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Temperature Evolution of Magnetic Structure in Fe–Co–Si–B–Mo–P Metallic Glass by Mössbauer Spectrometry

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Magnetic ordering in $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass is followed by ^{57}Fe transmission Mössbauer spectrometry performed at temperatures ranging from 4.2 K up to 415 K. Low temperature experiments were accomplished also in external magnetic field of 6 T oriented parallel to the ribbon plane. Evolution of Mössbauer spectra with sample temperature shows gradual vanishing of hyperfine magnetic fields. High temperature Mössbauer spectra exhibit clear transition from ferromagnetic to paramagnetic state. In this way, the Curie temperature can be determined. We have concentrated on samples annealed at 573 K and 673 K, i.e., well below the onset of crystallization. Measurements at 4.2 K revealed rearrangement of spins that is taking place both after the annealing, as well as in external magnetic field. From high temperature experiments, the Curie temperature of 400 K was determined for the sample annealed at 673 K.

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PACS/topics: metallic glass, Mössbauer spectrometry, magnetic microstructure

1. Introduction

Metallic glasses are still attracting the interest of researchers namely for their very good magnetic properties. Several new types of P-containing metallic glasses were recently scrutinized [1, 2]. To enhance their practical applications, microstructure and soft magnetic properties of novel compositions are checked, too. The role of B, P, and Si on thermal stability and glass forming ability was studied in $(Fe_{1-x}Co_x)_{78}Mo_1(B,P,Si)_{21}$ alloy [3]. Especially, addition of P has improved the investigated parameters. Further amelioration of saturation magnetization and the Curie temperature was obtained by substitution of small amounts of Co for Fe in this alloy. In a similar system of $Fe_{83-x}Si_4B_{10}P_2Cu_1Nb_x$, the addition of Nb was systematically investigated to ensure improved soft magnetic properties [4].

Recently, we have studied the microstructure and magnetic properties of $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass [5–8]. We have employed Mössbauer spectrometry at room temperature in addition to magnetic measurements. In this way, information was obtained about the structural arrangement of the as-quenched metallic glass [5], as well as samples annealed at temperatures below the onset of crystallization [6–8]. Here, we extend the previous studies towards Mössbauer measurements at extended temperature range to follow the evolution of microstructure, as well as magnetic order.

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2. Experimental details

The $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass ribbons were prepared by planar flow casting with the width of 6 mm and average thickness of 20 μm. Their amorphicity was checked using X-ray diffraction, diffraction of synchrotron radiation, as well as Mössbauer spectrometry. The latter technique was employed in transmission geometry using $^{57}Co/Rh$ source of radiation and conventional constant acceleration spectrometer. Temperature measurements at 4.2 K were performed in a Janis bath cryostat with optional magnetic field of 6 T oriented parallel to the ribbon plane. High temperature Mössbauer effect experiments up to 425 K were accomplished in a Wissel furnace. Mössbauer spectra were evaluated by the fitting software Confit [9] with distributed components that feature magnetic dipolar and electric quadrupole interactions. In this study, we focus on comparison of low temperatures and/or external magnetic fields upon as-quenched and annealed (573 K) samples. In addition, sample annealed at 673 K is investigated at temperatures higher than 300 K. Annealing of both samples was performed for 1 h in nitrogen protective atmosphere. According to the results of differential scanning calorimetry, these annealing temperatures are well below the primary crystallization temperature of 839 K [6, 8].

3. Results and discussion

Low temperature Mössbauer spectrum of the as-quenched $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass presented in the bottom part of Fig. 1, shows magnetically split absorption lines. To evaluate the results three sextets were

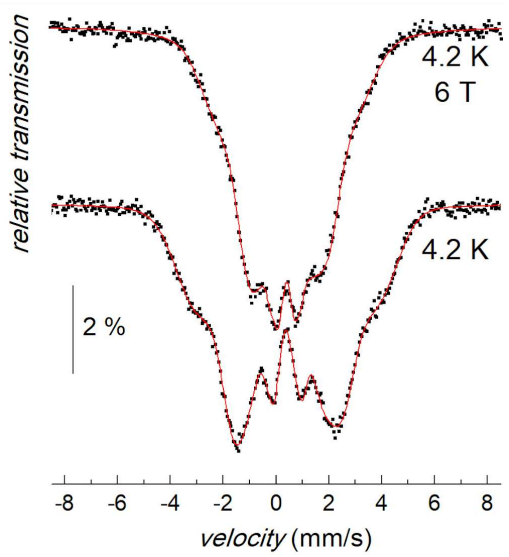

Fig. 1. Mössbauer spectra of the as-quenched $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass recorded at 4.2 K without and with external magnetic field.

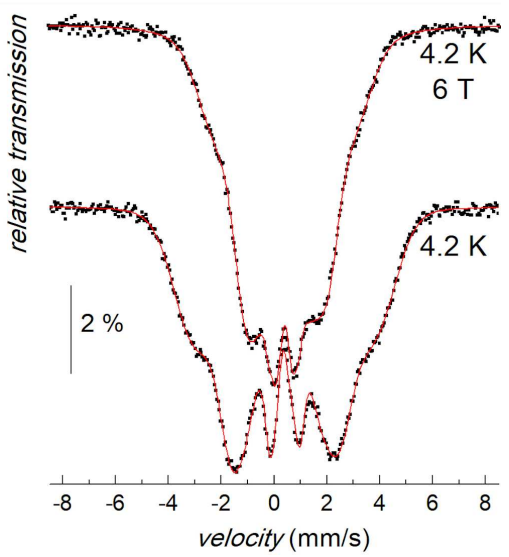

Fig. 2. Mössbauer spectra of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass annealed at 573 K/1 h recorded at 4.2 K without and with external magnetic field.

used. Each sextet was presenting Gaussian distribution of hyperfine magnetic fields, which were finally summed up, and then were characterized by an average value of the resulting hyperfine magnetic field $\langle B \rangle$. The used fitting software CONFIT [9] works with the so-called determining sextet and/or doublet of Lorentzian lines which are convoluted with a Gaussian distribution. Each spectral component represents one particular environment of the resonant Fe atoms. The number of the convoluted sextets and/or doublets is established by taking the quality of the fit into account. Relative area, isomer shift, quadrupole shift/splitting, hyperfine magnetic field, line intensity ratio of the sextets and/or doublets, and standard deviations of their Gaussian distributions were fitted parameters.

When external magnetic field was applied, the spectrum has collapsed into rather featureless shape, as seen in the upper part of Fig. 1. The average hyperfine magnetic field $\langle B \rangle$ has decreased from 17.3 T to 11.7 T ($\pm$0.4 T). The difference of 5.6 T coincides with the value of the external magnetic field ($B_{ext} = 6$ T). At the same time, the magnetic moments are oriented into the direction of B_{ext}. They have rotated from their originally canted orientation ($\Theta = 66.7°$) into the plane of the ribbons ($\Theta = 90°$).

The angle Θ determines the orientation of the net magnetic moment of the sample with respect to the direction of the γ-rays from the source. It can be calculated as:

$$\Theta = \sin^{-1}\left(\sqrt{\frac{3(A_{2,5}/A_{1,6})}{1+3(A_{2,5}/A_{1,6})}}\right),$$

where $A_{2,5}$ and $A_{1,6}$ are relative areas of the Mössbauer spectral lines 2, 5 and 1, 6, respectively. In case of randomly oriented spins (e.g., in powder) one can have the so-called magic angle $\Theta = 54.7°$. For $\Theta = 0°$ the spins are oriented perpendicular to the ribbon plane, whereas for $\Theta = 90°$ they acquire parallel directions. It is noteworthy that the angle Θ is an average value resulting from the contributions of all spins.

Similar situation occurs also in the sample that was annealed at 573 K for 1 hour, as demonstrated in Fig. 2. Nevertheless, even though the difference in $\langle B \rangle$ in this case is almost the same (5.7 T), rather pronounced deviations in the directions of the magnetic moments are observed. In the absence of B_{ext}, one can have $\Theta = 56.7°$, which means that the spins are oriented more in the outward direction with respect to the ribbon plane than in the as-quenched sample. In fact, they exhibit close-to-random arrangement that is characterized by $\Theta = 54.7°$. On the other hand, the applied B_{ext} was not strong enough to tilt the spins into a complete in-plane alignment. Therefore, they are oriented at $\Theta = 80.5°$. We can conclude that the annealing affects the structural short-range order which, in turn, is demonstrated in the behavior of the magnetic moments.

Mössbauer spectra of the sample annealed at 673 K were collected at temperatures ranging from 295 K up to 415 K. The obtained fits to the recorded experimental Mössbauer spectra are shown in Fig. 3. The fitting model consisted of a combination of distributed sextets and doublets. According to the temperature of measurement, only sextets, sextets plus doublets, and only doublets were adopted towards the increasing temperature. It is clearly seen that the broadened room-temperature sextet (thick black line) continuously narrows with rising temperature as indicated by the arrows. Finally, at $\sim$ 395 K the magnetic sextet collapses, and a distributed doublet appears (thick red line). With further temperature increase its contribution to the spectrum prevails.

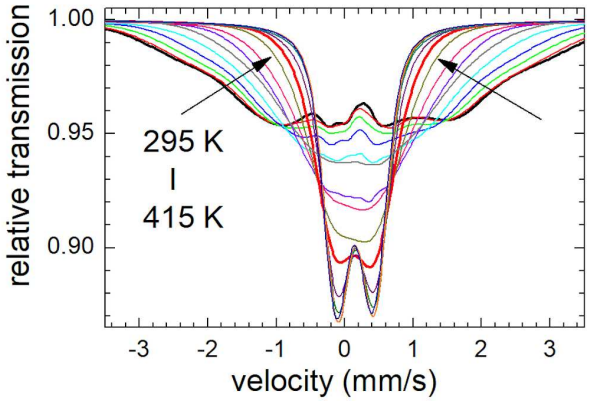

Fig. 3. Mössbauer spectra of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass annealed at 673 K/1 h recorded at the temperatures from 295 K to 415 K. The temperature rises in the direction of the arrows. For clarity, only the theoretically calculated fits are displayed.

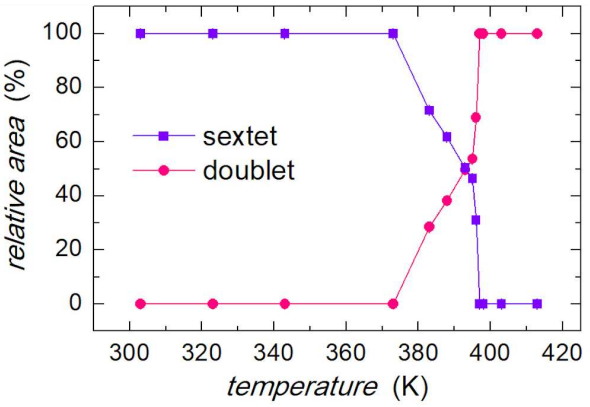

Fig. 4. Temperature dependence of relative spectral areas obtained from the evaluation of Mössbauer spectra of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass annealed at 673 K/1 h.

Consequently, the Mössbauer spectra were evaluated by a magnetic component, which was modelled by distributed sextets and a non-magnetic component. The latter represents electric quadrupole interactions of a distributed doublet, and belongs to paramagnetic regions in the metallic glass. Relative areas of both spectral components are plotted in Fig. 4 as a function of the temperature of measurement. At temperatures higher than 397 K, this sample becomes paramagnetic.

Average hyperfine magnetic fields were derived from the fits to the Mössbauer spectra. The results are plotted against the measurement temperature in Fig. 5 and marked by open symbols. Additionally, they were fitted with a temperature dependence of hyperfine magnetic field $B_{\rm hf}(T)$ applying an approach that assumes similar behavior of $B_{hf}(T)$ as that of magnetization at temperatures lower but close to the Curie point [6, 10] considering

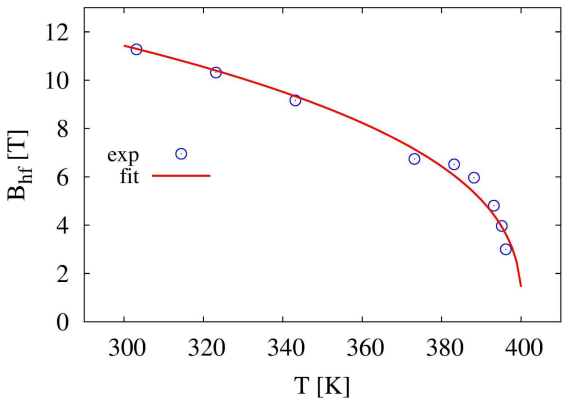

Fig. 5. Temperature dependence of average hyperfine magnetic field obtained from the evaluation of Mössbauer spectra of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass annealed at 673 K/1 h (see text).

the critical exponent $\beta = 36$. The resulting curve (red line in Fig. 5) gives $T_{\rm C} = 400$ K which is in accord with the temperature of dominant contribution of the doublet component in the Mössbauer spectra (Fig. 4). The obtained $T_{\rm C}$ is slightly higher than that of the as-quenched sample ($T_{\rm C} = 392$ K [5]).

The Curie temperature of 411 K was obtained from the temperature dependence of the normalized magnetization which was recorded in external magnetic $\mu_0 H = 25$ mT using the same metallic glass annealed at 673 K [8]. Namely the use of external magnetic field might be responsible for the differences observed in the $T_{\rm C}$-values. It should be noted that due to technical limitations it was possible to measure the magnetization only up to 400 K [8]. Consequently, $T_{\rm C}$ was determined by extrapolating the fit of the experimental data. Similar situation was encountered in the determination of $T_{\rm C}$ of the as-quenched alloy where the values of 400 K and 392 K [5] were obtained from magnetic measurements and Mössbauer data, respectively. The comparable differences in $T_{\rm C}$-values presumably stem from miscellaneous techniques applied for their determination. Nevertheless, the trend of increasing $T_{\rm C}$ after the annealing is maintained. This is an indication that after isothermal annealing, the local microstructure of this metallic glass is modified which affects also its magnetic parameters. It is noteworthy, that upon the studied samples we have performed also experiments of Conversion Electron Mössbauer Spectrometry (CEMS) which are sensitive to modifications of the surface microstructure. Because no traces of surface crystallization were found we can ascribe the observed effects to the modifications of the samples' bulk.

4. Conclusions

Evolution of magnetic ordering that takes place in $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass was followed by Mössbauer spectrometry performed at different

temperatures. Experiments at low temperature of 4.2 K pointed out differences in the spin arrangement between the as-quenched metallic glass and that of isothermally annealed at 573 K/1 h. In the latter, the spins acquired almost random arrangement. Even external magnetic field of 6 T oriented parallel to the ribbon plane was not able to rotate all spins into its direction.

Mössbauer effect measurements performed in temperature region from 295 K to 415 K exhibited dramatic evolution of the spectra. The absorption lines progressively varied from magnetically split sextets to paramagnetic doublets. Relative contribution of the individual spectral components, as well as average hyperfine fields of the magnetic sextet helped in the determination of the Curie temperature. Therefore, $T_C = 400$ K is the result obtained for $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass isothermally annealed at 673 K/1 h.

Acknowledgments

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