

LETTER TO THE EDITOR

A Mössbauer study of the crystallisation process of magnetic metallic glass $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$

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Abstract. Mössbauer spectra of amorphous $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ ribbons at temperatures 90 to 800 K and their isothermal time evolution have been recorded. The analysis of the experimental spectra reveals that crystallisation begins at about 600 K and crystalline Fe_2B , Fe metal and FeSi are formed either isothermally in time or by raising the temperature above 700 K.

Several recent publications [1-3] discuss the crystallisation dynamics of metallic glasses. Measurements of the resistivity [1] and the magnetisation [2, 3] of metallic glasses yield information on the crystallisation through the observed changes in the relevant bulk properties. Such a study of the magnetisation of the magnetic metallic glass $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ revealed many interesting features of the crystallisation process [2]. However, a bulk magnetisation study measures only the sum of the magnetisations of the magnetic components present in the sample. In the crystallisation process of the magnetic metallic glass $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ many crystalline materials can be formed, some of temporal nature and some permanent, and it is difficult to reach conclusions on the nature and properties of the single components. On the other hand, a Mössbauer spectroscopy study, which reveals the properties of and distinguishes between all iron nuclei belonging to different chemical components, becomes an ideal tool for the investigation of the crystallisation process.

Amorphous $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ in the form of ribbons from the same batch used for the magnetisation experiments [2], were studied using a Mössbauer spectrometer, the Co:Rh source running in the constant acceleration mode perpendicular to the ribbon foil. Spectra were taken with the absorber at 90, 300, 473, 588, 598 (after 46, 70, 96 and 120 h), 613, 628, 733 and 800 K. After the 628 K and the 800 K measurements the temperature was reduced and a room-temperature spectrum was recorded. Some of the spectra are shown in figure 1. All spectra were analysed in terms of two to three subspectra. For temperatures below 600 K one spectrum corresponded to pure iron metal and the other to the amorphous system. The amorphous subspectrum was fitted with a distribution of magnetic hyperfine fields, of Lorentzian shape having asymmetric widths at half maximum and cut-off fields below and above the average hyperfine field. The spectra above 600 K were analysed in terms of well defined magnetic hyperfine fields for two sites and an additional pure quadrupole split subspectrum. All parameters obtained from these least-squares fit procedures are given in table 1.

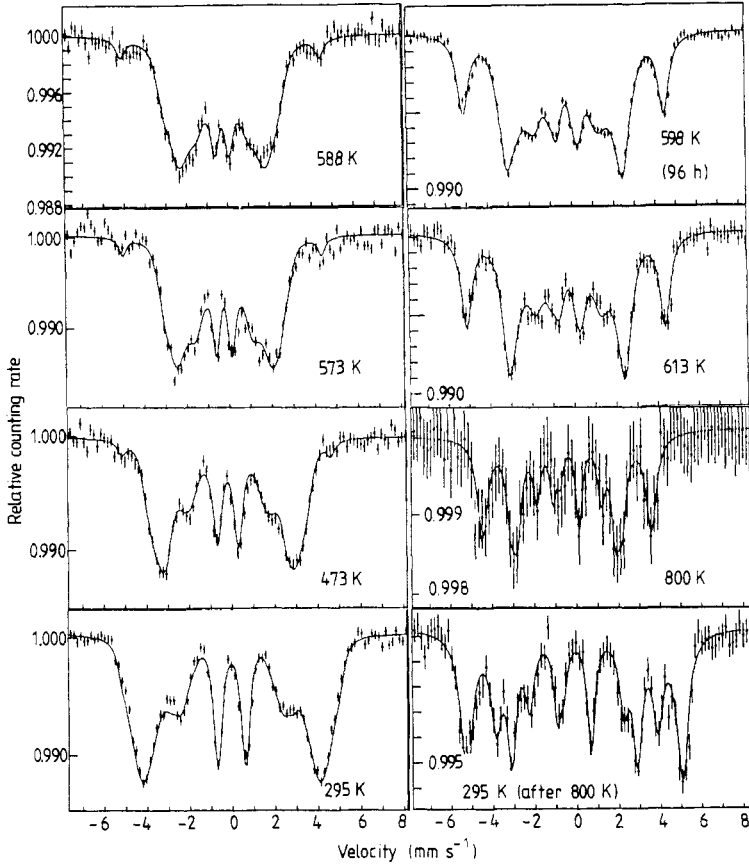


Figure 1. Mössbauer spectra of ^{57}Fe in $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ at various temperatures.

From the analysis of the spectra it is clear that within a period of a typical Mössbauer measurement (~ 24 h) the only surviving phases in the crystallisation process are the amorphous system, released pure iron, Fe_2B [4] and probably FeSi [5]. In figure 2 the temperature dependences of the experimental hyperfine fields and isomer shifts of the various phases are shown. In figure 3 the fraction of pure iron in the system as a function of temperature is displayed.

The analysis of the Mössbauer spectra of the amorphous ribbons also yields the amount of the partial orientation of the magnetisation in the ribbon. This orientation parameter, table 1 and figure 3, is the ratio of the intensity of the $\Delta m = 0$ nuclear transition to the intensity expected for a random distribution of magnetisation directions. When the magnetisation is perpendicular to the ribbon this parameter should take the value zero, and when it is in the plane of the ribbon it should take the value 2 [6]. From figure 3 it is clear that the magnetisation in the amorphous $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ is partly oriented perpendicular to the ribbon plane. At elevated temperatures this orientation disappears, in particular when crystallisation starts to take place.

The analysis of the spectra below 600 K show that the amorphous $\text{Fe}_{83}\text{B}_{12}\text{Si}_5$ ribbons contain a small fraction of the crystalline phase of pure iron ($\sim 2\text{--}3\%$). The iron nuclei in the amorphous phase at low temperatures experience a distribution of magnetic hyperfine fields extending from 80 to 345 kOe with an average magnetic field

Table 1. Hyperfine interaction parameters with which the ^{57}Fe in $\text{Fe}_{83}\text{B}_{17}\text{Si}_x$ Mössbauer spectra were fitted.

Temperature (K)	Amorphous phase					Pure iron					Fe ₃ B					FeSi ₃								
	Isomer shift (mm s ⁻¹)	Average hyperfine field (kOe)	Lower cut-off field (kOe)	Higher cut-off field (kOe)	Orientation parameter	Relative intensity (%)	Isomer shift (mm s ⁻¹)	Hyperfine field (kOe)	Hyperfine field (kOe)	Relative intensity (%)	Isomer shift (mm s ⁻¹)	Hyperfine field (kOe)	Hyperfine field (kOe)	Relative intensity (%)	Isomer shift (mm s ⁻¹)	Isomer shift (mm s ⁻¹)	Relative intensity (%)	Hyperfine field (kOe)	Hyperfine field (kOe)	Relative intensity (%)	Isomer shift (mm s ⁻¹)	Isomer shift (mm s ⁻¹)	Relative intensity (%)	Quadrupole interaction (mm s ⁻¹)
90	0.18(2)	275 ± 5	76	345	0.41(3)	2(1)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
295a	0.06	265	173	332	0.48	3	0.0	330 ± 3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
473	-0.08	191	83	250	0.39	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
573	-0.13	142	35	210	0.52	6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
588	-0.16	130	110	200	0.80	5	-0.23	295	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
598a‡	-0.16	145	110	200	0.90	21	-0.21	298	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
598b‡	-0.15	151	110	200	0.91	26	-0.21	298	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
598c‡	-0.14	154	110	200	0.95	30	-0.21	298	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
598d‡	-0.14	157	110	200	0.92	32	-0.21	298	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
613	-0.15	168	100	200	0.85	41	-0.23	295	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
628	-0.17	167	100	200	—	47	-0.21	292	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
733	—	—	—	—	—	64	-0.28	269	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
800	—	—	—	—	—	65	-0.34	249	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
295b§	0.06	267	—	—	0.83	30	0.0	330	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
295c§	—	—	—	—	—	66(3)	0.0	325	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

‡ Relative to Fe metal at 300 K.

§ After 46, 70, 96 and 120 h measurements respectively.

§ 295b and 295c are measurements after the sample was at 630 K and 800 K for two days respectively.

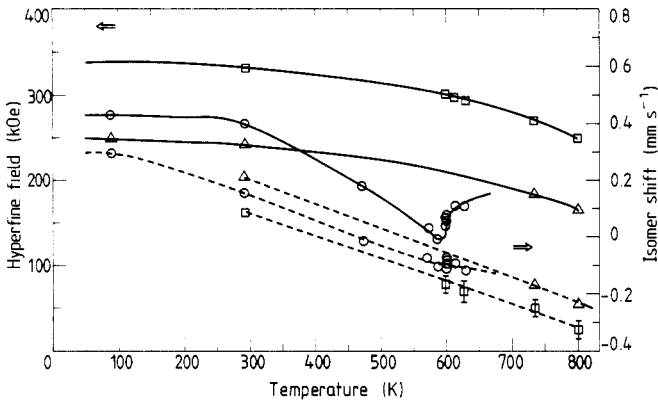


Figure 2. Temperature dependence of the isomer shift and of the magnetic hyperfine field acting on Fe nuclei in $\text{Fe}_{53}\text{B}_{12}\text{Si}_5$ and in crystalline Fe and Fe_3B . (\square , Fe; \triangle , Fe_3B ; \circ , $\text{Fe}_{53}\text{B}_{12}\text{Si}_5$).

of 275 kOe. The average orientation of this field is 36° relative to the normal to the ribbons plane.

The spectrum at 598 K was measured for several days. After 46 hours of measurement a large fraction of pure crystalline iron was observable ($\sim 20\%$) while in the 588 K spectrum only 7% iron was present (top curves in figure 1). The amount of pure iron increased with time, to 30% after 120 h of measurement. Since this 30% is an average over 120 h of measurement, the percentage of Fe present at the end is much larger. The spectra at 588 and 598 K could not be fitted without adding a third subspectrum composed of a pure quadrupole split doublet. The hyperfine interaction parameters and relative intensity, table 1, tend to indicate that this extra component is

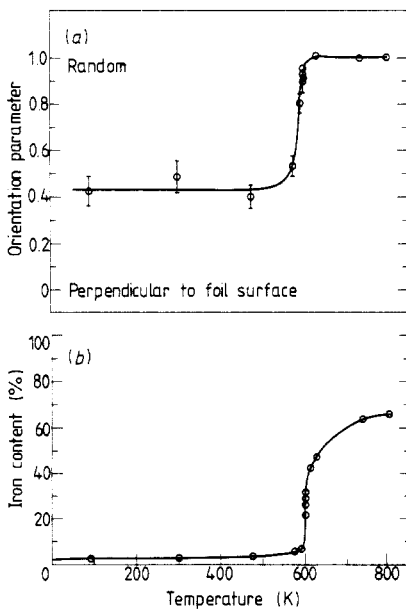


Figure 3. Degree of magnetic orientation (a) and temperature dependence of the metallic iron content (b) in $\text{Fe}_{53}\text{B}_{12}\text{Si}_5$.

a crystalline, Fe-poor, FeSi compound [5]. The hyperfine interaction parameters of the 'amorphous' subspectrum at 598 K change with time, indicating that this phase is undergoing crystallisation. The average magnetic hyperfine field is increasing with time, towards the value in the crystalline phase. The spectra at 733 and 800 K could be analysed in terms of well defined hyperfine field parameters indicating that the material has fully crystallised. Cooling the sample from 800 K to room temperature and re-measuring the spectrum (bottom curve in figure 1), yields the room-temperature parameters of the crystalline phase (table 1), proving that it is mainly Fe₂B [4]. Also the relative intensities of all subspectra prove that after full crystallisation three phases are present, Fe metal, Fe₂B and FeSi, their relative abundances being 65%, 29% and 6% respectively.

The presented results demonstrate the usefulness of Mössbauer spectroscopy for studies of crystallisation processes. In the case of diffusive, slow crystallisation processes the Mössbauer spectra even yield the time evolution of the process. In the case of Fe₈₃B₁₂Si₅ we have shown that a detectable crystallisation process starts at 588 K. First to be formed are pure Fe and FeSi. Above 598 K Fe₂B is also formed. These are the only crystalline phases formed.

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