

LETTER TO THE EDITOR

Chemical ordering in $Y_{66}(Fe_xMn_{1-x})_{34}$ metallic glasses

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Abstract. The compositional dependence of the ^{57}Fe Mössbauer effect spectra for the metallic glasses $Y_{66}(Fe_xMn_{1-x})_{34}$ has been studied. For high concentrations of Fe the spectra consist of two symmetric peaks with the spectra becoming progressively more complex as the Fe content decreases. The smooth variation of the parameters derived from the spectra indicates that Fe and Mn perform the same functions in the glass. We find evidence for chemical ordering in these glasses and we demonstrate the existence of two distinct atomic sites for Fe. Site 1 we attribute to Fe atoms having predominately Y near neighbours and site 2 is identified as Fe atoms having a larger number of Fe (Mn) near neighbours.

The nature and extent of the short-range order in metallic glasses is currently of great interest. Many techniques have been used to study the structure of these glasses (x-ray, neutron, electron scattering, EXAFS). These techniques can provide radial information on the average coordination number and average interatomic spacings. In metal-metalloid glasses (e.g. $Pd_{80}Si_{20}$) evidence for chemical ordering has been found. For the glasses Co-P (Blétry and Sadoc 1975), $Pd_{84}Si_{16}$ (Sadoc and Dixmier 1977) and $Pd_{78}Ge_{22}$ (Hayes *et al* 1978) the absence of metalloid-metalloid nearest neighbours has been claimed. By studying the compositional dependence of the Mössbauer effect (ME) spectra we find evidence for chemical ordering in $Y_{66}(Fe_xMn_{1-x})_{34}$ glasses. In particular, we report the first indication of the existence of two distinct atomic sites in a metallic glass. In the non-magnetic metallic glass system $Y_{66}(Fe_xMn_{1-x})_{34}$ we find that there are two distinct Fe sites for all compositions (X). One site has predominantly Y neighbours, while the other site has a larger number of Fe(Mn) neighbours. The other structural techniques (x-ray, neutron, electron scattering, EXAFS) would not be sensitive to the dual role Fe plays in this glass since their information is averaged over all Fe sites. The ME spectra, being sensitive to both the chemical and topological environment about the resonant atom, provide unique information about the arrangement of atoms in these glasses.

Ingots of $Y_{66}(Fe_xMn_{1-x})_{34}$ were prepared by levitation melting 99.99% pure Y and 99.9% pure Mn in a protective atmosphere of argon. Fe enriched to 10 wt% ^{57}Fe was used in the preparation of the $X = 0.25$ and 0.05 samples. Rapidly quenched foils were produced using the piston and anvil technique in a flowing helium atmosphere (Duwez 1966). The resulting foils were approximately 30 μm thick and 40 mg in weight. X-ray diffraction scans using $Cu K\alpha$ ($0.125^\circ \text{ min}^{-1}$) and $Mo K\alpha$ ($0.024^\circ \text{ min}^{-1}$) were taken. Those foils whose x-ray diffraction patterns consisted of a smooth

featureless band were classified as amorphous. Amorphous foils of $Y_{66}(\text{Fe}_x\text{Mn}_{1-x})_{34}$ were prepared for $X = 1.00, 0.75, 0.50, 0.25$ and 0.05 . Density measurements were made on the foils using a microbalance and a toluene bath. The values for atomic density (ρ) are listed in table 1. They increase smoothly with increasing Fe content, consistent with the smaller size of Fe compared to Mn.

Mössbauer effect (ME) experiments were performed at room temperature in a fixed well collimated geometry using a ^{57}Co (Rh) source and a constant acceleration electromechanical drive. The linewidth (Γ) observed for the inner two lines of a thin Fe foil using this system was 0.221 mm s^{-1} . Absorbers (for $X = 1.00, 0.75$ and 0.50) having a thickness of $0.06 \text{ mg } ^{57}\text{Fe cm}^{-2}$ were prepared from carefully powdered foils mixed with MgO. For $X = 0.25$ and 0.05 , because of the small amount of Fe in the samples, the as-quenched foils were used as absorbers. For all experiments the material from a single foil was used as an absorber, powders from different foils were not mixed.

The ME spectra for $X = 0.05, 0.50$ and 1.00 are shown in figure 1. The $X = 1.00$ spectrum consists of two reasonably symmetric peaks, while the spectra of the other compositions are somewhat more complex. As figure 2 shows, the $X = 1.00$ spectrum can be fitted to a single pair of Lorentzian lines; however a fit assuming two pairs of lines gives a visibly better representation of the data. Although it is difficult to justify the use of two pairs of lines for $X = 1.00$ on the basis of the quality of the fit, the other compositions shown in figure 1 clearly cannot be fitted to a single pair of lines. A minimum of two doublets is required to understand the data for $X \leq 0.75$. As figure 1 shows, a model which assumes two distinct Fe sites gives a good representation of the experimental data for all three compositions. As an approximation, we have constrained the two pairs of lines to have the same linewidth. Each pair is characterised by the spacing between its peaks (quadrupole splitting QS) and its centroid (isomer shift IS). The QS is related to the point symmetry about the resonant atom and the IS is a measure of the s electron density at the nuclear site. In table 1 we list the results of least-squares fitting the spectra to two Fe sites. Also included in table 1 are the parameters resulting from a one-site fit to the $X = 1.00$ spectrum. The systematic behaviour of QS and IS for both sites demonstrates that these two sites are present for all compositions of Fe and Mn. The fact that the intensity ratio (I_1/I_2) is always about 1 means that both sites are approximately equally populated and thus rules out the possibility that one of the sites is a crystalline phase. The x-ray scans would have detected such a large amount of crystals in the samples easily.

Table 1. Summary of ME data and atomic density measurements for $Y_{66}(\text{Fe}_x\text{Mn}_{1-x})_{34}$ metallic glasses.

Composition (X)	QS1 (mm s^{-1})	IS1 (mm s^{-1})	QS2 (mm s^{-1})	IS2 (mm s^{-1})	I_1/I_2	Γ (mm s^{-1})	ρ (atom cm^{-3})
0.05	0.467 (8)	-0.153 (8)	0.174 (8)	-0.094 (8)	0.89	0.29 (1)	3.97×10^{22}
0.25	0.468	-0.155	0.180	-0.113	0.88	0.29	3.97
0.50	0.466	-0.157	0.192	-0.130	0.96	0.29	3.99
0.75	0.467	-0.160	0.212	-0.147	0.95	0.28	4.00
1.00	0.472	-0.164	0.226	-0.165	1.07	0.28	4.04
1.00†	0.363	-0.164	—	—	—	0.34	—

† One-site fit.

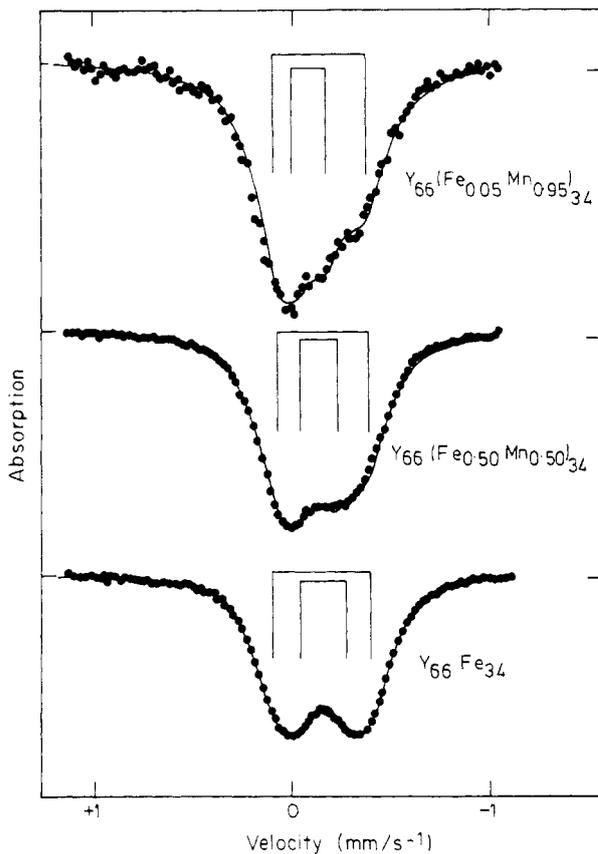


Figure 1. Room temperature ME spectra of $Y_{66}(Fe_xMn_{1-x})_{34}$ metallic glasses. The full curve passing through the data points represents a least-squares fit of the spectra to two pairs of lines. The peak positions and intensities of the pairs are shown above the data by the vertical bars. The zero of velocity is with respect to α -Fe.

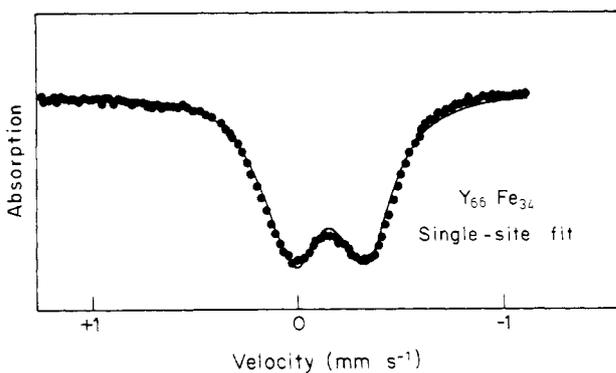


Figure 2. The $Y_{66}Fe_{34}$ data from figure 1 fitted to a single pair of Lorentzians.

The Γ values are somewhat smaller than those observed in other ME measurements on metallic glasses. This is due to the fact that we are able to separate clearly the two contributions to the spectra, and are therefore able to justify using a two-site fit. Although the lines are fairly narrow, some broadening exists indicating that fitting the spectra to two distinct sites is not quite correct. The simple approach taken here, however, is adequate to describe the data and provides a useful framework for understanding its implications.

As table 1 shows, the parameters of site 1 (QS_1 and IS_1) are nearly independent of composition (X). In contrast, the parameters of site 2 (QS_2 and IS_2) are very dependent on X . As figure 3 shows, IS_2 rapidly decreases with increasing Fe content while IS_1 remains nearly constant. This results in the increasingly asymmetric character of the spectra as X decreases. In fact, the dramatic changes we observe in the spectra can be attributed almost entirely to the dependence of QS_2 and IS_2 on X . Because its parameters are nearly independent of X , we identify site 1 as an Fe environment which has primarily Y near neighbours. Since the chemical and topological short-range order about this Fe site is dominated by Y, QS_1 and IS_1 are weak functions of X . Likewise, site 2 represents Fe atoms which have a significant number of Fe and Mn near neighbours. The identification of this site is based on its strong dependence on X and both the value and direction of the change of its IS . We have measured the IS of dilute impurities of ^{57}Fe in the Laves phase compound YMn_2 and have found that it is 0.10 mm s^{-1} higher than pure YFe_2 . We find that IS_2 for $X = 0.05$ is 0.071 mm s^{-1} higher than $X = 1.00$ and that IS_2 smoothly decreases as the Fe content is increased. This supports the claim that this site is Fe and Mn dominated. In addition, the smooth behaviour of ρ and the ME parameters (particularly the intensity ratio) supports the idea that the Mn and Fe atoms are randomly mixed and perform essentially the same functions in the amorphous structure.

A complete description of the two Fe environments in Y-Mn-Fe glasses cannot be

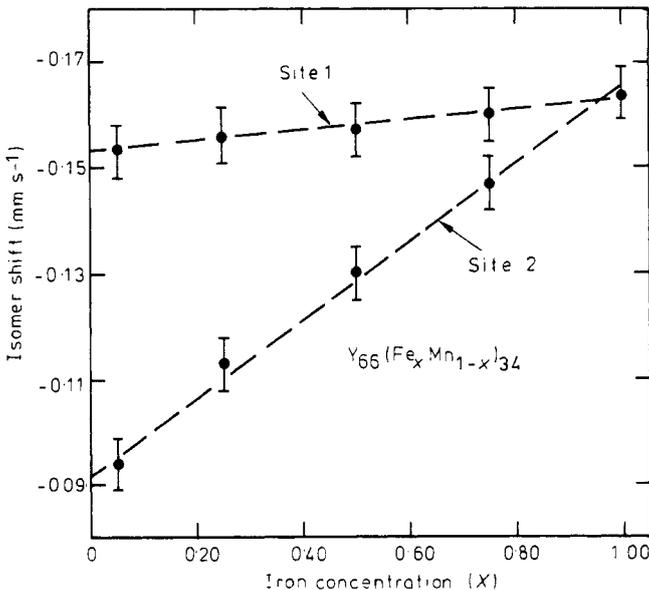


Figure 3. Isomer shifts obtained by fitting the ME spectra to two sites plotted against iron concentration (X). The designations site 1 and site 2 are discussed in the text. The IS is with respect to $\alpha\text{-Fe}$.

given with the limited information reported here. Other microscopic techniques (e.g. NMR) would be very helpful here. From the ME experiments we know that two Fe sites exist having roughly equal populations in which one site has a larger number of Fe(Mn) neighbours than the other. We suggest two descriptions of metallic glasses consistent with the ME data.

The first is that the glass is a single-phase material in which Fe performs two functions. In the description of metal-metalloid glasses (e.g. $\text{Pd}_{80}\text{Si}_{20}$) one commonly uses the Polk (1972) model in which the metal atoms (Pd) are randomly dense packed and the metalloid atoms (Si) occupy the holes in the metal packing. This leads to metalloid atoms having only metal near neighbours. Evidence for the qualitative correctness of this kind of picture has been reported (Hayes *et al* 1978). This is the type of environment we imagine Fe has in site 1. Having only Y near neighbours its contribution to the ME spectrum would be independent of composition (X). The number of these kinds of holes is limited and because of the high concentrations of Fe(Mn) in these alloys some of the small atoms (Fe, Mn) are forced to have small atom near neighbours (i.e. site 2).

The second description is that the glass is intrinsically inhomogeneous. In particular, the glass consists of two amorphous phases having different types of short-range order. Such a two-phase amorphous material has been reported in the Pb-Sb-Au system on the basis of x-ray and superconducting data (Kim and Johnson 1980). In addition, the idea was mentioned in a discussion of the ME experiments on $\text{Y}_{1-x}\text{Fe}_x$ glasses (Tenhover 1980b).

The equilibrium phase diagrams of Y-Mn and Y-Fe are very similar. In both cases the solubility of Fe(Mn) in HCP Y is very small (less than 0.1 at%) and the Fe(Mn) richest compound is the cubic Laves phase YFe_2 (YMn_2). In equilibrium, the alloy is two-phase (HCP Y + YFe_2 (YMn_2)). We imagine the metallic glass to be composed of two amorphous phases related to the two equilibrium phases. The interstitial solubility of Fe(Mn) in HCP Y is very small due primarily to size effects which should not be as important for the amorphous structure. We identify site 1 as the contribution from Fe atoms in a Y-rich amorphous phase (something like amorphous $\text{Y}_{80}\text{Fe}_{20}$) which is similar in structure to the metal-metalloid glasses mentioned earlier. As a first approximation to the structure a Polk model would perhaps be appropriate. Site 2 results from Fe atoms in an Fe(Mn) richer amorphous phase based possibly on the kind of short-range order found in the Laves phase compound. The kind of model suggested by Sadoc and Liénard (1978) for rare-earth-transition-metal glasses might be a reasonable starting point. The problem with a two-phase model is that if these domains are small a fair number of atoms are on the interface and they must make a contribution to the ME spectra. We mentioned before that the lines are somewhat broad, and we suggest that Fe atoms at the interface may be the origin of this broadening.

Whatever the details of the two Fe sites are, the fact that there are two distinct sites having equal populations is very interesting. There are many transition-metal-transition-metal alloys which form metallic glasses at high concentrations of small atoms (e.g. $\text{Zr}_{57}\text{V}_{43}$ (Tenhover 1980a), $\text{Nb}_{58}\text{Rh}_{42}$ (Johnson and Poon 1975), $\text{Nb}_{60}\text{Ni}_{40}$ (Ray *et al* 1968)). This may simply be the result of the fact that the small atom has two specific roles in these metal-metal glasses as opposed to the single role the metalloid plays in a metal-metalloid glass (like Si in $\text{Pd}_{80}\text{Si}_{20}$). The ME work is being extended to include the systems $\text{Y}_{66}(\text{Fe}_x\text{M}_{1-x})_{34}$ ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and these results will be reported soon.

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