¹⁹Sn Mössbauer spectra, indicating that the transverse components are indeed locally correlated. Furthermore, because $\langle B_{hf} \rangle$ (T) clearly changes slope at T_{ry}, it is possible to separate the contributions of the longitudinal and transverse components. Extrapolating the high temperature region $(T_{xy} \leq T \leq T_C)$ to T=0 allows the average longitudinal moment to be estimated, while the value actually measured at T=0 reflects the contributions from both the longitudinal and transverse components. Comparing the ratios of these two values as measured at the magnetic and non-magnetic sites allows the degree of correlation to be estimated. Assuming that the transferred hyperfine field at the non-magnetic atom site (¹⁹⁷Au or ¹¹⁹Sn) is due only to the moments on the nearest-neighbor iron atoms leads to the conclusion that the transverse components are strongly correlated over first neighbor disinces, indeed, in one case better than perfect correlation is required [92].

One problem with the measurements on the AuFe system is the rather low iron concentration in the region of interest. This leads to over one third of the nonmagnetic probe atoms having less than two iron nearest-neighbors and therefore being insensitive to any correlations. We have prepared a-Fe₉₂Zr₇Sn₁ to study the spin correlations in Fe-Zr system. The greatly increased iron concentration means that any probe atom will typically have 10-11 magnetic neighbors allowing the spin correlations to be more clearly examined.

As shown before, there is no evidence of significant changes of structural or mag-

netic properties due to the addition of 1 at.% of Sn. Furthermore, from Fig. 3.31, the average transferred hyperfine fields at the ¹¹⁹Sn and ⁵⁷Fe sites show similar temper-



Figure 3.31: Average hyperfine fields for $Fe_{92}Zr_7Sn$ derived from ⁵⁷Fe and ¹¹⁹Sn Mössbauer spectra in zero field showing a smooth temperature dependence with no apparent break in slope at T_{zy} .

ature dependences, indicating that the sample is homogeneous and no segregation of Sn has occurred.

The ⁵⁷Fe and ¹¹⁹Sn Mössbauer spectra at different temperatures are shown with fits in Fig. 3.32 (a) and (b). As can be seen, the six lines in the ¹¹⁹Sn spectra are poorly resolved and the spectra appear to consist of only two peaks. It is not possible to obtain a unique value for R by fitting a spectrum under these conditions, and we



Figure 3.32: Mössbauer spectra of $Fe_{92}Zr_7Sn$ at different temperatures with (a) ⁵⁷Fe and (b) ¹¹⁹Sn sources. The solid lines are fitted curves.

can not simply assume R=2 since we have proved that this assumption is wrong. The fitted shape of $P(B_{hf})$ (and hence its average value) depends somewhat on the value of R used in the fit, therefore an uncertainty in R translates into an uncertainty in $\langle B_{hf} \rangle$. The magnitude of this uncertainty has been estimated by comparing the average hyperfine field obtained using R=2 (appropriate for a random spin orientation) with the value obtained using R derived from fitting the ⁵⁷Fe spectrum at the same temperature. In the temperature range from 5K to 90K, the difference was found to be less than 2%.

 $\langle B_{hf} \rangle$ (T) increases smoothly with falling temperature for both ⁵⁷Fe and ¹¹⁹Sn, and does not show a break in slope at T_{xy} (see Fig. 3.31). Since no break in slope of $\langle B_{hf} \rangle$ (T) is observed at T_{xy}, we cannot attempt to separate the longitudinal and transverse spin components as has been done previously [90-92]. However, an analysis of the temperature dependence of the average hyperfine fields on the magnetic and non-magnetic atom sites is still possible and information about spin correlations can be obtained. It was shown before that the population of the spins with the preferred direction opposite to the net magnetization is quite small for this sample, as a first order approximation, we can assume that m = n in the equation (3.5). Using the average iron moment μ_{av} and its component in z direction M₂, the average transverse component is estimated to be about 0.53 μ_{av} . If we assume the transverse spin components have a 2D spin glass order below T_{xy} , then the ratio of average ¹¹⁹Sn hyperfine field to the 57 Fe hyperfine field should exhibit a 15% drop below T_{xy} . The temperature dependence corresponding to this situation is plotted as a solid line in Fig. 3.33. Within the quoted uncertainty, the ratio is temperature independent over the whole range covered here, as indicated by the dotted line. The observed temperature dependence therefore indicates that in the nearest-neighbor scale, the transverse spin components are strongly correlated rather than having the two-dimensional spin glass order.

It is instructive to repeat our analysis on the 197 Au and 119 Sn Mössbauer data from the AuFe alloys. Fig. 3.34 shows a plot of the ratios of average hyperfine fields



Figure 3.33: Ratio of the average transferred hyperfine field at ¹¹⁹Sn sites to that at the ⁵⁷Fe sites as a function of temperature for $Fe_{92}Zr_7Sn$.

as function of temperature for the two data sets. Comparison with the Fe-Zr data in Fig. 3.33 shows that the behaviour of the transferred field ratio is quite different. The two AuFe alloys have similar values of T_c and T_{xy} both to each other and to the present a-Fe-Zr alloy and may be expected to be magnetically similar. However, in the AuFe data, the hyperfine field ratio falls steadily with cooling. For the ¹⁹⁷Au Mössbauer measurement on Au_{83.2}Fe_{16.8}, the ratio drops about 26% between 80K and 0K. Even if random ordering of the transverse spin components is assumed, the expected reduction of the ratio is much smaller than that observed: both longitudinal



Figure 3.34: Ratios of the average transferred hyperfine field at ¹⁹⁷Au and ¹¹⁹Sn sites to that at the ⁵⁷Fe sites in two AuFe alloys.

and transverse component of the iron moment can be estimated from ⁵⁷Fe Mössbauer spectra and average transferred hyperfine field at ¹⁹⁷Au site can be calculated, the decrease of ratio is expected to be 14%, and the decline should only start at T_{xy} . The observed behavior is quite distinct from that of the Fe-Zr system and suggests a decrease in the correlation length of longitudinal spin components on cooling. Recent neutron depolarization measurements on Fe-Zr and AuFe alloys[88,93,94] are also consistent with this conclusion. Although neutron depolarization is not sensitive on length scales smaller than the order of a micron, it does allow measurement of the size and average internal magnetisation of domains. For $\text{Fe}_{x} Zr_{1-x}$, the polarization decreases strongly at T_{c} for alloys with x < 0.92 indicating the formation of domains, and these domains persist through $T_{xy}[88]$. Only a small depolarisation signal was observed for the alloy with x=0.92 suggesting the development of an imperfect ferromagnetic state. However, for all samples, the polarization decreases down to 15K and gives no evidence of a reduction of the correlation length as the temperature is lowered. By contrast, in the AuFe alloys, the polarisation first decreases at T_{c} as expected, then starts to increase again [93,94]. The increase of polarization indicates a reduction of either the mean domain size or the internal domain magnetization, which in turn suggests a decrease in correlation length of the longitudinal spin components. Our Mössbauer measurements on $Fe_{92}Zr_7Sn$ indicate that the transverse spin components are strongly correlated on a nearest neighbor scale and the correlations of longitudinal components show no detectable change on cooling through T_{xy} .

Despite the strong similarities between the magnetic phase diagrams of the AuFe and a-Fe-Zr systems and the values of the transition temperatures of the particular alloys studied here, quite different spin correlation behaviour is observed. It is possible that the stiffness of the spin system plays a role in stabilising the spin correlations in the presence of exchange frustration and a-Fe-Zr has been shown to exhibit displaced hysteresis loops [19] whereas AuFe does not [54]. Another possibility is the proximity of the AuFe alloys to the percolation threshold which may lead to a fragmentation of the order at low temperatures. While the origin of the difference remains unclear, the effect is well defined and further work on a variety of similar systems is needed to identify the controlling factor.

3.3 Magnetic Properties of a-FeHf alloys

From the temperature dependence of the average hyperfine field obtained from zero field Mössbauer spectra (see Fig. 3.35), the magnetic ordering temperature T_c of Fe_{92.5}Hf_{7.5} was determined to be 175±5K. T_c obtained from magnetization measure-



Figure 3.35: Temperature dependence of the average hyperfine field obtained from zero field Mössbauer spectra for $Fe_{92.5}Hf_{7.5}$.

ments is $186\pm7K$, in agreement with that from Mössbauer measurements.

Transverse spin freezing is clearly observed in this system. Mössbauer spectra measured in a 3.5T field parallel to the γ -beam show the presence of lines 2 and 5 at low temperature (see Fig. 3.36). Due to its high level of exchange frustration, the subtraction procedure can not be used. The Mössbauer spectra were fitted by Window's methods and the fitted R is plotted in Fig. 3.37. T_{xy} is determined to be $47\pm8K$ from Fig. 3.37.

High field slopes were observed for all magnetization curves (Fig. 3.38) below T_c . The difference between the μ_{av} and M_z begins to increase around T_{xy} (Fig. 3.39), showing behavior typical of transverse spin freezing.

Since T_c and T_{xy} of $Fe_{92.5}Hf_{7.5}$ are both close to those for $Fe_{92}Zr_7Sn$ (see Table 3.4),



Figure 3.36: Mössbauer spectra in a 3.5T field parallel to the γ -beam at different temperature for Fe_{92.5}Hf_{7.5}.



Figure 3.37: Temperature dependence of R derived from Mössbauer spectra in a 3.5T field parallel to the γ -beam for Fe_{92.5}Hf_{7.5}.

we expect that the frustration level and therefore the spin structures below T_{xy} are quite similar for the two samples. It was shown that single cone model is a reasonable approximation for Fe₉₂Zr₇Sn and the half-angle ϕ was estimated to be $34\pm3^{\circ}$ from R, the model may also work in Fe_{92.5}Hf_{7.5}. R is 0.25 ± 0.04 at 5K, corresponding a cone with half-angle of $29\pm3^{\circ}$. Using the magnetization value at 2T (which results in a similar internal field compared with the Mössbauer measurements to determine R), half-angle ψ is estimated to be $30\pm4^{\circ}$. It agrees very well with the value obtained from R (see Table 3.4).



Figure 3.38: Magnetization curves at different temperatures for Fe92.5Hf7.5.

Table 3.4: Summary of our main results on $Fe_{92.5}Hf_{7.5}$: the average iron moment μ_{av} , ferromagnetic transition temperature T_c , transverse spin freezing temperature T_{xy} , R derived from Mössbauer spectra in parallel fileds, cone half-angle from R ψ_R , ratio of magnetization M_s to μ_{av} as well as cone half-angle ψ_M estimated from M_x/μ_{av} . ψ_M (B=2T) is obtained from the ratio of the magnetization in a field of 2T to μ_{av} .

Samples	μαυ	T _c	T _{xy}	R	ψ_R	M_z/μ_{av}	ψ_M	ψM
	$(\mu_B/{ m Fe})$	(K)	(K)				(B=0T)	(B=2T)
Fe _{92.5} Hf _{7.5}	1.51 ± 0.04	175±5	47±8	0.25±0.04	29±3°	0.88±0.03	41±4°	30±4°

3.4 Magnetic Properties of a-FeSc alloys

Mössbauer spectra measured in zero field for $Fe_{91}Sc_9$ (see Fig. 3.40) show typical magnetic splitting at low temperatures. The spectra were fitted by Window's method. The temperature dependence of the average hyperfine field and the absorption yield almost the same ordering temperature (105 and 106K respectively, as shown in Fig. 3.41). Mössbauer spectra in a 6T field parallel to the γ -beam are shown in Fig. 3.42. The external field has strong effects on the magnetic structure of the sample. Above the ordering temperature (105K), the spectra measured in the field clearly exhibit magnetic splitting, and average hyperfine field of more than 10T are obtained, providing evidence of strong magnetic cluster relaxation. From Fig. 3.42, it can be seen that the intensities of lines 2 and 5 increase at low temperature. The field spectra were fitted by using Window's model since the subtraction procedure again does not work for this system. The fitted values of R is plotted against temperature in Fig. 3.43. The temperature at which R begin to increase from zero is obtained by fitting the low temperature R with a linear function, and it is 97 ± 10 K. This means that the noncollinearity starts to develop as soon as the magnetic order appears. Therefore, unlike the Fe-Zr and Fe-Hf alloys, which first enter a collinear state at T_c and develop noncollinearity only below the second transition, Fe91Sc9 undergoes a single transition and enters the non-collinear state directly.



Figure 3.39: Comparison of component of iron moment in the field direction, M_z , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 3T field for Fe_{92.5}Hf_{7.5}.

Magnetization curves for $Fe_{91}Sc_9$ (Fig. 3.44) show the largest high field slopes among all materials studied here, consistent with it being the most frustrated system. M_z is compared with μ_{av} in Fig. 3.45. Above the ordering temperature, both μ_{av} and M_z are not zero due to the slowing down of cluster relaxation by external fields. μ_{av} is larger than M_z since Mössbauer measurements also include contributions from rapidly relaxing clusters. From the ordering temperature down to 5K, M_z increases only about 10%. The ratio of M_z to μ_{av} at 5K is 0.55, revealing a very high degree of noncollinearity. Non-zero M_z were obtained at all temperature from 5 to 200K. It seems that the ground state is an asperomagnetic state characterized by noncollinearity and finite magnetization. However, M_z was obtained by extrapolation of the high



Figure 3.40: Mössbauer spectra in zero field for Fe91Sc9.



Figure 3.41: Temperature dependence of (a) the average hyperfine field and (b) absorption obtained from zero field Mössbauer spectra of $Fe_{91}Sc_{9}$.



Figure 3.42: Mössbauer spectra in a 6T field parallel to the γ -beam at different temperature for Fe91Sc9.



Figure 3.43: Temperature dependence of R derived from Mössbauer spectra in a 6T field parallel to the γ -beam for Fe₉₁Sc₉.

field part ($2T \le B \le 5.5T$) of the magnetization curves. Such big fields can cause significant changes in magnetic structure. This is clearly seen from Fig. 3.45 where M_z is not zero above the ordering temperature. Although M_z is the extrapolation to B=0T, it still includes the contribution induced by the large magnetic fields.

From the modified Arrott plots (see Fig. 3.46), it can be seen that the ferromagnetic order does not set in at least down to 5K. Therefore, we conclude that $Fe_{91}Sc_9$ exhibit a single transition to spin glass rather than asperomagnetic state. This is the reason that we have labeled the transition temperature as T_{sg} rather than T_c in Fig. 3.41.



Figure 3.44: Magnetization curves at different temperatures for $Fe_{91}Sc_9$.



Figure 3.45: Comparison of component of iron moment in the field direction, M_x , and iron average moments, μ_{av} , obtained from Mössbauer spectra measured in a 6T field for Fe₉₁Sc₉. The dashed line is a guide to eyes.



Figure 3.46: Modified Arrott plots at different temperatures for Fe91Sc9.

Chapter 4

Discussion

4.1 Magnetic Relaxation around T_c

Fitting procedures combining the static disorder and cluster relaxation have been developed and they can give reasonable fits to the observed Mössbauer spectra. However, this approach does not allow us to obtain much new insight into the magnetic properties of the materials studied here due to some rather artificial assumptions made in our relaxation models. Indeed, the static disorder in amorphous materials make the relaxation problem much more complicated. The static magnetic disorder becomes dominant almost as soon as magnetic order sets in, and it leads to a wide distribution of apparent cluster sizes and moments. Both the initial shape and the temperature dependence of the cluster moment distribution are unknown. In our models, the distribution of hyperfine field has been used to represent the distribution of cluster moments, which assumes that the cluster moments are proportional to the hyperfine fields (or atomic moments), and further assumes that the all clusters have the same numbers of spins. Moreover, the cluster moment distribution has been fixed to be that observed at T=5K. This implies that relaxation is the only mechanism by which order is lost -i.e. all demagnetizing processes found in normal ferromagnets are neglected. Although it is reasonable to assume that there is a distribution of cluster relaxation rates, expressing the relaxation rate as a exponential function of hyperfine field (or cluster moment) is somewhat artificial. These artificial assumptions prevent us from following the relative change of the average cluster size with temperature.

It should be noted that the presence of slowly relaxing clusters does not necessarily lead to anomalous behaviour at T_c . The critical exponents obtained from magnetization measurements on iron-rich Fe-Zr alloys agree well with the theoretical predictions for the homogeneous three-dimensional Heisenberg model and indicate the ferromagnetic nature of the transition at T_c [74,75]. In Monte Carlo simulations[95,96], finite-size scaling analysis also yields critical exponents in good agreement with those of the three-dimensional Heisenberg ferromagnets.

4.2 Nature of The Second Transition

The magnetic phase diagram of the a-Fe-Zr series has been constructed (see Fig. 4.1) based on our measurements. It is clear that the second transition temperature T_{xy} is strongly dependent on the Fe concentration. This concentration dependence of T_{xy} is inconsistent with both the AFM cluster and FM cluster models. It has been argued [25] that the second transition temperature of $Fe_{93}Zr_7$ (78K) is close to the Néel temperature of γ -Fe precipitates in Cu (~70 K) [15], which suggests that the second transition could be due to the ordering of the AFM clusters. However, we have found that the second transition temperature decreases monotonically from 78 K at x=93 to ~ 0 K (or at least is below 5K) at x=89. For alloys with x ≤ 92 , the second transition temperatures are equal to or smaller than 46 K, well below the expected Néel temperature of γ -Fe. Furthermore, it is extremely unlikely that decreasing of Fe content by 4 at.% would cause such large changes in the precipitated minority phase that its ordering temperature is reduced by almost 80 K. No explanation for the concentration dependence of the second transition temperature is provided by the FM cluster model. Actually, although the second transition is explained in terms of freezing of the FM clusters, no mechanism for the cluster freezing has been provided or even suggested. Thus, it is impossible to predict any concentration dependence



Figure 4.1: Magnetic phase diagram of a-Fe_xZr_{100-x}

for the transition temperature. Furthermore, the FM cluster model has several more points which are hard to understand. Firstly, it has been assumed that the existence of the FM clusters is due to the density fluctuations. The average nearest-neighbor Fe-Fe distance in the clusters is larger than that in the FM matrix, and this leads to a higher Curie temperature for the clusters (T_c^{cl}) . Indeed, T_c^{cl} has been assumed to be larger than the observed ferromagnetic transition temperature $T_c^{ob}[26]$. It is also reported that for Fe₂₀Zr₁₀, the effective population of the FM clusters increases with temperature and reaches about 90 % at $T\simeq T_c^{ob}$. It is difficult to understand that the system with 90% of spins belong to the FM clusters does not order at the Curie temperature of the clusters (T_c^{cl}) , and that "only 11% of the total Fe spins are actually participating in the FM-PM (paramagnetic) phase transition for this glassy alloy"[26]. Secondly, according to this model, the exchange interactions in the FM clusters are stronger but the atomic moments are smaller than those in the FM matrix, so that the low-field Gaussian components of hyperfine field distribution can correspond to the FM clusters. However, there is no physical justification for the spins in the FM clusters being smaller, and this point is very important to the FM cluster model. Thirdly, it is claimed that the freezing process does not start abruptly at the second transition temperature, but proceeds gradually over a wide temperature range extending from 130K down to 4.2K for $Fe_{90}Zr_{10}$. This is inconsistent with our observation that the noncollinearity (R) begins to develop at a well defined temperature T_{xy} . Finally, it is reported that at low temperatures, about 30% Fe atoms belong to the low density clusters while 70% are in the high density matrix. Both parts are quite large and can not be neglected. However, there is no microscopic evidence that such distinction is meaningful.

Based on our systematic measurements on amorphous Fe-Zr alloys, we can rule out the two cluster models completely and conclude that the second transition marks the homogeneous freezing of the transverse spin components due to the exchange frustration.

4.3 Effects of Exchange Frustration On Magnetic Ordering

4.3.1 Partially Frustrated Materials

a-FeZr alloys

1. Drop of T_c

From the magnetic phase diagram of the a-Fe-Zr alloys (Fig. 4.1), we can see that as the Fe concentration is increased from 89 at.% to 93 at.%, T_c drops from 260K to 137K, more than 120K. In contrast to the substantial drop in T_c, the average iron moment, μ_{av} , remains essentially unchanged (Fig. 4.2). It has been shown that T_c actually starts to drop when Fe content is larger than 85


Figure 4.2: Average iron moment at 5 K derived from Mössbauer spectra measured in external magnetic fields for a-Fe_x Zr_{100-x} alloys with different Fe content x

at.%, while the average iron moment increases with the Fe content[97]. The ferromagnetic transition temperature (T_c) is determined by the average moment and average exchange interaction for amorphous materials, and a large moment with strong exchange leads to high T_c . Since the average iron moment does not show any decrease when the Fe concentration is raised from 85 to 93 at.%, the decrease of T_c is expected to be due to a decrease of average exchange strength. The Monte Carlo simulations of Heisengerg spin system with exchange frustration[95,96] (which will be described in detail later) indicate that as soon as the antiferromagnetic interactions are present, two magnetic transitions are expected. Since there is no evidence of second transition for alloys with Fe concentration between 85 and 89 at.%, it is expected that exchange interactions in these alloys are all ferromagnetic (FM), and that the decrease of T_c in this range is mainly due to the reduction of FM interaction strength. For alloys showing two magnetic transitions ($x \ge 90$), the drop of T_c and therefore the reduction of exchange strength is mainly due to the presence of AFM interactions.

This view is supported by various experimental observations on the system. Anomalous X-ray scattering indicates that the Fe-Fe separation in Fe_xZr_{100-x} alloys with x around 90 is about 2.6Å[11,12], which is close to the the critical separation 2.55Å where the exchange interaction change sign from FM to AFM. The exchange interactions are strongly dependent on the distance between Fe atoms. This means that the wide distribution of Fe-Fe separations in these amorphous alloys will lead to a wide distribution of exchange interactions which may including both FM and AFM components. When the iron concentration is increased, the average Fe-Fe separation becomes smaller since the radius of Fe atoms is smaller than those of alloying elements (Zr, Hf, and Sc), consequently the strengths of the FM interactions are reduced first and then the AFM interactions are present. Moreover, a strong pressure effect on the Curie temperature of iron-rich a-Fe-Zr alloys has been observed[98]. For a-Fe₉₀ Zr_{10} , T_c drops after applying hydrostatic pressure with a pressure coefficient of about 4K/kbar. Smaller pressure coefficients were found for alloys with less Fe. Since compressing the sample leads to shorter Fe-Fe separations, the same effect induced by increasing Fe concentration, the drop of T_c is consistent with the frustration picture. Finally, increasing the distance between Fe atoms by hydrogenation greatly increases the Curie temperatures of these alloys and converts them to conventional ferromagnets as a result of reducing the number of AFM bonds[23,99-102]. T_c of the a-Fe₉₀Zr₁₀ is increased by about 150K. All alloys with their magnetizations being not saturated in fields up to 19T, are good soft ferromagnets after hydrogenation: the magnetization readily saturates in 0.1T with no apparent high-field slope[23]. It was also found that both the Curie temperature T_c and the average iron moment (proportional to the average hyperfine field obtained from Mössbauer spectra) increase with the hydrogen content in the alloys. Therefore, we conclude that the reduction of T_c with the increase of Fe content must be largely due to the decrease of the nearest-neighbor Fe-Fe separations, which first reduces the strengths of the FM interactions and then leads to the presence of AFM interactions.

2. Spin Correlations

Both Lorentz transmission electron microscopy and neutron depolarization measurements [86-89] indicate the existence of magnetic domains. For weakly frustrated $\text{Fe}_{x}\text{Zr}_{100-x}$ alloys (87 $\leq x \leq 91$), magnetic domains in the order of $10\mu m$ are formed below the first transition at T_c , and the domain structures remain essentially unchanged down to about 15K, demonstrating the presence of long-range ferromagnetic correlation in longitudinal spin components. However, nc domain structure was observed in Fe₉₂Zr₈ by Lorentz transmission electron microscopy, while the neutron depolarization measurements shows very small but noticeable depolarization [88]. From the neutron depolarization, the domain sizes are estimated to be about 2000Å, which is comparable to thickness of a domain wall. This suggests that Fe92Zr8 does not behave like a conventional ferromagnet below T_c. We have shown (in Chapter 3) that for partially frustrated materials, not all spins are parallel as $T_{xy} < T < T_c$ and some spins point opposite to the net magnetization. With increasing Fe concentration (thus raising the level of frustration), more and more spins would be antiparallel to the net magnetization. This kind of spin configuration is of course different from that of a conventional ferromagnet and is probably responsible for the observed imperfect ferromagnetic state in Fe₉₂Zr₈. It should be emphasized that for all three $Fe_{x}Zr_{100-x}$ alloys (x=90, 91 and 92) studied by neutron depolarization, the polarization decreases steadily down to 15K and gives no evidence of reduction in the longitudinal components correlation length as the temperature is lowered, indicating that the ferromagnetic order is not lost after the transverse spin freezing.

For the transverse spin components, our measurements on $Fe_{92}Zr_7Sn$ by ⁵⁷Fe and ¹¹⁹Sn Mössbauer spectroscopy clearly indicate that they are strongly correlated on the nearest-neighbor scale. On the other hand, the transverse spin components have to be random on a scale which is not larger than the domain sizes, otherwise the magnetization will not be smaller than the average total moment derived from Mössbauer spectrascopy. The observation of ripples (~100Å) in the domains[86,89] and the of short range correlations on the scale of 100Å revealed by small angle neutron diffraction[80] suggest that the correlation lengths of the transverse components may extend to the order of 100Å.

3. Increase of T_{zy} and Noncollinearity

We have shown that except for a-Fe₈₉Zr₁₁, all of the other Fe-Zr alloys studied here exhibit two magnetic transitions and have a non-collinear ground state. From Fig. 4.1, it can be seen that T_{xy} increases from about 0K at x=89 at.% to 78K at x=93 at.%. The transverse spin freezing is a result of exchange frustration, therefore, the increase of the freezing temperature T_{xy} will reflect the increase of the frustration level with Fe content.

The noncollinearity is found to increase with the Fe concentration. The noncollinearity may be characterized by R obtained from the spectra with a field parallel to the γ -beam. R is zero if the sample is in a collinear state, and is equal to 2 for a random spin orientation in spin glass. R at 5 K for all Fe-Zr alloys are plotted in Fig. 4.3. R increases from ~0 at x=89 at.% to 0.53 at x=93 at.%. According to the derived phase diagram (Fig. 4.1), T_c and T_{xy} meet at x=94.5 and after that point, a spin glass ground state with R equal to 2 is expected. E is relatively small for x≤93 and would exhibits an abrupt increase from the measured 0.53 at x=93 to the expected 2 at x=94.5, suggesting that the degree of non-collinearity obtained in this manner is underestimated. Indeed, quite large external fields (typically ~3T) have been used in the measurements and



Figure 4.3: R as a function of Fe content x for a-Fe_x Zr_{100-x} , indicating the increase of non-collinearity with Fe concentration. The dashed lines are a guide to eyes.

the fields may suppress the non-collinearity by rotating the spins towards the field direction. Furthermore, different fields were used for different alloys in order to achieve technical saturation above the second transition, which means that R were obtained under slightly different conditions.

The increase of non-collinearity with Fe content can be seen clearly in Fig. 4.4. For Fe₈₉Zr₁₁, the magnetization changes little when $B \ge 2T$, while Fe₉₀Zr₁₀ begins to show a measurable high field slope. The slope become bigger for samples with even higher Fe concentrations. Since the slope reflects the aligning of spins in field direction, the large slope indicates a higher level of noncollinearity. Compared to R, M_z provides a better measure of the noncollinearity as they were obtained in the same conditions: extrapolation of high field part ($2T \le B \le 5.5T$) magnetization curves to B=0T. Furthermore, since it is the extrapolated value



Figure 4.4: Magnetization curves at 5K for a-Fe_xZr_{100-x}

at B=0T, the field effect of aligning spins is smaller compared to the case of obtaining R. M_z is divided by average atomic moment μ_{av} to take account of the small change in μ_{av} . The normalized M_z drops with the increase of Fe concentration (Fig. 4.5), indicating the increase of noncollinearity. Although M_z is the extrapolation value at B=0T, it may still include the contributions from the field aligned spins. Thus, M_z may be overestimated and this leads to an underestimate of the non-collinearity.

In summary, the increase of T_{xy} with Fe concentration indicates that the frustration level is raised when increasing Fe content. This conclusion is consistent



Figure 4.5: Normalized magnetization as a function of Fe content x for $a-Fe_xZr_{100-x}$

with the observation that noncollinearity increases with Fe content.

4. Properties of Amorphous Iron

The average iron moment remains essentially unchanged (~1.55 μ_B /Fe) when the Fe concentration is in the range of 89 to 93 at.% (see Fig. 4.2). Therefore, the the extrapolation to x=100 is fairly straightforward, and amorphous Fe is expected to have a average moment about $1.55\mu_B$ /Fe. On the other hand, As the Fe content is increased, T_c drops smoothly while both T_{xy} and the degree of noncollinearity increase (Fig. 4.1). T_c and T_{xy} can be approximated as linear functions of Fe content, and the lines meet at x~94.5 and T=100K, suggesting that this alloy will show a single transition to a spin glass at this point. According to the mean-field theory[6], after the intersection of T_c line and T_{xy} line, the system would remain a spin glass and the freezing temperature would not change. Thus, we expect that amorphous iron would be a spin glass with an ordering temperature of ~100K and an average moment of about $1.55\mu_B/\text{Fe}$.

a-FeHf alloy

For the a-FeHf group, only Fe92.5 Hf7.5 was studied here. The magnetic behavior of the alloy is very similar to those of a-FeZr alloys: magnetic relaxation around first transition T_c, large high field slopes in magnetization curves as well as the transverse spin freezing at second transition T_{xy} . Moreover, the two magnetic transition temperatures (175K and 47K) are very close to those of $Fe_{92}Zr_7Sn$ (180K and 46K). It was also reported that on hydrogenation, the iron-rich a-FeHf alloys exhibiting two magnetic transitions with a noncollinear ground state become soft ferromagnets with substantially increased T_c [28,99]. Even early studies on a-FeHf alloys in a wide range of Fe concentration found that the first transition temperature T_c increases from zero above a critical Fe concentration of ~ 45 at.%, and then drops from the maximum around 86 at.% with further increasing the Fe contents[103]. The magnetization measured during heating after zero-field cooling and that obtained after field-cooling begin to separate below a certain temperature, which is field dependent[20]. All of these properties have been observed in a-FeZr alloys. The close similarity between the two systems suggests that the magnetic ordering behavior of the two systems is controlled by the same mechanism: exchange frustration. Since the transition temperatures of Fe92.5Hf7.5 and Fe32Zr7Sn are quite close, it is expected that the magnetic phase diagram of a-FeHf system is similar to that of a-FeZr system but shifted to higher Fe content by about 0.5 at.%. This can be easily understood according to the frustration picture. Hf atoms have a greater atomic radius (1.67Å) than that of Zr atoms (1.60Å), which leads to less AFM interactions and therefore a lower level of exchange frustration for Fe-Hf alloys compared to Fe-Zr alloys with the same Fe concentration. Thus the phase diagram will shift to high Fe content.

4.3.2 Strongly Frustrated Materials

The magnetic ordering behavior of $Fe_{91}Sc_9$ is quite different from that of a-FeZr and a-FeHf alloys studied here. Our results indicate that it exhibits a single transition to a spin glass at $105\pm5K$. A sharp peak in ac susceptibility (χ_{ac}) has been observed at 99K[29] and 95K[104] for $Fe_{90}Sc_{10}$, which is a characteristic feature of spin glass. It was also found that for Fe_xSc_{100-x} with x=89, 90 and 91, the transition temperature are almost the same ($\simeq 104K$). Based on these measurements, we expect that the Fe_xSc_{100-x} alloys (x=89, 90 and 91) are all spin glasses with the same transition temperature. This behavior is consistent with the mean-field theory[6] and Monte Carlo simulations[95,96], which predict that if the frustration level is above a critical point at which the system become a spin glass, the transition temperature will remain constant.

While $Fe_{91}Sc_9$ is clearly a highly frustrated material, the origin of the high level frustration in the system seems not clear. The radius of Sc atoms is 1.62Å, slightly larger than that of Zr atoms (1.60Å), so the average distance between nearest neighbor Fe atoms in $Fe_{91}Sc_9$ is expected to be somewhat bigger than that in $Fe_{91}Zr_9$. Since the direct exchange interactions are determined by the nearest neighbor Fe-Fe separations, the frustration level due to the direct interactions is expected to be lower in $Fe_{91}Sc_9$ as a result of the larger Fe-Fe separations.

One possible origin of this extra frustration could be indirect exchange via conduction band polarization, which is suggested by the spin glass behavior observed in Sc-RE alloys (RE is an rare earth element, such as Gd, Dy, Er, Tb) [105-112]. Although for RE=Dy, Er, and Tb, the spin glass behavior results from anisotropy[105-107], Sc-Gd alloys have been shown to be almost isotropic spin glasses[108], indicating that the anisotropy in Sc-Gd system is quite small. Temperature dependence of ac susceptibility for Sc13%Gd shows a cusp at a certain temperature, a characteristic feature of spin glasses[110], and the resistivity of Sc15%Gd and Sc20%Gd at low temperature follows a $T^{3/2}$ behavior calculated by Rivier and Adkins[113] for a spin glass. Furthermore, specific heat measurements on crystalline Sc-Gd alloys with Gd concentration up to 1 at.% indicates that the scaling law are approximately obeyed, thus suggesting that RKKY exchange interactions are dominant[109,112]. This means that Sc atoms can carry the oscillating RKKY interactions between magnetic moments of Gd atoms. If this is true in amorphous $Fe_{91}Sc_{9}$, it is expected that this indirect exchange would further enhance the exchange frustration since the direct exchange is already partially frustrated. Moreover, the indirect interactions would not be affected significantly by hydrogenation. However, recent neutron diffraction study on Dy/Sc superlattices reveals that while individual Dy layers order ferromagnetically, the magnetic coherence length along the growth direction is less than the Dy layer thickness[114]. This suggests that Sc can not carry the long-range exchange interactions, inconsistent with the above explanation.

It is also not clear whether hydrogenation (which expands the lattice, increasing the Fe-Fe distance and reducing the incidence of antiferromagnetic couplings) can convert Fe-Sc alloys into ferromagnets. As described before, hydriding Fe-Zr and Fe-Hf alloys lifts the exchange frustration and converts them into collinear ferromagnets with greatly increased T_c . Hydriding the Fe-Sc alloys does reduce the degree of noncollinearity and raise the ordering temperatures[30,104], and the magnetization of these alloys saturates readily in fields of about 0.2T like soft ferromagnets. However, ac susceptibility does not shows the structure associated with critical fluctuations, and thus fails to confirm the ferromagnetic character of the transition[104].

The experimental data on amorphous Fe-Y alloys [115,116] indicates that the magnetic ordering behavior of iron-rich Fe-Y alloys is similar to that of Fe-Sc alloys. For Fe-Y alloy with only 71 at.% Fe, the Mössbauer spectrum measured in a 5T field parallel to the γ -beam clearly shows the presence of lines 2 and 5, and thus revealing a noncollinear ground state[116]. Magnetization as a function of applied field for Fe₈₈Y₁₂ shows a large high-field slope, and the magnetization fails to saturate in fields of up to 15T at 4.2K, indicating it is also a noncollinear system[115]. These observations are consistent with the spin glass behavior in Fe₉₁Sc₉, but in contrast to the nearly ferromagnetic nature of Fe₈₉Zr₁₁. The similarity between the magnetic properties of Fe-Sc and those of Fe-Y alloys suggests that the indirect exchange may be also present in Fe-Y alloys and enhance the degree of frustration. Indeed, evidence of indirect exchange through the polarization of yttrium conduction band has been observed in Y-Gd alloys (Gd atoms have localized 4f moments)[111,112,117]. It was also reported that in c-axis Y-RE superlattices (RE is an rare earth elements), magnetic coherence can extend over several bilayers where the layers of locallized RE spins are separated by layers of nonmagnetic Y[118-121]. The long range coupling between the RE layers is believed to result from the indirect RKKY interaction[118,119]. Careful examination of the Arrott plots for Fe₈₈Y₁₂ suggests that Fe-Y alloys are less frustrated than Fe-Sc alloys with the same Fe concentration. As mentioned above, Fe₈₉Sc₁₁ is expected to be a spin glass, whereas extrapolation of the low-field Arrott plots for Fe₈₈Y₁₂ yields a finite T_c, below which the spontaneous magnetization become non-zero. It is quite possible that the larger radius of Y atoms (1.78Å compared to 1.62Å of Sc atoms) leads to bigger average Fe-Fe separation in Fe-Y alloys, and therefore a lower level of frustration.

As in the a-FeZr and a-FeHf systems, a cluster model has also been suggested as a description of the ordering in a-FeSc. Indeed, we have shown that both the average hyperfine field and M_z are not zero above the transition temperature T_{sg} , providing some evidence of magnetic cluster relaxation around T_{sg} . However, the observed transition at T_{sg} cannot simply reflect the blocking of superparamagnetic clusters as is suggested in Ref.[32], since measurements on very different time-scales give almost identical values of transition temperature. As mentioned in Chapter 3, for Fe_xSc_{100-x} ($89 \le x \le 91$), the transition temperatures ($104\pm 5K$) measured by Mössbauer spectroscopy, which is sensitive on a time scale of $10^{-7} \sim 10^{-9}$ s, are almost the same as those obtained from χ_{ac} measurements where a driving field of several kHz was used (99K[29] and 95K[104] for Fe₉₀Sc₁₀). The relaxation rate for magnetisation reversal in zero field (the field is really zero in Mössbauer spectroscopy and only 0.05 Oe in the χ_{ac} measurements) may be written:

$$r^{-1} = \tau_0^{-1} exp(-\Delta E/k_B T)$$
(4.1)

where τ_0 is the attempt frequency (assumed constant) and ΔE is an energy barrier. χ_{ac} measurements give $T_c \sim 100$ K at $\tau^{-1} \sim 1$ kHz, from these we estimate ΔE to be ~ 1800 K (assuming a "reasonable" value of 10^{11} Hz for τ_0^{-1} [122]). For Mössbauer measurements where $\tau^{-1} \sim 10$ MHz, the blocking temperature is then predicted to be ~ 200 K, far above the experimentally observed value of ~ 100 K. This result is relatively insensitive to the actual choice of ΔE or τ_0^{-1} and thus we can rule out a simple blocking transition as the origin of the ordering at T_{eg} .

Since $Fe_{91}Sc_9$ is already a spin glass, increasing the Fe concentration further will not change the magnetic structure and the transition temperature according to the mean-field theory and Monte Carlo simulations. Thus, the amorphous iron extrapolated from the Fe-Sc series would be a spin glass with freezing temperature about 105K and an average moment ~1.63 μ_B /Fe. This is in good agreement with the extrapolation from Fe-Zr alloys, although the magnetic ordering behavior of Fe₉₁Sc₉ is very different from that of Fe-Zr alloys with Fe content equal or less than 93 at.%.

4.4 Comparison With Theory And Simulations

Our experimental observations are clearly inconsistent with the Ising spin model of Sherrington and Kirkpatrick (SK model), which predicts that when the frustration level is high enough, the system would exhibits two magnetic transitions with the first ferromagnetic transition followed by a transition to spin glass state with a loss of FM order. While the nature of the first transition is in good agreement with experimental results on frustrated materials showing two magnetic transitions, the second transition is definitely not to spin glass state since magnetic domains have been observed in these materials and the magnetization is not zero.

The mean-field theory developed by Gabay and Toulouse (GT model)[6], where infinite-ranged exchange interactions between Heisenberg spins are assumed, is found to be comparable to our results. This theory predicts that for partially frustrated materials, three magnetic transitions are expected. The first transition is from a paramagnetic to a ferromagnetic state. The second transition marks the onset of spin glass order of the transverse spin components, but the ferromagnetic order of the longitudinal components established at the first transition is not lost. The state below the third transition has the same coexistence of ordering as the phase above the transition, and in addition has the spontaneous breaking of replica symmetry, which is associated with the strong irreversibility in the system. At high level of frustration, the system is expected to be a spin glass. Our measurements have shown that all partially frustrated materials studied here possess a finite magnetization below the second transition, which agrees with the presence of ferromagnetic order of longitudinal spin components in GT model. Furthermore, GT model predicts that the second transition reflects the ordering of the transverse spin components, which is just what we have observed. Finally, the highly frustrated Fe91Sc9 exhibits a single transition to spin glass, in good agreement with the model. However, as can be seen, differences between the theory and our experiment results do exist. There is no evidence of a well defined third transition in all of our partially frustrated samples. In fact, it has been argued that the replica-symmetry breaking, which is related to the irreversibility, occurs as soon as the transverse spin components order[8]. This therefore suggests that the third transition may not exist. Dc magnetization measurements on iron-rich Fe-Zr alloy by others [19,20] do reveal irreversibility. Magnetization obtained when the samples were cooled with and without a small dc field begin to separate below a certain temperature. But this temperature is strongly dependent on the dc field and can be higher or lower than the freezing temperature of the transverse components. Another shortcoming of GT model is that although it has shown that the transverse spin components order randomly like a two-dimensional spin glass below the second transition, it is not clear whether the transverse components are present above the second transition but precess rapidly and thus exhibit no order (transverse spin freezing model) or the transverse components appear only below the second transition since spins are canting away from the direction of the net magnetization (spin canting model).

It has been mentioned that the exchange interactions are assumed to be infiniteranged in GT model. This is definitely invalid for iron-rich amorphous alloys studied here, because for these materials, the dominant magnetic couplings are the nearestneighbor direct exchange. Moreover, the mean-field approximation inevitably misses local fluctuations. Therefore, we do not expect that this model can gives a very detailed description of magnetic ordering in these alloys.

All of our experimental observations have been reproduced by Monte Carlo simulations[95,96] where classical Heisenberg spins with nearest neighbor interaction have been considered. The localized spins are placed on a simple-cubic lattice and the exchange frustration is modeled by randomly replacing a fraction, f, of the FM interactions by AFM bonds. The exchange distribution is assumed to be a two δ -function form (+J and -J) for simplicity. Several parameters have been defined and calculated in the simulations. S_{rms} stands for the average moment while M the magnetization is as usual. Q_{\perp} is the root-mean-square transverse spin, which is a measure of the average component of the spins which lies perpendicular to the z axis independent of angular motion in the xy plane. It is defined as

$$Q_{\perp} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} m_{\perp i}^2}$$
(4.2)

where i is the site index and $m_{\perp i}^2$ is expressed as

$$m_{\perp i}^{2} = \frac{1}{\tau} \sum_{t=1}^{\tau} [\mathbf{S}_{i} - (\mathbf{S}_{i} \cdot \hat{\mathbf{z}})\hat{\mathbf{z}}]^{2}$$
(4.3)

where time $\tau = 4000$ Monte Carlo steps. Q_{xy} is the mean square transverse spin length, which averages over rotational motion of the spins in the xy plane and measures the ordering of transverse spin components. It is written as

$$Q_{xy} = \frac{1}{N} \sum_{i=1}^{N} [\mathbf{m}_{i} - (\mathbf{m}_{i} \cdot \hat{\mathbf{z}})\hat{\mathbf{z}}]^{2}$$

$$(4.4)$$

with $\mathbf{m_i} = \tau^{-1} \sum_t \mathbf{S_i}(t)$ is the time average of the spin at each site. For f=0, there are only FM exchange interactions and the system is found to be a conventional ferromagnet with transition temperature $\mathbf{T_c}=\mathbf{T_H}$. $\mathbf{S_{rms}}$ is identical to M at all temperature below $\mathbf{T_c}$, indicating that it is a collinear order. Above $\mathbf{T_c}$, $\mathbf{Q_{\perp}}$ is equal to

 $\sqrt{2/3}$, corresponding to isotropic motion of the spins for a paramagnetic system. It decreases on lowering the temperature and reaches zero at T=0K, as expected for a collinear ferromagnet. Q_{xy} remains zero at all temperatures, which indicates that there are no ordered transverse components. New features appear for f>0 and this can be see from the simulation results for f=0.115 (Fig. 4.6). Q_{\perp} decrease from $\sqrt{2/3}$ below T_c as for f=0, indicating that on average the spins are becoming less isotropic and spending less time in the xy plane. However, it does not reach zero, suggesting that noncollinearity may be established at T=0K. More significantly, although Q_{xy} is initially zero below T_c , as in the ferromagnetic case, it becomes finite below T_{xy} . The increase of Q_{xy} indicates that the transverse components of the spins are no longer averaging to zero and thus indicates the presence of noncollinear order. On the other hand, Q_{\perp} continues to decrease below T_{xy} . The only possible mechanism which would accommodate these two results is the freezing of the transverse degree of freedom. If the transverse spin components rotate rapidly about the z axis, Q_{xy} averages to zero in spite of the large Q_{\perp} . After the transverse components freeze, Q_{xy} becomes finite, although Q_{\perp} continues to decrease as the spins become more aligned to the z direction. The decrease of Q_{\perp} below T_{xy} is not consistent with the spin canting model[9,10] where spins are canting away from z direction after the second transition. Moreover, magnetization M increases steadly on lowering the temperature and does not show a sudden drop at T_{xy} as expected in the spin canting model. Therefore, the

not show a sudden utop at T_{xy} as expected in the spin canting model. Therefore, the spin canting model can be ruled out. It is also found that S_{rms} is larger than M at all temperature below T_c . While the difference between them is essentially unchanged above T_{xy} , it begins to increase below T_{xy} . This increase marks the freezing of the transverse spin components. When the transverse components order, they contribute to the total moments but do not affect the magnetization since they are perpendicular to the field direction, leading to the increase of the difference between S_{rms} and M. Compared to the corresponding measured parameters in Fig. 4.7 where average iron moment, magnetization and R (it characterizes the non-collinearity in the system and corresponds to Q_{xy} in the simulations) for $Fe_{92}Zr_7Sn$ are shown as functions of



Figure 4.6: Above: Behavior of the calculated averages in Monte Carlo simulations for f=0.115. Below: A projection along the z-axis of average spin configurations at temperatures: T=0.0TH, T=0.4591TH, T=0.7142TH.

temperature, strong similarities between our results and the simulations can be seen, particularly the two characteristic features of transverse spin freezing: (i) increase of R (or Q_{xy}) from zero and (ii) the rapid increase of μ_{av} (S_{rms} in the simulations) compared to M at T_{xy} .

The simulations predict that increasing the fraction of AFM bonds (thus the degree of frustration) causes T_c to fall, reflecting the decrease of the average exchange interaction, whereas T_{xy} rises due to the increase of frustration level. For a simple cubic lattice, T_c and T_{xy} meet at a critical fraction $f_c=0.25$. After that point, the system undergoes a single transition from paramagnetic to spin glass state with $T_{sg} \simeq 0.42T_H$ (ferromagnetic transition temperature for f=0). The phase diagram from the simulations shown in Fig. 4.8 is very similar to that we have obtained for a-Fe-Zr alloys (Fig. 4.1). It is interesting to note that the expected T_{sg} for Fe_xZr_{100-x} with $x\leq 94.5$ is ~100K. This temperature is just about 0.4 times T_c (260K) of $Fe_{sg}Zr_{11}$ (which is e-sentially a ferromagnet), a remarkable agreement between the simulations and our experimental data. For bcc and fcc lattices with higher coordination numbers (8 for bcc and 12 for fcc), the critical fraction is raised to 0.30 and 0.32 respectively, but the sequence of the ordering remains unchanged.

In the simulations, spin structure can be observed directly. It is clear that spins are not all parallel above T_{xy} as in a normal ferromagnet, some spins point in the direction opposite to the net magnetization. As a consequence, the average moment S_{rms} is larger than the magnetization M due to the partial cancellation when averaging over the system to obtain M. The difference between S_{rms} and M becomes larger as the fraction of AFM bonds, f, is increased (Fig. 4.9). This is exactly what we have observed in the Fe-Zr alloys.

Quantitative comparison between the simulations and our experiments is somewhat difficult since it not easy to exactly correlate the compositions of our samples to the fraction of AFM bonds in the simulations. An alternative is to use the ratio of T_{xy} to T_c as a measure of degree of frustration. R obtained from our experiments and the simulations are plotted as a function of T_{xy}/T_c in Fig. 4.10. For $T_{xy}/T_c < 0.3$, the



Figure 4.7: Temperature dependence of average iron moment, μ_{av} , magnetization, M, and R for Fe₉₂Zr₇Sn



Figure 4.8: Magnetic phase diagram from Monte Carlo simulations. FM: ferromagnetic phase; PM: paramagnetic phase; SG: spin-glass-like phase.

results from our measurements and the simulations are in good agreement. However, as T_{xy}/T_c become larger, R calculated from simulations is much greater than that from the experiments. This is due to several reasons. First, in our measurements, R is derived from spectra with external fields around 3T, which would rotate the spins towards the field direction and thus yield smaller R. Second, for the simulations, R is calculated from an expression: $R = 4sin^2\theta/(1 + cos^2\theta)$ and an approximation $sin\theta = \sqrt{Q_{xy}}/S_{rms}$ has been used. This approximation is only valid for small θ (thus small Q_{xy} and R) and low level frustration (small T_{xy}/T_c) where almost all longitudinal spin components are parallel.

Since magnetization can be obtained directly from the simulations, it is more meaningful to compare the magnetization. The results are shown in Fig. 4.11. The simulations agree very well with our experimental results up to $T_{xy}/T_c \sim 0.6$. Fe₉₁Sc₉ has a ratio T_{xy}/T_c of 1 and the measured magnetization is zero. According to the simulations, the system with $T_{xy}/T_c=1$ is in a spin-glass-like state and exhibits a



Figure 4.9: Above: Behavior of the calculated averages in Monte Carlo simulations for f=0.174. Below: A projection along the z-axis of average spin configurations at temperatures: T=0.0TH, T=0.4591TH, T=0.7142TH.



Figure 4.10: Comparison of R between the Monte Carlo simulations and our experiment results

finite magnetization. Since it is not clear that whether the lower critical dimension of the Heisenberg spin glass model is greater than three, the non-zero magnetization may be real or may be due to finite-size effects. Nevertheless, the remakable agreement between our experimental results and the simulations, at least up to $T_{xy}/T_c \sim 0.6$, strongly support the view that the exchange frustration alone (the only mechanism in the simulations) is sufficient to account for the observed magnetic ordering behavior of the iron-rich amorphous binary alloys studied here.



Figure 4.11: Comparison of M between the Monte Carlo simulations and our experiment results

Chapter 5

Conclusions

The magnetic properties of iron-rich amorphous alloys in the form of $\operatorname{Fe}_{x} \operatorname{T}_{100-x} (T=Zr, Hf, Sc; 89 \le x \le 93)$ have been systematically studied mainly by Mössbauer spectroscopy and magnetization measurements. The presence of both ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions in these alloys leads to exchange frustration and therefore complex magnetic ordering behavior. Our research on these frustrated systems yields the following conclusions:

- There is evidence of magnetic cluster relaxation around the ferromagnetic transition temperature T_c for all of the FeZr and FeHf alloys studied here. Two relaxation models combining the static disorder and cluster relaxation have been developed and they can give reasonable fits to Mössbauer spectra measured around T_c . Due to the complexity caused by static disorder, some artificial assumptions have to be made in the relaxation models, which prevent us from obtaining much new insight into the magnetic properties of these materials.
- Two magnetic transitions have been observed in $Fe_{92.5}Hf_{7.5}$ and FeZr alloys with Fe content between 90 and 93 at.%, and the nature of the second transition has been clarified. Subtraction of zero field Mössbauer spectra from the spectra recorded in a s. tall polarizing field yields two-line patterns, which allow us to obtain reliable hyperfine field distributions $(P(B_{hf}))$ for $Fe_{90}Zr_{10}$ by minimizing

the line overlap and eliminating the problem caused by the presence of uncontrolled magnetic texture. The analysis of $P(B_{hf})$ enables us to rule out the both cluster models, which attribute the second transition either to the ordering of AFM clusters or to the freezing of FM clusters, and to confirm that the second transition is due to the homogeneous freezing of the transverse spin components as a result of exchange frustration.

- Detailed information about the evolution process from a ferromagnet to a spin glass under the influence of increasing exchange frustration has been obtained. $Fe_{x}Zr_{100-x}$ alloys with x between 85 and 89 exhibit essentially conventional ferromagnetic behavior (there is no evidence of a second transition down to 5K for x=89), although the Curie temperature T_c drops with increasing the Fe content. When x is raised to 90, a second transition is clearly observed at $T_{xy}=28\pm 3K$, and the system enter a noncollinear state below the transition, which indicates the presence of AFM interactions and therefore the exchange frustration. As we increase the Fe content further (and thus raise the frustration level), the second transition temperature T_{xy} and the noncollinearity of the ground state increase, while T_c continues to drop. T_c and T_{xy} are expected to meet at T=100K when Fe concentration is about 94.5 at.%, suggesting that Fe94.5Zr5.5 (which can not be made by melt-spinning) would be a spin glass with spin freezing temperature of ~ 100 K. For highly frustrated Fe_x Zr_{100-x} alloys with $x \ge 92$, there is evidence that the ferromagnetic phase below T_c is different from that of a conventional ferromagnet in that some spins point in the direction opposite to the net magnetization. $Fe_{91}Sc_9$ is the most frustrated system and it exhibits a single transition to a spin glass at T_{sg} =105K. The observed evolution process is comparable to that predicted by the mean-field theory[6].
- Extrapolation of the magnetic properties of all systems (FeZr, FeHf and FeSc alloys) gives a common limit as Fe concentration approaches 100%. The amorphous Fe is expected to be a spin glass with the spin freezing temperature about

100K and an average iron moment of $\sim 1.6 \mu_B$.

- Below the second transition, the transverse spin components are strongly correlated on a nearest neighbor scale in $Fe_{92}Zr_7Sn$. The fact that magnetization is smaller than the average iron moment derived from Mössbauer spectrascopy indicates that the transverse components have to be random on a scale not larger than domain sizes. This scale is estimated to be in the order of 100Å from Lorentz transmission electron microscopy and the neutron scattering measurements. The correlation length of the longitudinal components shows no detectable change on the local scale, in contrast to a similar frustrated system, crystalline AuFe alloys, where the longitudinal correlation length decreases sizeadily below T_c .
- All of the experimental observations have been reproduced by Monte Carlo simulations, where the only mechanism is the exchange frustration modeled by randomly replacing a fraction of FM interactions with AFM interactions. The simulations give all of the characteristic features of the transverse spin freezing and a magnetic phase diagram very similar to what we have obtained. The quantitative agreement between our results and the simulations demonstrates that the magnetic ordering behavior of the alloys studied here is controlled primarily by the exchange frustration.

References

- D.H. Ryan, Recent progress in random magnets, D.H. Ryan ed. (World Scientific Publishers (Singapore), 1992).
- [2] K. Moorjani and J.M.D. Coey, Magnetic Glasses (Elsevier, Amsterdam, 1984).
- [3] S.F. Edwards and P.W. Anderson, J Phys. F 5, 965 (1975).
- [4] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. 35, 1792 (1975).
- [5] S. Kirkpatrick and D. Sherrington, Phys. Rev. B 17, 4384 (1978).
- [6] M. Gabay and G. Toulouse, Phys. Rev. Lett. 47, 201 (1981).
- [7] G. Toulouse and M. Gabay, J. de Phys. (Paris) 42 L-103 (1981).
- [8] D.M. Cragg, D. Sherrington and M. Gabay, Phys. Rev. Lett 49, 158 (1982).
- [9] W.M. Saslow and G. Parker, Phys. Rev. Lett. 56, 1074 (1986).
- [10] G.N. Parker and W.N. Saslow, Phys. Rev. B 38, 11718 (1988).
- [11] H.U. Krebs, W. Biegel, A. Bienenstock, D.J. Webb and T.H. Geballe, Materials Science and Engineering 97, 163 (1988).
- [12] M. Przybylski, K. Krop, T. Stobiecki and L. Dargel-Sulir, Hyperfine Interactions 27, 425 (1986).
- [13] J.S. Kouvel and R.H. Wilson, J. Appl. Phys. 32, 435 (1961).
- [14] W. Kümmerle and U. Gradmann, Solid State Commun. 24, 33 (1977).
- [15] G.J. Johanson and M.B. McGirr, Phys. Rev. B 1, 3208 (1970).
- [16] J.G. Wright, Phlosophical Magazine 24, 217 (1971).
- [17] U. Gonser, C.J. Meechan, A.H. Muir and H. Wiedersich, J. Appl. Phys. 34, 2373 (1963).
- [18] J.B. Newkirk, Trans. AIME 209, 1214 (1957).
- [19] H. Hiroyoshi and K. Fukamichi, Physics Letters 85A, 242 (1981).
- [20] H. Hiroyoshi and K. Fukamichi, J. Appl. Phys. 53, 2226 (1982).
- [21] N. Saito, H. Hiroyoshi, K. Fukamichi and Y. Nakagawa, J. Phys. F: Met. Phys. 16, 911 (1986).
- [22] D.H. Ryan, J.O Ström-Olsen, R. Provencher and M. Townsend, J. Appl. Phys. 64, 5787 (1988).
- [23] D.H. Ryan, J.M.D. Coey, E. Batalla, Z. Altounian and J.O. Ström-Olsen, Phys. Rev. B 35, 8630 (1987).
- [24] D.H. Ryan and Hong Ren, J. Appl. Phys. 69, 5057 (1991).
- [25] D.A. Read, T. Moyo, S. Jassim, R.A. Dunlap and G.C. Hallam, J. Magn. Magn. Mater. 82, 87 (1989).

- [26] S.N. Kaul, V. Siruguri and G. Chandra, Phys. Rev. B 45, 12343 (1992).
- [27] S.N. Kaul, C. Bansal, T. Kumaran and M. Havalgi, Phys. Rev. B 38, 9248 (1983).
- [28] D.H. Ryan, J.M.D. Coey and J.O. Ström-Olsen, J. Magn. Magn. Mater. 67, 148 (1987).
- [29] R.K. Day, J.B. Dunlop, C.P. Foley, M. Ghafari and H. Pask, Solid State Commun. 56, 843 (1985).
- [30] D.H. Ryan, J.O. Ström-Olsen, J.M. Cadogan and J.M.D. Coey, Phys. Rev. B 40, 11208 (1989).
- [31] M. Ghafari, R.K. Day, J.B. Dunlop, W. Keune and A.C. Mcgrath, Hyperfine Interactions 54, 533 (1990).
- [32] M. Ghafari, R.K. Day, J.B. Dunlop and A.C. McGrath, J. Magn. Magn. Mater. 104-107, 1668 (1992).
- [33] M. Avirovic, P. Ziemann, B. Huck and J. Hesse, Europhys. Lett 8, 281 (1989).
- [34] B.V.B. Sarkissian, J. Phys. F: Met. Phys. 11, 2191 (1981).
- [35] B.H. Verbeek and J.A. Mydosh, J. Phys. F: Met. Phys. 8, L109 (1978).
- [36] J. Lauer and W. Keune, Phys. Rev. Lett. 48, 1850 (1982).
- [37] F. Varret, A. Hamzić and I.A. Campbell, Phys. Rev. B 26, 5285 (1982).
- [38] I.A. Campbell, S. Senoussi, F. Varret, J. Teillet and A. Hamzić, Phys. Rev. Lett. 50, 1615 (1983).
- [39] S. Crane and H. Claus, Phys. Rev. Lett. 46, 1693 (1981).
- [40] E. Dartyge, H. Bouchiat and P. Monod, Phys. Rev. B 25, 6995 (1982).
- [41] J.W. Cable, G. Parette and Y. Tsunoda, Phys. Rev. B 36, 8467 (1987).
- [42] C.E. Violet and R.J. Borg, Phys. Rev. Lett. 51, 1073 (1983).
- [42] R.J. Borg and C.E. Violet, J. Appl. Phys. 55, 1700 (1984).
- [44] P. Monod and I.A. Campbell, Phys. Rev. Lett. 52, 2096 (1984).
- [45] R.A. Brand and W. Keune, Phys. Rev. Lett. 52, 2097 (1984).
- [46] R.A. Brand, J. Lauer and W. Keune, Phys. Rev. B 31, 1630 (1985).
- [47] J.A. Geohegan and S.M. Bhagat, J. Magn. Magn. Mater. 25, 17 (1981).
- [48] T. Miyazaki, I. Okamoto, Y. Ando and M. Takahshi, J. Phys. F: Met. Phys. 18, 1601 (1988).
- [49] Y. Yeshurun, M.B. Salamon and K.V. Rao, Phys. Rev. B 24, 1536 (1981).
- [50] G. Aeppli, S.M. Shapiro, H. Maletta, R.J. Birgeneau and H.S. Chen, J. Appl. Phys. 55, 1628 (1984).

- [51] M. Hennion, B. Hennion, I. Mirebeau, S. Lequien and F. Hippert, J. Appl. Phys. 63, 4071 (1988).
- [52] R.W. Erwin, J.W. Lynn, J.J. Rhyne and H.S. Chen, J. Appl. Phys. 57, 3473 (1985).
- [53] J.W. Lynn, R.W. Erwin, J.J. Rhyne and H.S. Chen, J. Appl. Phys. 52, 1738 (1981).
- [54] S. Senoussi, J. de Phys. 45, 315 (1984).
- [55] I Mirebeau, S. Itoh, S. Mitsuda, T. Watanabe, Y. Endoh, M. Hennion and R. Papoular, Phys. Rev. B 41, 11405 (1990).
- [56] R.W. Erwin, J. Appl. Phys. 67, 5229 (1990).
- [57] V. Manns, R.A. Brand, W. Keune and R. Marx, Solid State Commun. 48, 811 (1983).
- [58] I. Mirebeau, G. Jehanno, I.A. Campbell, F. Hippert, B. Hennion and M. Hennion, J. of Magn. Magn. Mater. 54-57, 99 (1986).
- [59] H. Maletta, J. Appl. Phys. 53, 2185 (1982).
- [60] H. Maletta, G. Aeppli and S.M. Shapiro, Phys. Rev. Lett. 48, 1490 (1982).
- [61] H. Maletta, W. Zinn, H. Scheuer and S.M. Shapiro, J. Appl. Phys. 52, 1735 (1981).
- [62] H. Maletta, Heidelberg Colloquium on Spin-Glasses, J.L. van Hemmen and I. Morgenstern ed. (Springer Verlag, Berlin, 1983), p. 90.
- [63] S.M. Shapiro, H. Maletta and F. Mezei, J. Appl. Phys. 57, 3485 (1985).
- [64] H.G. Bohn, W. Zinn, B. Dorner and A. Kollmar, Phys. Rev. B 22, 5447 (1980).
- [65] N.N. Greenwood and T.C. Gibb, Mössbauer Spectroscopy (Chapman and Hall Ltd, London, 1971).
- [66] P.E.D. Dominic and J.B. Frank, Mössbauer Spectroscopy, P.E.D. Dominic and J.B. Frank ed. (Cambridge University Press, 1986), p. 1.
- [67] U. Gonser, Proceedings of the School on Application of Nuclear Gamma Resonant Spectroscopy (Mössbauer Spectroscopy), N.A. Eissa and G. Denardo ed. (World Scientific, 1986), p. 1.
- [68] P.C.M. Gubbens, J.H.F.van. Apeldoorn, A.M.van.der. Kraan and K.H.J. Buschow, J. Phys. F 4, 921 (1974).
- [69] M. Blume and J. A. Tjon, Phys. Rev. 165, 446 (1968).
- [70] D.G. Rancourt, Hyperfine Interactions 40, 183 (1988).
- [71] D.G. Rancourt, H.H.A. Smit and R.C. Thiel J. Magn. Magn. Mater. 66, 121 (1987).
- [72] B. Window, J. Phys. E4, 401 (1971).

- [73] D. Kaptas and I. Vincze, Hyperfine Interactions 55, 987 (1990).
- [74] R. Reisser, M. Fähnle and H. Kronmüller, J. Magn. Magn. Mater. 75, 45 (1988).
- [75] S.N. Kaul, J. Phys. F: Met. Phys. 18, 2089 (1988).
- [76] J.C.Le Guillou and J. Zinn-Justin Phys. Rev. Lett. 39, 95 (1977).
- [77] S.M. Fries, C.L. Chien, J. Crummenauer, H.G. Wagner and U. Gonser, Hyperfine Interactions 27, 405 (1986).
- [78] S.M. Fries, J. Crummenauer, U. Gonser, P. Schaaf and C.L. Chien, Hyperfine Interactions 45, 301 (1989).
- [79] H. Yamamoto, H. Onodera, K. Hosoyama, and H. Yamauchi, J. Magn. Magn. Mater.31-34,1579 (1983).
- [80] J. J. Rhyne, R. W. Erwin, J. A. Fernandez-Baca, and G. E. Fish, J. Appl. Phys. 63, 4080 (1988).
- [81] J.M.D. Coey, J. Appl. Phys. 49, 1646 (1978).
- [82] J.R. Thomson, Ph.D. thesis
- [83] H. Tange, Y. Tanaka, M. Goto and K. Fukamichi J. Magn. Magn. Mater. 81,L243 (1989).
- [84] H. Ma, H.P. Kunkel and G. Williams, J. Phys.: Condens. Matter 3, 5563 (1991).
- [85] S.N. Kaul, J. Phys.: Condensed Matters 3, 4027 (1991).
- [86] S. Senoussi, S. Hadjoudj, R. Fourmeaux and C. Jaouen, J. de Phys. Colloque (Paris) 49, C8-1163 (1988).
- [87] S. Senoussi, S. Hadjoudj, P. Jouret, J. Bilotte and R. Fourmeaux, J. Appl. Phys. 63, 4086 (1988).
- [88] S. Hadjoudj, S. Senoussi and I. Mirebeau, J. of Magn. Magn. Mater. 93, 136 (1991).
- [89] S. Hadjoudj, S. Senoussi and D.H. Ryan, J. Appl. Phys. 67, 5958 (1990).
- [90] M.M. Abd-Elmeguid, H. Micklitz, R.A. Brand and W. Keune, Phys. Rev. B 33, 7833 (1986).
- [91] A. Aït-Bahammou, C. Meyer, F. Hartmann-Boutron, Y. Gros, I.A. Campbell,
 C. Jeandey and J.L. Oddou, J. de Phys. Colloque (Paris) 49, C8-1075 (1988).
- [92] A. Aït-Bahammou, C. Meyer, F. Hartmann-Boutron, Y. Gros and I.A. Campbell, J. de Phys. Colloque (Paris) 49, C8-1157 (1988).
- [93] S. Mitsuda, H. Yoshizawa, T. Watanabe, S. Itoh, Y. Endoh and I. Mirebeau, J. Phys. Soc. Japan 60, 1721 (1991).
- [94] B.V.B. Sarkissian, J. Phys: Condens. Matter 3, 961 (1991).

- [95] J.R. Thomson, G. Hong, D.H. Ryan, M.J. Zuckermann and G. Martin, Phys. Rev. B 45, 3129 (1992).
- [96] J.R. Thomson, G. Hong, D.H. Ryan, M.J. Zuckermann and G. Martin, J. Appl. Phys. 69, 5231 (1991).
- [97] K.M. Unruh and C.L. Chien, Phys. Rev. B 30, 4968 (1984).
- [98] T. Kaneko, K. Shirakawa, S. Ohnuma, M. Nose, H. Fujimori and T. Masumoto, J. Appl. Phys. 52, 1826 (1981).
- [99] J. Tanaka, K. Nomura, Y. Ujihira, A. Vértes, H. Kimura and T. Masomoto, Hyperfine Interactions 55, 1071 (1990).
- [100] A.H. Morrish, R.J. Pollard, Z.S. Wronski and A. Calka, Phys. Rev. B 32, 7528 (1985).
- [101] S.M. Fries, C.L. Chien, J. Crummenauer, H.G. Wagner and U. Gonser, Journal of Less-Common Metals 130, 17 (1987).
- [102] E. Kuzmann, A. Vértes, Y. Ujihira, P. Kovács, T. Ando and T. Masomoto, Hyperfine Interactions 45, 279 (1989).
- [103] S.H. Liou, G. Xiao, J.N. Taylor and C.L. Chien, J. Appl. Phys. 57, 3536 (1985).
- [104] H. Ma, Z. Wang, H.P. Kunkel, G. Williams, D.H. Ryan and J.O. Ström-Olsen, J. Magn. Magn. Mater. 104-107, 89 (1992).
- [105] M.F. Opheys and E.F. Wassermann, Physica B 169, 471 (1991).
- [106] P. Pureur, G.L. Fraga, D.E. Brandão, R. Caudron, H. Safa and G. Nieva, J. Magn. Magn. Mater. 68, 213 (1987).
- [107] K. Baberschke, P. Pureur, A. Fert, R. Wendler and S. Senoussi, Phys. Rev. B 29, 4999 (1984).
- [108] R. Wendler, P. Pureur, A. Fert and K. Baberschke, J. Magn. Magn. Mater. 45, 185 (1984).
- [109] L.L. Isaacs, Phys. Rev. B 8, 3301 (1973).
- [110] B.V.B. Sarkissian, J. Phys. F: Met. Phys. 7, L139 (1977).
- [111] B.V.B. Sarkissian and B.R. Coles, Communications on Physics 1, 17 (1976).
- [112] B. Levesque, R. Caudron and P. Costa, Journal de Physique, Colloque C5 40, C5-266 (1979).
- [113] N. Rivier and K. Adkins, J. Phys. F: Met. Phys. 5, 1745 (1975).
- [114] F. Tsui, C.P. Flynn, R.S. Beach, M.B. Salamon, J.A. Borchers, R.W. Erwin and J.J. Rhyne, J. Appl. Phys. 73 6904 (1993)
- [115] J.M.D. Coey, D. Givord, A. Liénard and J.P. ' bouillat, J. Phys. F 11, 2707 (1981).

- [116] J. Chappert, J.M.D. Coey, A. Liénard and J.P. Rebouillat, J. Phys. F 11, 2727 (1981).
- [117] L.E. Wenger, G.W. Hunter, J.A. Mydosh, J.A. Gotaas and J.J. Rhyne, Phys. Rev. Lett. 56, 1090 (1986).
- [118] C.F. Majkrzak, J.W. Cable, J. Kwo, M. Hong, D.B. McWhan, Y. Yafet, J.V. Waszczak and C. Vettier, Phys. Rev. Lett. 56, 2700 (1986).
- [119] M.B. Salamon, S. Sinha, J.J. Rhyne, J.E. Cunningham, E. Ross, J. Borchers and C.P. Flynn, Phys. Rev. Lett. 56, 259 (1986).
- [120] J. Borchers, M.B. Salamon, R.W. Erwin, J.J. Rhyne, R. Du and C.P. Flynn, Phys. Rev. B 43, 3123 (1991).
- [121] R.W. Erwin, J.J. Rhyne, M.B. Salamon, J. Borchers, S. Sinha, R. Du, J.E. Cunningham and C.P. Flynn, Phys. Rev. B 35, 6808 (1987).
- [122] D.H. Jones, Hyperfine Interactions 47, 289 (1989).