Atomic rearrangements during structural relaxation in $Fe_{78}Si_9B_{13}$

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Structural relaxation in a magnetic metallic glass having composition $Fe_{78}Si_9B_{13}$ has been studied using Mössbauer spectroscopy. Information about the atomic-level changes occurring in the specimen has been obtained through the correlated distributions of the hyperfine-interaction parameters. Increasing annealing temperature causes a decrease in the geometrical distortions as well as a change in topological short-range order. These changes involve (i) a decrease in the average interatomic spacing, and (ii) topological rearrangement of atoms resulting in significant changes in the population of transition-metal sites with different numbers of metalloid near neighbors.

I. INTRODUCTION

Metallic glasses exhibit considerable variation in their material properties with thermal annealing at temperatures well below the crystallization temperature. This has been attributed to structural relaxation occurring in the glassy state, resulting in significant changes in the short-range order (SRO) in the system. Studies on the structural relaxation in metallic glasses have mainly been done by monitoring changes in properties like Curie temperature, electrical resistivity, density, etc.[1–3] Such studies yield detailed information about the kinetics of the structural relaxation process. However, kinetic measurements are generally not sufficiently critical to discriminate between different forms of atomic rearrangements. In a rather limited number of studies, microscopic techniques like Mössbauer spectroscopy and x-ray diffraction (XRD) have also been used to get information about variations in short-range order.[4,5] Three possible atomic rearrangement events associated with structural relaxation may be recognized as the following: (i) a change in the mean near-neighbor distance, (ii) a change in the mean coordination number, and (iii) a change in the mean chemical order.[2] It has been shown that irreversible relaxation is accompanied by densification, whereas reversible relaxation shows only changes in local atomic order at constant density.[4] A combination of the results of XRD, Mössbauer, and differential scanning calorimetry measurements in a nonmagnetic metallic glass $Pd_{40}Ni_{40}P_{20}$ (Ref. 5) suggests that apart from the elimination of free volume, associated only with irreversible relaxation, reversible and irreversible relaxation involve essentially similar microscopic changes.

In the present work we have used Mössbauer spectroscopy to study irreversible structural relaxation in a magnetic metallic glass $Fe_{78}Si_9B_{13}$, occurring during isochronal annealing at successively higher temperatures. In a transition-metal–metalloid (TM-M) metallic glass, the hyperfine field at a TM site is significantly affected by its metalloid environment. Therefore, in a magnetic metallic glass, variations in the metalloid environment as a result of structural relaxation can be effectively studied using Mössbauer spectroscopy.

II. EXPERIMENT

A metallic glass specimen having composition $Fe_{78}Si_9B_{13}$, available in the form of ≈ 40 μm thick and 20 mm wide ribbon from Vacuumschmelze GmbH, Germany was studied. Annealing was done in a salt bath consisting of 50% KNO_3, 10% $NaNO_3$, and 40% $NaNO_2$. Temperature of the bath was kept constant to within ± 1 K of the set temperature. ^{57}Fe Mössbauer spectra were measured at room temperature with a Wissel MD-1200 Mössbauer spectrometer and a 25 mCi ^{57}Co source in a Rh matrix. The spectrometer gave a linewidth of 0.22 mm/s for the inner lines of a thin α-Fe absorber.

III. RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectra of the specimen $Fe_{78}Si_9B_{13}$ isochronally annealed at different temperatures for 30 min each, and the corresponding distributions of hyperfine fields obtained using the method of Le Caer *et al.*[6] The results of fitting are summarized in Table I. From the figure one may note that with increasing annealing temperature, the relative intensity of the second and fifth lines *b* decreases monotonically, which may be attributed to the increasing surface crystallization or oxidation of the specimen.[7] Besides this, small but significant changes in the hyperfine field distribution also take place with increasing annealing temperature, indicating a change in the short-range order in the system.

It is well accepted that the hyperfine field at a TM site is mainly determined by its metalloid environment, its magnitude varying approximately linearly with the number of metalloid near neighbors.[8,9] Thus a broad hyperfine field distribution essentially reflects the variety of possible metalloid environments about the TM site. Therefore, the spectra were also analyzed assuming an overlap of four sextets corresponding to iron sites with one, two, three, and four metalloid near neighbors.[9] The results of fitting are shown in Table II. One may note that with increasing annealing temperature, the population of iron sites with two and three metalloid near neighbors increases at the expense of other sites, while the mean number of metalloid near neighbors remains essen-

tially unchanged. The mean hyperfine field corresponding to each type of site also varies with annealing temperature. While the mean field corresponding to the Fe sites with four metalloid near neighbors exhibits a small decrease with increasing annealing temperatures, i.e., a negative $(\Delta H/\Delta T)$, the other three sites exhibit a positive $(\Delta H/\Delta T)$ with its magnitude increasing with the decreasing number of metalloid near neighbors. This variation with temperature in the mean hyperfine field of different sites may be understood in terms of two effects. (i) Increasing annealing temperature results in a decrease in the mean interatomic distance via annihilation of excess free volume, and a decrease in Fe-M distances would result in a decrease in Fe moment causing the hyperfine field to decrease.[10] (ii) With increasing annealing temperature, the geometrical distortions are expected to decrease, causing an increase in the mean hyperfine field at a given site.[11] Since the first effect would be more pronounced for sites with a larger number of metalloid near neighbors, the net $(\Delta H/\Delta T)$ is expected to be smaller for sites with a higher number of metalloid near neighbors, as observed experimentally. Thus, the observed variations in the hyperfine field may be understood in terms of (i) a decrease in geometrical distortions causing $H_{\rm hf}$ at a site to increase, (ii) a decrease in interatomic distance causing $H_{\rm hf}$ to decrease, and (iii) atomic rearrangements resulting in redistribution of TM sites with different number of M near neighbors.

The above inference gets further support from the observed changes in the variances of and correlations among isomer shift, quadrupole interaction, and hyperfine field, obtained using the method of Lines and co-workers.[12] Following Pollard, Wronski, and Morrish[13] one can write

$$\langle L_i\rangle=\langle\delta\rangle+jg_k\mu_N\langle H\rangle+1\langle\alpha_m\rangle\ , \tag{1}$$

$$\sigma^2(L_i)=\langle(\Delta\delta)^2\rangle+\langle(\Delta u^2)\rangle+g_k^2\mu_N^2\langle(\Delta H)^2\rangle +2m\langle\Delta u\Delta\delta\rangle+2jg_k\mu_N(\langle\Delta H\Delta\delta\rangle+1\langle\Delta H\Delta\alpha_m\rangle +m\langle\Delta H\Delta u\rangle)\ , \tag{2}$$

where all the symbols have been defined in Ref. 13. The spectra were fitted with six independent lines having Voigt line profiles in order to obtain six line positions $\langle L_i\rangle$ and their variances $\sigma^2(L_i)$. The values of various parameters determined by least-square fitting of the obtained values of $\langle L_i\rangle$ and $\sigma^2(L_i)$ using Eqs. (1) and (2) are presented in Table III.

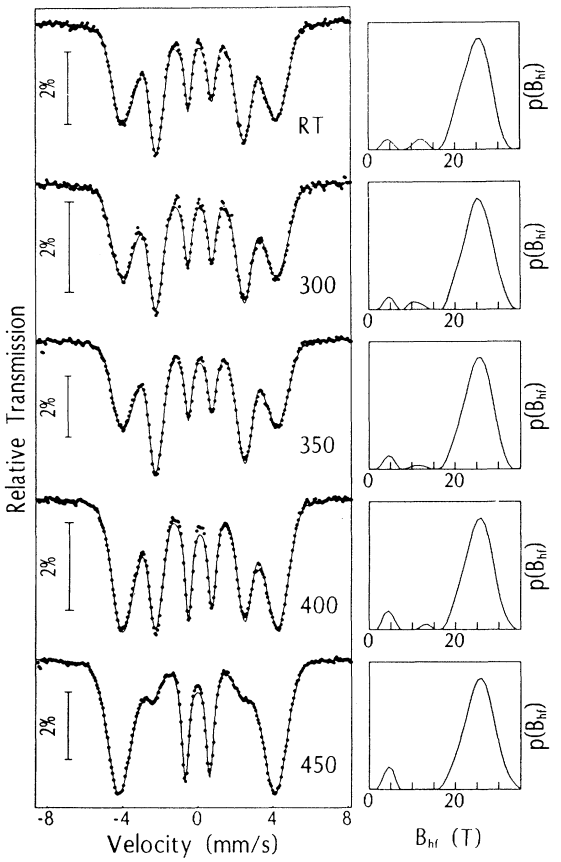

FIG. 1. Room-temperature Mössbauer spectra of $Fe_{78}Si_9B_{13}$ after isochronal annealing at different temperatures (given in °C) for 30 min each.

From Table III one may note that the most significant variation with annealing temperature is observed in the variance of u. $\sigma(\Delta u)$ decreases with increasing annealing temperature, indicating that the effect of structural relaxation is to decrease the geometrical disorder (distribution of bond angles and bond lengths) in the system. On the contrary, the variance of isomer shift exhibits a small increase with annealing temperature. This may be attributed to a decrease in the TM-M bond length as a result of

TABLE I. Parameters obtained by fitting of the Mössbauer spectra using the method of Le Caer *et al.* Isomer shift (δ) is relative to α-Fe.

Annealing temperature (°C)	$\langle H\rangle$ (kOe)	ΔH (kOe)	δ (mm/s)	QS (mm/s)	b
RT	245.8(5)	46.9(5)	0.10(1)	−0.06(5)	0.84(2)
300	248.8	47.2	0.08	−0.06	0.84
350	248.4	46.8	0.09	−0.02	0.97
400	248.2	48.8	0.08	−0.02	0.61
450	252.9	47.3	−0.04	−0.01	0.15

TABLE II. Results of fitting of the Mössbauer spectra with four overlapping sextets with Voigt line profile.

Annealing temperature (°C)	4M nn $\langle H \rangle$ (kOe)	4M nn Area	3M nn $\langle H \rangle$ (kOe)	3M nn Area	2M nn $\langle H \rangle$ (kOe)	2M nn Area	1M nn $\langle H \rangle$ (kOe)	1M nn Area	$\bar{n}_B$
RT	212.7(10)	0.184(5)	238.3(10)	0.269(5)	269.1(10)	0.328(5)	284.0(10)	0.219(5)	2.42(5)
300	211.0	0.143	239.5	0.304	262.0	0.324	288.3	0.228	2.36
400	211.4	0.131	238.3	0.303	263.9	0.368	288.5	0.199	2.37
450	210.2	0.133	240.9	0.328	267.7	0.360	294.8	0.179	2.42

the densification of the system. It may be noted that, while the quadrupole interaction is strongly influenced by the geometrical symmetry around the transition-metal atoms, isomer shift depends mainly upon the number and distances of metalloid near neighbors and is not sensitive to the actual geometrical arrangement of the metalloid atoms. Therefore, a decrease in the average bond length would cause a higher distribution in the isomer shift for the same distribution in the bond lengths. Thus, a decrease in geometrical disorder (distribution in local symmetries) associated with structural relaxation causes $\sigma(\Delta u)$ to decrease, while it does not have a significant effect on the distribution of isomer shift. On the other hand, a decrease in the average TM-M bond length would cause an increase in the distribution of isomer shift without having a significant effect on the distribution of quadrupole interaction.

From Tables I and III one may note that the effect of higher annealing temperatures is to cause an increase in the average hyperfine field and a decrease in its variance. Various factors which would affect the hyperfine field during the annealing process are (i) a decrease in geometrical distortions causing the hyperfine field to increase (ii) a decrease in interatomic distances (densification) which should cause the hyperfine field to decrease, and (iii) a change in the average number of metalloid near neighbors. As the average number of metalloid near neighbors remains essentially unchanged with annealing, the observed change in $\langle H \rangle$ may be attributed to the first two factors. Therefore, the present results suggest that the effects of a decreased geometrical disorder on a hyperfine field is stronger as compared to that of a decreased interatomic distance.

Extensive studies have been done on the structural relaxation in metallic glasses. In most of the studies, the irreversible changes in various physical properties on annealing have been attributed to structural changes associated with annihilation of excess free volume. However, a detailed qualitative analysis of the dependence of Curie temperature and electrical resistivity in metallic glasses on near-neighbor distances done by Gibbs and Hygate[2] suggests that changes in the SRO related to near-neighbor distances are not sufficient to account for observed changes in the physical properties when metallic glasses are annealed. Thus, they conclude that besides the changes in near-neighbor spacing, the structural relaxation also involves some other effects. However, no information about the nature of these additional changes could be obtained from their studies. The present Mössbauer measurements provide clear evidence that besides the annihilation of free volume and the decrease in the geometrical distortions, the annealing also results in changes in topological short-range order (TSRO) such that the population of Fe sites with two and three metalloid near neighbors increases, although the average number of M near neighbors remains essentially unchanged. Thus our studies support the results of Gibbs and Hygate and also provide information about the nature of the structural changes occurring on annealing of metallic glasses.

IV. CONCLUSIONS

Structural relaxation in metallic glass $Fe_{78}Si_9B_{13}$has been studied. Mössbauer spectroscopy provides clear evidence about the atomic-level changes occurring in the

TABLE III. Correlation parameters obtained using the method of Lines and Eibschütz. $\langle x \rangle$ and $\sigma\langle \Delta x \rangle$ are the mean and standard deviation of hyperfine parameter x where $\Delta x = x - \langle x \rangle$, and terms like $\langle \Delta x \Delta y \rangle$ represent the correlation between the fluctuations of parameters x and y.

Annealing temperature °C	$\langle \delta \rangle$ mm/s	$\langle H \rangle$ kOe	$\sigma(\Delta\delta)$ mm/s	$\langle \alpha_- \rangle$ mm/s	$\sigma(\Delta u)$ mm/s	$\frac{\sigma(\Delta H)}{\langle H \rangle}$	$\mu_N\langle \Delta H \Delta\delta \rangle$ (mm/s)^2	$\mu_N(\Delta H \Delta u)$ (mm/s)^2	$\langle \Delta u \Delta\delta \rangle$ (mm/s)^2
RT	0.10(1)	249.0(5)	0.17(3)	0.022(5)	0.19(2)	0.217(3)	0.015(10)	0.052(10)	−0.18(1)
300	0.09	252.6	0.16	0.015	0.16	0.209	0.013	0.037	−0.16
350	0.10	253.6	0.20	0.008	0.11	0.204	0.014	0.040	−0.16
400	0.10	253.6	0.22	0.007	0.11	0.202	0.016	0.053	−0.15
450	0.09	255.1	0.38	0.006	0.02	0.203	0.034	0.074	−0.16

specimen with isochronal annealing at successively increasing temperature. Structural relaxation is accompanied by (i) a decrease in geometrical distortions (ii) a decrease in interatomic spacing, and (iii) a topological rearrangement of atoms resulting in significant changes in the population of TM sites with different numbers of metalloid near neighbors, while keeping the average number of metalloid near neighbors essentially unchanged. These results support the conclusion of Gibbs and Hygate that a change in near-neighbor spacing is not sufficient to describe the irreversible structural relaxation.

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[1]J. O. Ström-Olsen, R. Brüning, Z. Altounian, and D. H. Ryan, J. Less-Common Metals **145**, 327 (1988).
[2]M. R. J. Gibbs and G. Hygate, J. Phys. F **16**, 809 (1986).
[3]T. Egami, IEEE Trans. Magn. **17**, 1600 (1981).
[4]R. Brüning and J. O. Ström-Olsen, Phys. Rev. B **41**, 2678 (1990).
[5]R. Brüning, D. H. Ryan, and J. O. Ström-Olsen (unpublished).
[6]G. Le Caer and J. M. Dubois, J. Phys. E **12**, 1083 (1979).
[7]H. N. Ok and A. H. Morrish, Phys. Rev. B **23**, 2257 (1981); S. Habibi, A. Gupta, and G. Principi, Hyperfine Interact. **69**, 623 (1991).
[8]P. Panisod, J. Durand, and J. I. Budnik, Nucl. Instrum. Methods **199**, 99 (1982).
[9]Ajay Gupta and S. Habibi, Mater. Sci. Eng. A **133**, 375 (1991).
[10]M. E. Lines, Solid State Commun. **36**, 457 (1980).
[11]P. Allia, A. Ferro Milone, F. Vinai, G. Fratucello, and F. Ronconi, J. Appl. Phys. **53**, 7750 (1982).
[12]M. Eibschütz, M. E. Lines, and H. S. Chen, Phys. Rev. Lett. **28**, 425 (1983); M. E. Lines and M. Eibschütz, Solid State Commun. **45**, 435 (1983).
[13]R. J. Pollard, Z. S. Wronski, and A. H. Morrish, Phys. Rev. B **29**, 4864 (1984).