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STRUCTURE AND MAGNETISM OF METASTABLE Bi–Fe ALLOY FILMS*

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Summary

Metastable alloy thin films in the insoluble Bi–Fe system were formed by means of electron beam co-evaporation at substrate temperatures of 140 K. Backscattering of 2.0 MeV helium ions and transmission electron microscopy showed that films with 45 - 60 at.% Fe were of a uniform amorphous phase. The mutual solute concentrations of iron and bismuth in the $Bi_{65}Fe_{35}$, $Bi_{60}Fe_{40}$ and $Bi_{35}Fe_{65}$ films were determined by X-ray diffraction and amounted to 0.2% Bi in b.c.c. iron and 1% - 2% Fe in rhombohedral bismuth depending on composition. Magnetic measurements were performed using a Faraday balance. Some samples showed minor ferromagnetic effects at measuring temperatures of 77 - 290 K. The characteristics of the metastable Bi–Fe alloy films obtained were compared with those observed in previous experiments with ion mixing and magnetron co-sputtering and with a model of the magnetic properties of amorphous 3d-base alloys.

1. Introduction

The behaviour of metastable phases in binary alloy systems with positive heat of formation has attracted considerable interest in recent years [1 - 7]. From a fundamental point of view little is still known about the underlying rules of the phase formation and stability in these systems, compared with systems with negative heat of formation. Furthermore, it is of interest to study these new alloys in view of their material properties,

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which may be of importance for various applications. Bi–Fe is such a typical system, as the phase diagram shows null miscibility both in the solid and in the liquid state [8]. The heat ΔH of formation is calculated to be +18 kJ mol^{-1} [9]. In a recent communication [10] it was reported for the first time that metastable Bi–Fe films of two compositions were formed by ion mixing. Subsequently, in the same investigation alloys formed by magnetron co-sputtering were used to find the composition range of amorphous phase formation.

In this paper, more detailed results are presented on the formation and stability of metastable phases in Bi–Fe films produced by electron beam co-evaporation and compared with previous results on co-sputtered alloys [10]. The diffraction angle parameters of the amorphous Bi–Fe films and the solute concentrations of Bi–Fe supersaturated solid solutions will be given. Also, the differences in the structures of the Bi–Fe metastable alloy films and in the transition temperatures T_{a-c} from the amorphous to the crystalline phase between various methods of film fabrication will be discussed. Furthermore, we have for the first time investigated the magnetic properties of Bi–Fe alloys. The results on magnetic properties are compared with a model described by Buschow of magnetic properties of amorphous 3d-base alloys [11]. This comparison is interesting, as experimental support of this model in iron-base glassy alloys with positive ΔH has been reported only in very few systems up to now.

2. Experimental details

Thin Bi–Fe alloy films were prepared by electron beam codeposition in a base vacuum of less than 5×10^{-6} Pa at a typical deposition rate of 1 Å s^{-1}. During deposition, the NaCl and silicon wafer substrates of the films were kept at a temperature of 140 K. The thickness of each film was between 300 and 400 Å. After deposition the NaCl substrate was dissolved in deionized water and the films were placed on molybdenum grids for transmission electron microscopy (TEM). The actual composition and thickness of the samples were determined by Rutherford backscattering spectroscopy. It was noted that the beam current of helium ions should be kept at less than 15 nA in order to avoid beam-induced diffusion of bismuth atoms to the film surface and to the interface between film and substrate. TEM observations were performed on samples as deposited and annealed. For vacuum thermal annealing, the vacuum level was less than 5×10^{-5} Pa and the annealing time was 1 h at each temperature. Some samples were analysed by X-ray diffraction (XRD) using Cu Kα radiation.

The samples with silicon wafer substrates were used for magnetic measurements in a Faraday balance with a sensitivity better than 1×10^{-4} e.m.u.

3. Results and discussion

3.1. Structure and stability

As-deposited films of six overall compositions are shown in Fig. 1. In this figure a series of transmission electron diffraction patterns and micrographs taken at 300 K is presented. The pattern of $Bi_{65}Fe_{35}$ films can be identified as a superposition of patterns for rhombohedral bismuth and b.c.c. iron. In the $Bi_{60}Fe_{40}$ films, the boundary between black agglomerates and white background in the micrograph becomes sharper than that in the Bi_{65}-Fe_{35} films, and in the diffraction pattern a weak halo appears at an approximate interatomic spacing of 2.4 Å. The diffraction patterns and the micrographs of the $Bi_{55}Fe_{45}$, $Bi_{50}Fe_{50}$ and $Bi_{40}Fe_{60}$ films are almost the same and show a typical amorphous structure. For these compositions the diffraction angle parameters $s = 2\pi \sin\theta/\lambda$ were determined as $s_1 = 1.12$ Å^{-1} (strong), $s_2 = 1.90$ Å^{-1} (weak) and $s_3 = 2.15$ Å^{-1} (medium). The strongest but diffuse diffraction ring corresponds to an interatomic distance of 2.80 Å. This value approximately equals the sum of atomic radii of bismuth and iron. For Bi_{35}-Fe_{65} films, black agglomerate grains about 1000 Å in diameter are dispersed over the amorphous bulk. From the diffraction pattern these agglomerates can be determined to be a bismuth rich rhombohedral phase.

Compared with the diffraction patterns in ref. 10, Fig. 2, it is clear that in co-evaporated alloys the radius ratio and the relative intensity of the amorphous halo rings are very different from those in the case of magnetron co-sputtering. This indicates that the two preparation techniques give rise to different microstructures. The results on phase formation obtained from the present work and those of ref. 10 are generalized in Fig. 2.

After the films were aged for 3 months at room temperature, they were again observed by TEM. It was found that the halo rings still remained. No change in the micrographs could be distinguished by TEM except for the $Bi_{60}Fe_{40}$ films. In the micrograph of these films the individual black zones appear to have aggregated into random clusters. These clusters are currently being investigated as fractal patterns. Thermal annealing tests indicated that T_{a-c} of $Bi_{40}Fe_{60}$ is 420 K whereas T_{a-c} of $Bi_{50}Fe_{50}$ and $Bi_{55}Fe_{45}$ is 500 K. It is noted that T_{a-c} of co-evaporated alloys is higher than that of co-sputtered alloys reported in ref. 10. The reason may be connected with the difference in microstructures revealed by TEM. For the alloy films with crystalline material, the solute concentrations were determined by XRD. Figure 3 is an XRD pattern of the $Bi_{60}Fe_{40}$ films after room temperature aging. Reflections from the silicon wafer were used as a reference. From the shift in the angular positions of the iron and bismuth reflections with respect to those of pure iron and bismuth the solute concentrations of the metastable Fe–Bi solutions were calculated using a procedure described in refs. 1 and 7. Results are shown in Fig. 4. In all samples the solubilities of bismuth in b.c.c. iron are already 0.2 at.%, while the solubilities of iron in rhombohedral bismuth are still as high as 1 - 2 at.%, depending on the composition of the films.

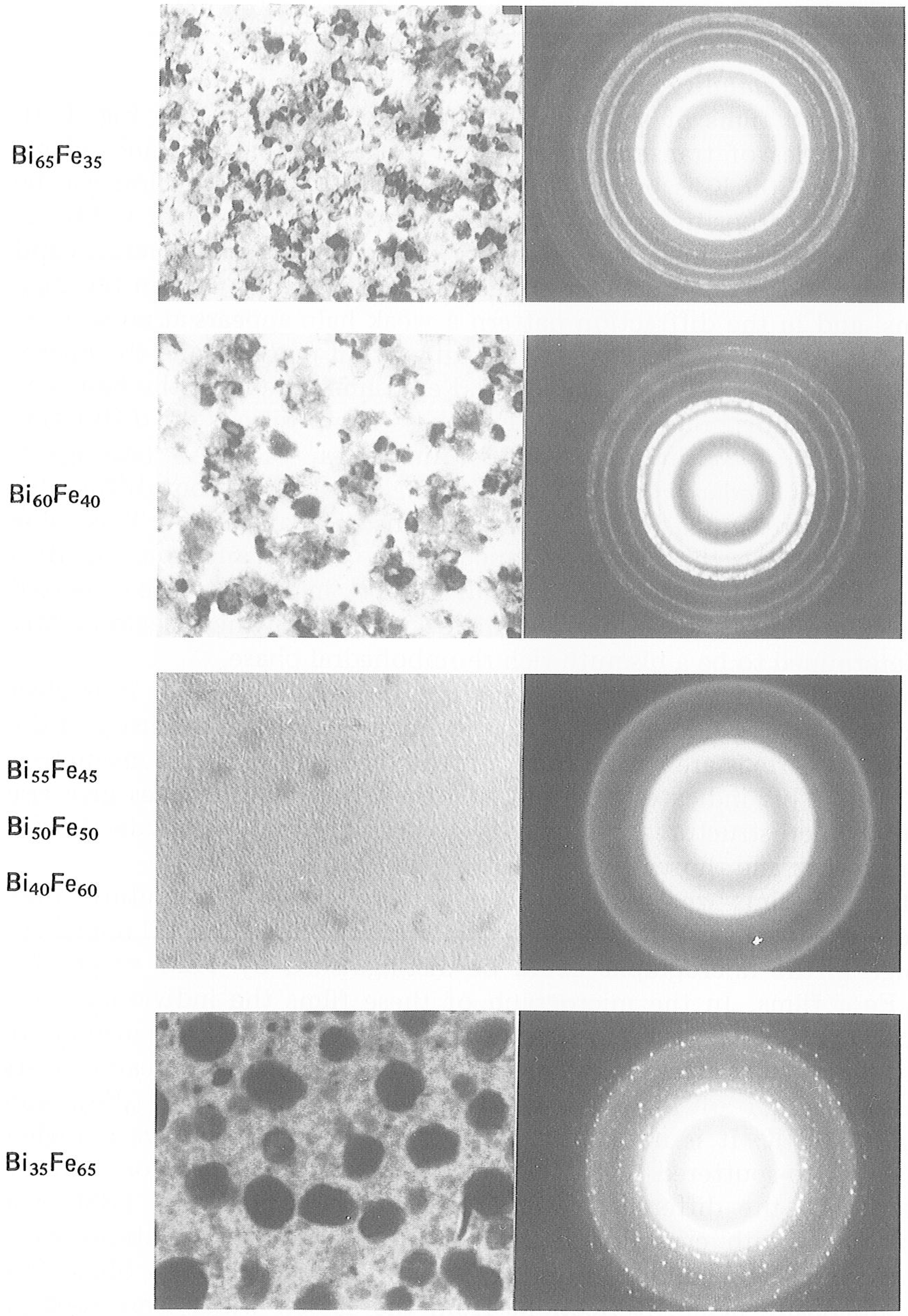


Fig. 1. Electron diffraction patterns and micrographs of as-deposited Bi–Fe films with six compositions. The scale marker indicates 300 Å.

3.2. Magnetic properties

The magnetization curves of the samples were measured in an applied field of 0 - 1.5 T and at temperatures ranging from 77 to 290 K. The applied

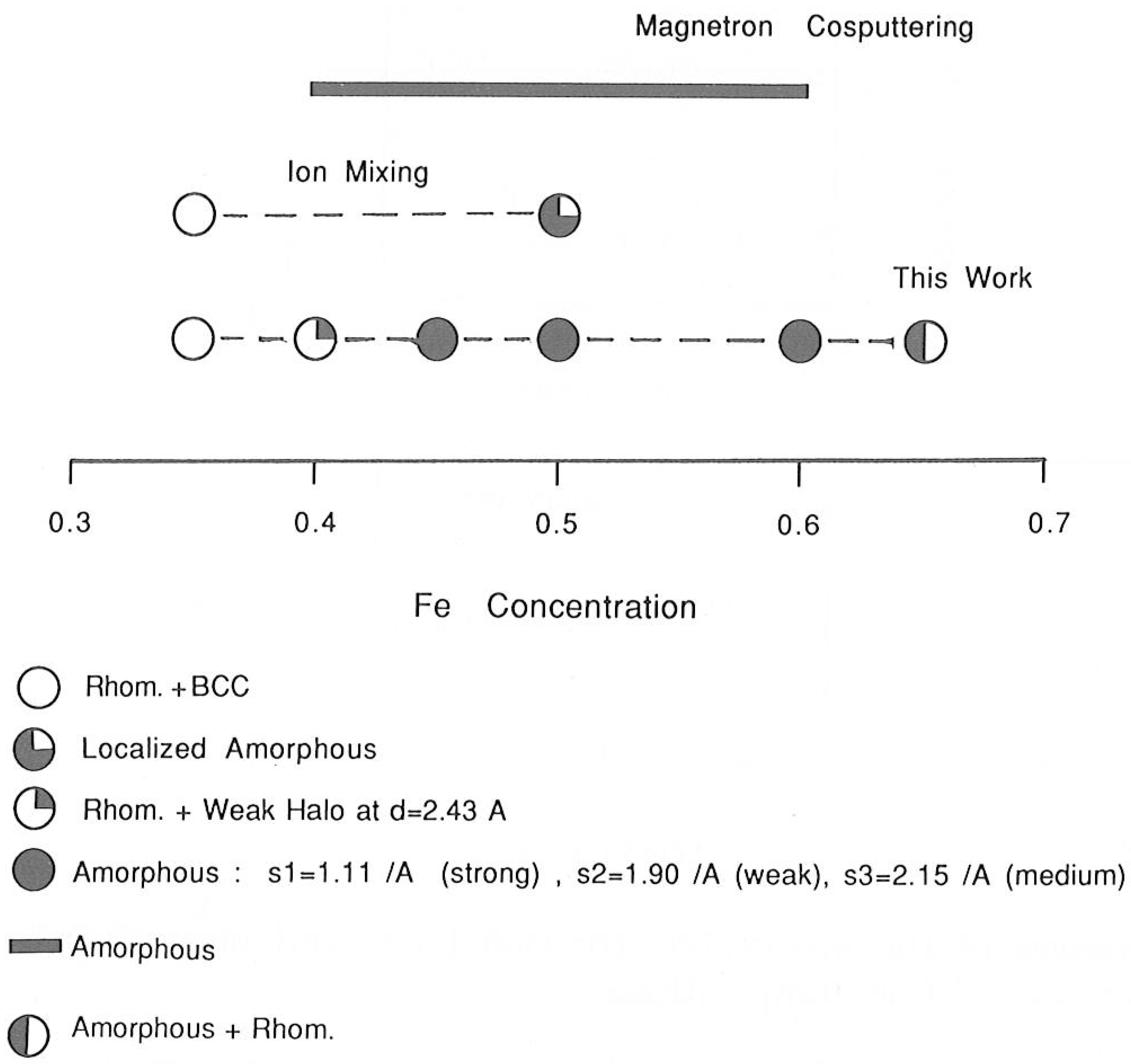


Fig. 2. Diagram indicating composition dependence of metastable phases identified in Bi–Fe (from the present work and that of ref. 10).

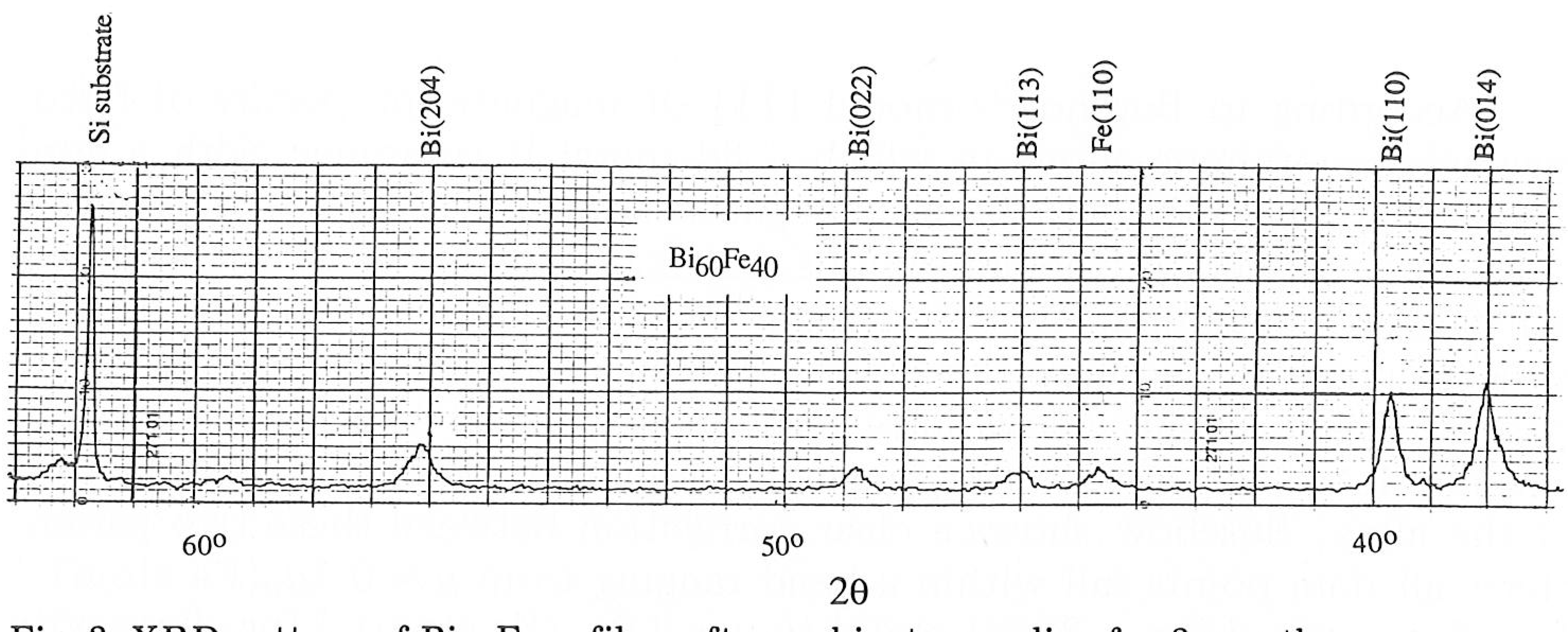
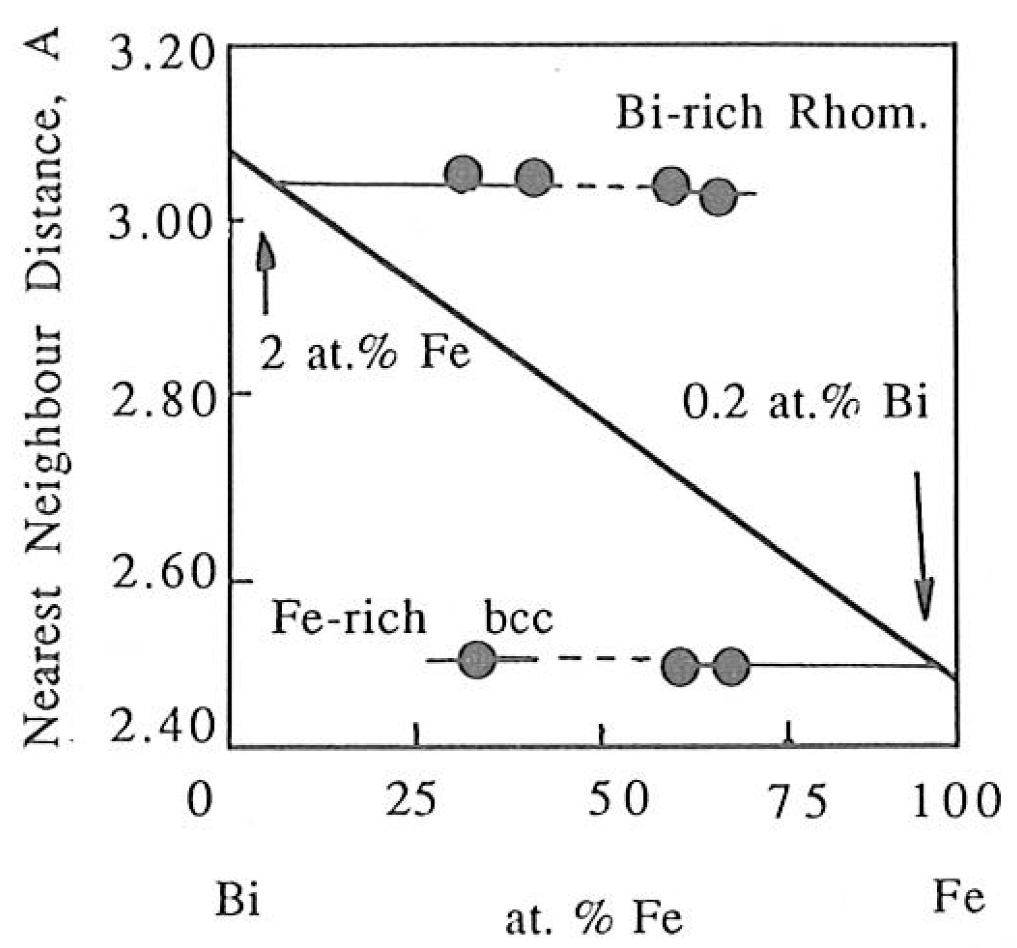


Fig. 3. XRD pattern of $Bi_{60}Fe_{40}$ films after ambient annealing for 3 months.

magnetic field was parallel to the film surface. Because the sample holder and the silicon substrates were all diamagnetic, we estimated the magnetic moments of the alloy films by extrapolating the data to zero applied field, thus eliminating the diamagnetic background contribution. Composition and temperature dependence of the average iron moment in all samples are shown in the upper and lower parts respectively of Fig. 5. At 77 K, the average iron moment for all compositions is less than $0.3\mu_B(\text{Fe atom})^{-1}$, where μ_B is the Bohr magneton.



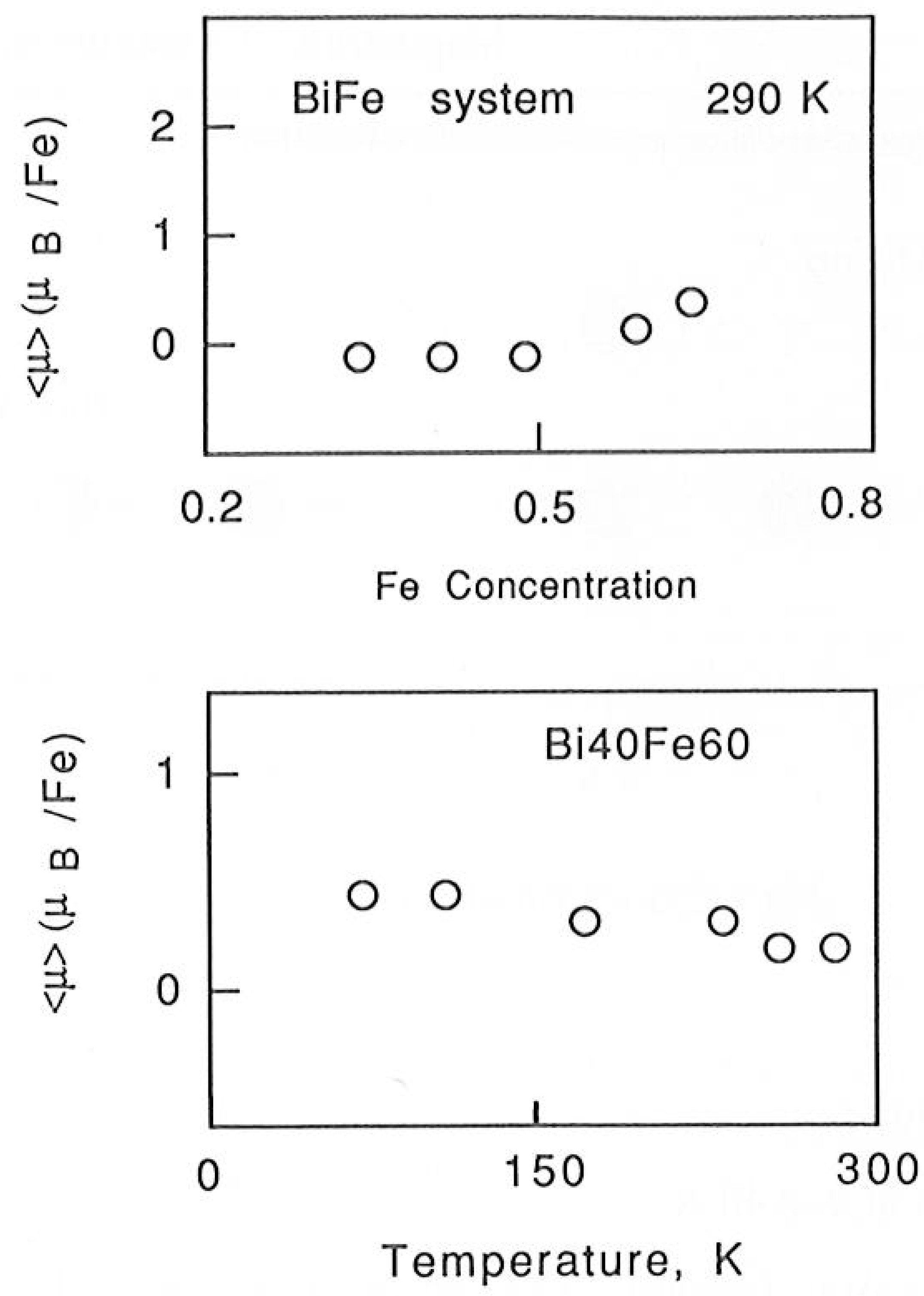


Fig. 4. Nearest-neighbour distances of the metastable iron-rich b.c.c. and bismuth-rich rhombohedral solid solutions *vs.* overall film compositions.

Fig. 5. Composition and temperature dependences of the average iron moment $\langle\mu\rangle$ in Bi–Fe films. μ_B denotes the Bohr magneton. In the lower figure, $Bi_{40}Fe_{60}$ films are in the amorphous state.

According to Buschow's model [11] of magnetic properties of ferromagnetic amorphous alloys in which a 3d metal is combined with a non-magnetic partner element, the iron magnetic moment is dependent on short-range order effects in the amorphous matrix. A positive heat of formation will favour a surrounding of iron atoms by other iron atoms, resulting in a higher magnetic moment than in the case of more uniform mixing. Some iron-based amorphous alloys have indeed been found to show such a behaviour. In a plot of the iron magnetic moment *vs.* the heat of formation of the alloy, Buschow shows a clear correlation between these two parameters: all data points fall within a band ranging from $\mu \approx 0.4\mu_B(\text{Fe atom})^{-1}$ for alloys with $\Delta H = -35$ kJ mol^{-1} to $\mu \approx 2.0\mu_B(\text{Fe atom})^{-1}$ for alloys with $\Delta H = +20$ kJ mol^{-1} [11]. For fair comparison, the local atomic concentration in all these alloys is 0.5. The local concentration differs from the overall concentration when the two alloying species have different atomic volumes. The relation between the two concentrations is expressed in ref. 11, formula (3). According to this formula, a local concentration of 0.5 in the case of Bi–Fe yields an overall composition of 35 at.% Bi. So, for amorphous $Bi_{35}Fe_{65}$ (ΔH of Bi–Fe, + 18 kJ mol^{-1}) one would expect an average iron moment $\langle\mu\rangle$ close to $2.0\mu_B(\text{Fe atom}^{-1})$. Although an amorphous phase of this composition has not been obtained, a uniform amorphous state in $Bi_{40}Fe_{60}$ films is observed. Clearly, our experimental value of $\langle\mu\rangle$ for $Bi_{40}Fe_{60}$ films does not support the model mentioned above. However, as has been pointed out in an earlier paper of van der Kraan and Buschow [12], more systems have been observed to deviate from Buschow's model. Amorphous Fe–Mg for instance ($\Delta H = +21$ kJ mol^{-1}), exhibits a magnetic moment of only $1.1\mu_B$(Fe atom)$^{-1}$, much smaller than expected from the model. Van der Kraan and Buschow ascribed this deviation to a non-collinear moment arrangement which obscures the derivation of the magnetic moment from magnetic measurements. Rather, they take the magnitude of the ^{57}Fe hyperfine field obtained by means of Mössbauer spectroscopy as a measure of the size of the iron moments, which appears to fit in the model much better. Unfortunately, such data are at present not available for the Fe–Bi system.

However, there may be another reason for the difference between the measured and expected μ values. Whereas van der Kraan and Buschow investigated amorphous alloys quenched from the melt [12], the samples used for the present investigation were vapour deposited. It is known that during vapour deposition quench rates are orders of magnitude higher than during melt-spinning-induced solidification. These differences may give rise to different local atomic arrangements after solidification: whereas the solidification time during quenching from the melt may allow some short-range ordering to occur, the high vapour–solid quench rates may bring about a more uniform atomic mixture. The magnetic moment will be different accordingly: for Bi–Fe melt spinning would result in a higher iron moment than vapour quenching. At present, however, the data available prevent further conclusions. For this, additional experiments, *e.g.* Mössbauer spectroscopy, have to be carried out.

4. Conclusion

In the Bi–Fe films synthesized by electron beam co-evaporation at 140 K, a uniform amorphous phase exists at concentrations of 45 - 60 at.% Fe. These alloy glasses are stable at room temperature. T_{a-c} of $Bi_{55}Fe_{45}$ and $Bi_{50}Fe_{50}$ films in 500 K whereas that of $Bi_{40}Fe_{60}$ films is 420 K. After ambient aging for 3 months the solute concentration of bismuth in the iron-rich b.c.c. structure is less than 0.2 at.%, while that of iron in the bismuth-rich rhombohedral structure is 1 - 2 at.% depending on composition. The average iron moment of the $Bi_{40}Fe_{60}$ glass is only $0.3\mu_B$(Fe atom)$^{-1}$. In order to study more thoroughly short-range order effects according to Buschow's model and to enable comparison with amorphous Fe–Bi alloys obtained by other methods, *e.g.* ion beam mixing, additional determinations of the iron moment, such as Mössbauer spectroscopy measurements of the hyperfine field, have to be performed.

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