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Mössbauer study of Fe–Pb films prepared by thermal evaporation

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Abstract. Although several alloys from some immiscible elements such as Fe/Cu, Fe/Ag have been obtained by vapour quenching techniques, so far there have been no reports on the Fe/Pb system. In this work, $\text{Fe}_x\text{Pb}_{1-x}$ films ($x = 0.10, 0.12, 0.20, 0.40, 0.42, 0.50, 0.63$ and 0.70) with a thickness of about 300 nm have been prepared at different deposition temperatures (20, 200 and 300 K) by a thermal co-evaporation technique. The *in situ* Mössbauer measurements were performed to study the alloying process, the magnetic properties and the structural variation with temperature. The results indicate that a solubility of 3% for Fe in Pb can be obtained by depositing an Fe diluted film ($x = 0.10$) at 20 K. For the highly Fe concentrated films, granular systems (Fe clusters) seem to be formed at all deposition temperatures.

1. Introduction

In the past decade vapour quenching, based on sputtering and thermal evaporation techniques, has been widely used to obtain metastable alloys from immiscible elements. Through sputtering deposition onto liquid-nitrogen (LN) cooled substrates, Chien *et al* (1986) and Kataoka *et al* (1985) were able to prepare Fe/Cu and Fe/Ag disordered alloys in the whole composition range. In previous work (Larcia *et al* 1992) we studied the Fe/Ag alloys obtained by thermal evaporation onto liquid-helium (LH) cooled substrates and we found that the reduction of the substrate temperature results in a wide solubility region. Moreover, Fe atoms seem to be more homogeneously dispersed in the host as compared with the films prepared at LN temperatures.

Fe/Pb is another immiscible system. The solubility of Fe in liquid Pb at 600 °C was reported to be 2.7×10^{-4} at.% by Araki (1963) and the solubility of Pb in liquid Fe at 1550–1600 °C is 0.05 at.%, as reported by Weeks (1963). Until now, there has been no report concerning the formation of Fe–Pb alloys by the vapour condensation technique.

Recently, Sielemann (1992, 1993) studied the behaviour of Fe implanted in a Pb host by in-beam Mössbauer spectroscopy. It is known that the implantation technique usually leads to very dilute alloys, and in principle it can be performed into any host material regardless of solubility limits. The results were interpreted assuming that Fe goes into the interstitial sites in the Pb host. Moreover, it was shown that Fe undergoes a dramatic diffusion process at elevated temperatures.

In this work, combining *in situ* ^{57}Fe Mössbauer spectroscopy and thermal evaporation techniques, we study the formation of Fe/Pb alloys as well as the effect of substrate temperature on the alloy-formation ability. In order to learn about the thermal stability

of the samples, the dynamic behaviour of Fe in a Pb host is studied in a temperature range 7–350 K.

2. Experimental details

Fe/Pb films were prepared by thermal co-evaporation of pure Fe and Pb metals out of two independent resistively heated Ta ovens; the deposition was performed onto kapton substrates kept at fixed temperatures (20, 200 and 300 K) during the depositions. Crystal oscillators were used to control the deposition rates and the compositions, which were finally confirmed by energy dispersive analysis (EDS) with an accuracy of 5%. The details of the evaporator set-up were given by Baggio-Saitovitch *et al* (1990). During the depositions, the pressure was kept at 5×10^{-8} Torr. All the films had a thickness of the order of 3000 Å.

The Mössbauer measurements were performed *in situ* in transmission geometry and in sinusoidal mode, using a 50 mCi ^{57}Co ;Rh source over a temperature range 7–350 K, with the film surface tilted at an angle of 45° with respect to the gamma-ray direction. The source and absorber were kept at the same temperature during the measurements. For each spectrum obtained *in situ*, the time of measurement was 12 h. The average signal-to-noise ratio was about 10 : 1. Also, *ex situ* Mössbauer measurements with the usual perpendicular geometry were performed for some samples at 4.2 K, using a He bath cryostat, or at room temperature (RT).

The Mössbauer spectra were fitted with Brand's program (1988) using the histogram method for hyperfine field (B_{hf}) superimposed with one or two crystalline sites. The linear correlation between the hyperfine field and isomer shift (IS) was assumed to fit the asymmetry of the magnetic spectra. The texture effects were taken into account allowing a free intensity ratio of the absorption lines 2–3 (D23) of the magnetic sextet. The isomer shift (IS) values are relative to an α -Fe absorber at room temperature (RT).

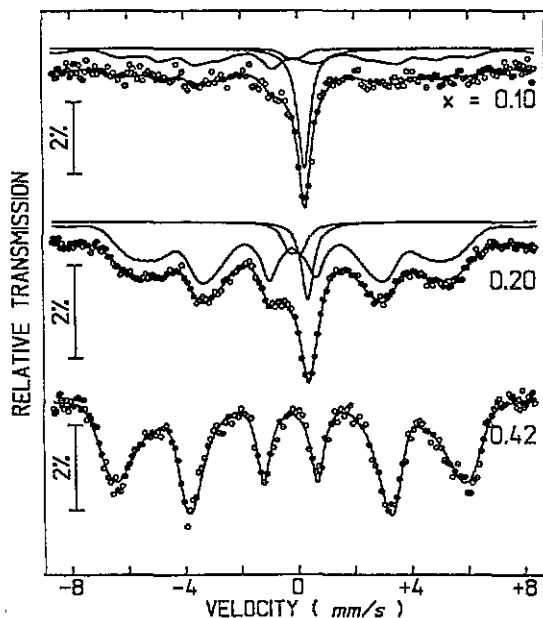


Figure 1. *In situ* ^{57}Fe Mössbauer spectra obtained at 7 K for $\text{Fe}_x\text{Pb}_{1-x}$ ($x = 0.10, 0.20$ and 0.42) films deposited at 20 K (the full curves are obtained from fits using the least-squares method).

3. Results and discussion

Figure 1 shows the *in situ* Mössbauer spectra measured at 7 K for the $\text{Fe}_x\text{Pb}_{1-x}$ films ($x = 0.10, 0.20$ and 0.42) prepared at 20 K. It can be clearly seen that the spectra are best fitted assuming a three-component model for $x = 0.10$ and 0.20 : a singlet (S), a doublet (D) and a magnetic sextet (M). For the film with $x = 0.42$, the measurement displays only a broad magnetic spectrum.

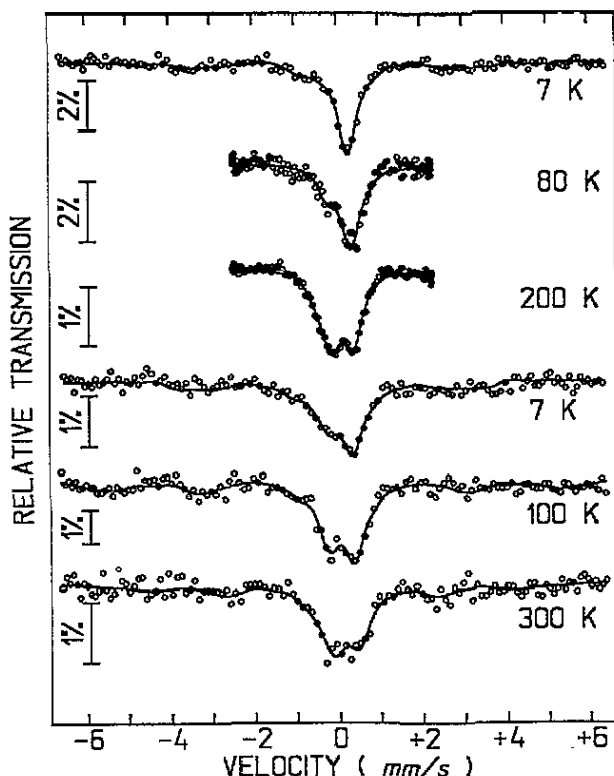


Figure 2. *In situ* ^{57}Fe Mössbauer spectra of a $\text{Fe}_{0.10}\text{Pb}_{0.90}$ film prepared at 20 K as a function of temperature ($T_m = 7, 80, 100, 200$ and 300 K) (the full curves are obtained from fits using the least-squares method).

The S component, which is better defined in the lower Fe concentration samples, has an $\text{IS} = 0.59 \text{ mm s}^{-1}$, similar to the value obtained for Fe implanted into a Pb host, but with a broader linewidth $\Gamma = 0.55 \text{ mm s}^{-1}$. According to Sielemann (1992, 1993), this singlet is assigned to Fe atoms placed on interstitial sites. Therefore the present results indicate that the preparation method used here is able to produce individual Fe atoms on interstitial sites, despite the relatively large iron content in our samples. The broader linewidth in our case may be due to structural defects, which are a general characteristic of vapour-quenched materials. From the fraction of the S component in the total absorption area of the spectrum obtained for the $\text{Fe}_{0.10}\text{Pb}_{0.90}$ film, we estimate the solubility of Fe in the Pb to be about 3 at. %. This value was confirmed by a sample prepared at 20 K with 3% of Fe, and the results will be published elsewhere by Peña Rodríguez *et al* (1995).

Another component (D) with a quadrupole interaction can be seen in our measurement with $IS = 0.12$ and $QS = 0.6 \text{ mm s}^{-1}$. Only the spectra for the lower iron concentration samples, 10% and 20%, exhibit the D component (figure 1). This component was not observed in the Fe implantation experiments of Sielemann (1992, 1993).

Figure 2 shows the *in situ* Mössbauer measurements at several temperatures for the $\text{Fe}_{0.10}\text{Pb}_{0.90}$ film. An analysis of these spectra indicates that the D component increases at the expense of the singlet S as the temperature increases. The transformation is almost complete at 200 K. To test if this interpretation was correct, the sample was cooled down again to 7 K (see figure 2). The spectrum showed a partial recovering of the S component. Therefore, with an increasing temperature, part of the S component transforms to D due to the diffusion of Fe atoms in the Pb host, while part of it is still present. However, it does not contribute appreciably to the total area at higher temperatures, which indicates that it has a lower Debye temperature than the D component. Sielemann (1993) have estimated the Debye temperature for the S component to be about 135 K from the temperature dependence of the Mössbauer absorption area.

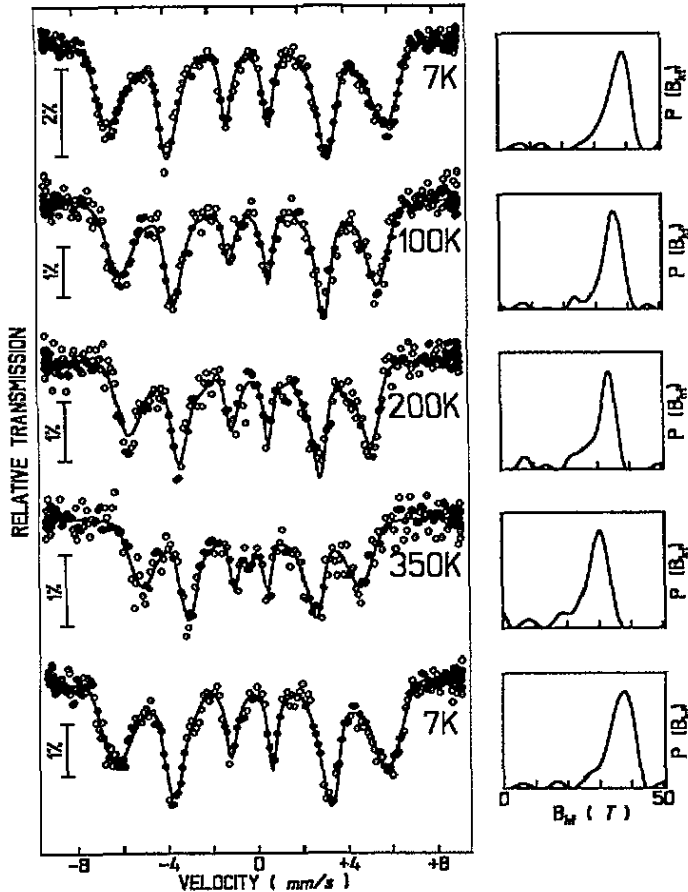


Figure 3. *In situ* ^{57}Fe Mössbauer spectra and the corresponding hyperfine magnetic field distribution of $\text{Fe}_{0.42}\text{Pb}_{0.58}$ films prepared at 20 K as a function of temperature (the full curves are obtained from fits using the least-squares method).

Since the S component is related to the as-quenched state, one may expect that the Fe atoms sit on sites completely surrounded by Pb atoms which have a cubic local symmetry. On the other hand, because the increase of the D component is associated with the Fe diffusion process, the D component may correspond to some type of very small Fe cluster with non-cubic local symmetry. This point will be discussed intensively by Peña Rodríguez *et al* (1995) in relation to the electronic structure calculation of Fe in a Pb matrix.

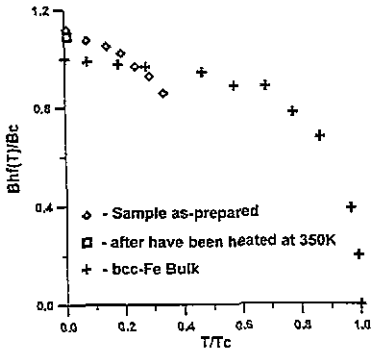


Figure 4. Hyperfine magnetic field (B_{hf}) as a function of temperature for $Fe_{0.42}Pb_{0.58}$ film prepared at 20 K and bulk α -Fe. The reduced temperature and B_{hf} are obtained from the bulk α -Fe ferromagnetic transition.

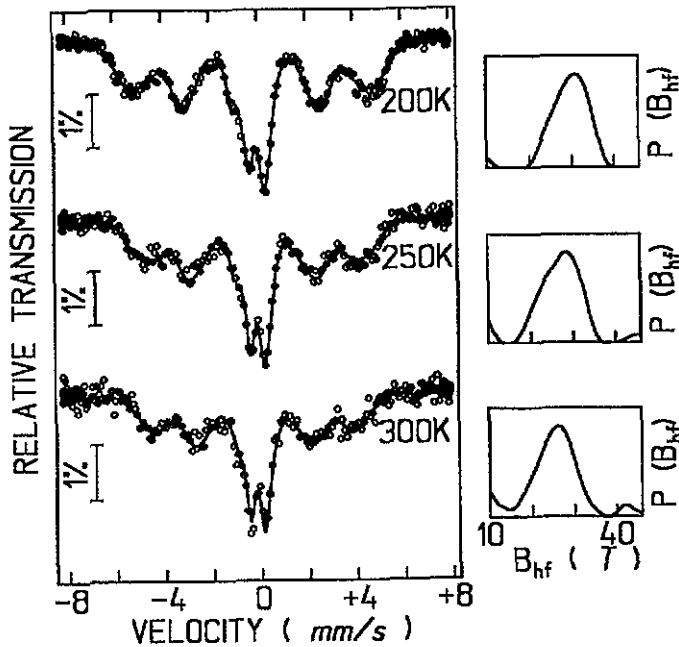


Figure 5. *In situ* ^{57}Fe Mössbauer spectra and corresponding hyperfine magnetic field distributions of $Fe_{0.12}Pb_{0.88}$ films, prepared at 200 K, as a function of temperature ($T_m = 200, 250$ and 300 K) (the full curves are obtained from fits using the least squares-method).

The magnetic component of the spectra (the M component) exhibits a broad magnetic hyperfine field distribution. This component, in principle, could be due to an amorphous

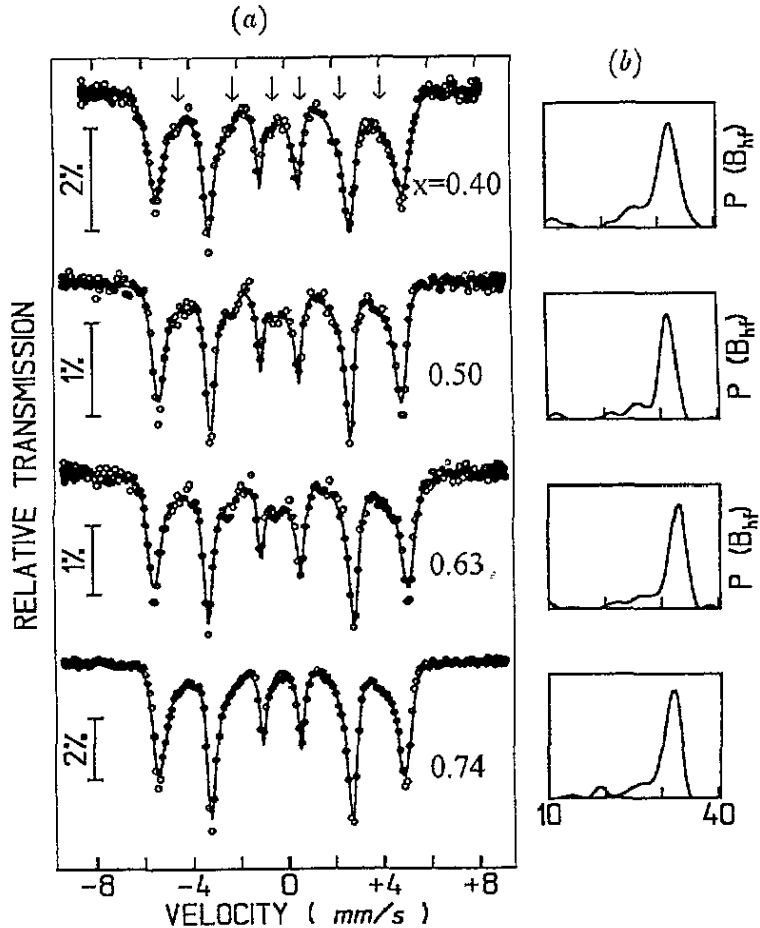


Figure 6. *In situ* ^{57}Fe Mössbauer spectra and corresponding hyperfine magnetic field distributions of $\text{Fe}_x\text{Pb}_{1-x}$ ($x = 0.40, 0.50, 0.63$ and 0.74) films prepared at 300 K and measured at the same temperature.

phase of Fe. In the following we will discuss why we think this is not the case, and that this component is due to small Fe particles. At the peak of the hf distribution, the isomer shift is $\text{IS} = -0.03 \text{ mm s}^{-1}$ and the magnetic hyperfine field value is 39 T at 7 K (figure 1). This value is larger than that for $\alpha\text{-Fe}$. In order to characterize this component, we obtained spectra as a function of temperature for an $\text{Fe}_{0.42}\text{Pb}_{0.58}$ film (see figure 3). Cycling the temperature from 7–350 K and cooling back to 7 K does not affect the spectrum, indicating that in this temperature range the heating process does not change the Fe site configuration corresponding to the M component. Figure 4 shows the temperature dependence of the peak value of the hf distribution for the $\text{Fe}_{0.42}\text{Pb}_{0.58}$ film in comparison with the bulk $\alpha\text{-Fe}$. It is higher at lower temperatures, but it reduces faster than $\alpha\text{-Fe}$, which results in smaller fields above 250 K. This behaviour has already been seen in Fe granular system by Bødker *et al* (1992). Therefore, we assign the M component to small Fe particles with bcc structure.

Figure 5 shows the *in situ* Mössbauer measurement, at the indicated temperatures, for

the $\text{Fe}_{0.12}\text{Pb}_{0.88}$ film prepared at 200 K. Under these conditions the S component was not formed, despite the fact that we observed that the doublet D had already been obtained after heating up the $\text{Fe}_{0.10}\text{Pb}_{0.90}$ sample prepared at 20 K (figure 2). This indicates that, at higher deposition temperatures, Fe clusters can be formed in the deposition process due to the fact that at 200 K there is a large mobility of Fe atoms.

Films with high Fe concentrations ($x = 0.40, 0.50, 0.63$ and 0.74) were prepared with the substrate temperature at room temperature (RT), as shown in figure 6(a). The magnetic spectra indicate the presence of two components. The main component (88%), which corresponds to the main peak of the hf distribution curves (figure 6(b)), is the M component, mentioned above, which is attributed to small Fe particles. The component with a lower intensity may be seen at the positions indicated by the arrows in the figure 6(a). This may imply that there is some solubility of Pb in the Fe matrix, which reduces the magnetic moment of the Fe atom. Compared with low-temperature deposition, figure 6(a) and (b) shows better-defined spectra of bulk α -Fe. This indicates the formation of larger α -Fe particles when a sample is deposited at RT.

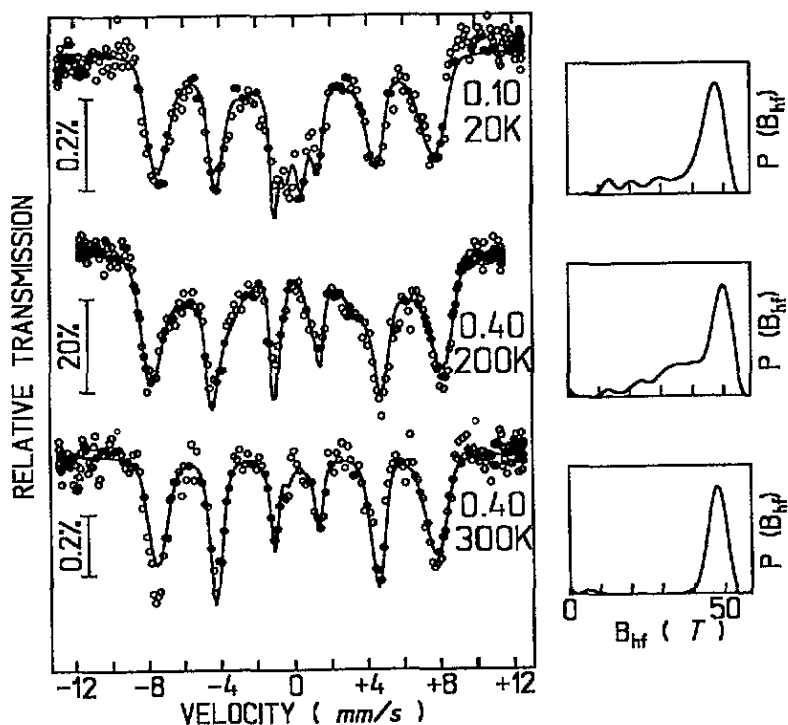


Figure 7. *Ex situ* ^{57}Fe Mössbauer spectra obtained at 4.2 K and the corresponding hyperfine magnetic field distributions of $\text{Fe}_x\text{Pb}_{1-x}$ ($x = 0.10, 0.40$ and 0.40) films prepared at 20, 200 and 300 K, respectively.

Since Fe/Pb films exhibit granular behaviour, the samples are easily oxidized at a partial pressure above 10^{-4} torr. Figure 7 shows the 4.2 K Mössbauer spectra of several samples prepared at different substrate temperatures after being exposed to the air. In this case, those samples with a higher Fe composition and having been deposited at high temperatures exhibit magnetically split spectra of Fe_2O_3 . However, those samples with a lower Fe composition

and having been deposited at low temperatures exhibit spectra composed of both magnetic subspectra of bulk Fe_2O_3 and the superparamagnetic doublet of small Fe_2O_3 particles. The latter can be understood, since the lower composition value and the lower preparation temperature partially inhibit the formation of big oxide clusters of Fe.

We have shown above that alloy-forming ability is very sensitive to substrate temperature. The low-temperature deposition has a higher quenching rate, so the mobility is small and a random disordered state can be frozen-in. Such an effect leads to the formation of an Fe/Pb alloy only at 20 K, although the solubility is low. For some other immiscible systems, where the alloys may be formed over the whole composition range, the substrate temperature can still affect the homogeneity of the films. For example, for the Fe/Ag system, films prepared at 20 K have lower hyperfine fields compared with those prepared at liquid nitrogen temperatures. This is because the Fe atoms are more homogeneously dispersed in the matrix in the former case; in the latter case they may form Fe clusters.

4. Conclusions

Although Fe and Pb are immiscible in both the solid and liquid states, it has been found that Fe/Pb alloys with a solubility of 3% of Fe in Pb can be obtained by thermal co-evaporation onto a substrate kept at 20 K. Such alloys are thermally unstable and a diffusion process is observed after warming to temperatures even lower than RT. The diffusion leads to the formation of some type of Fe clusters which are rather small for diluted films deposited at room temperature. For high deposition temperatures, such clusters are formed during the deposition. For films with a higher Fe content, the clusters become larger and the systems show a magnetic ordering independent of the deposition temperature.

Acknowledgments

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References

- Araki T 1963 *Trans. Nat. Res. Inst. Metals (Tokyo)* 5 91
- Baggio-Saitovitch E, Drago V, Elmequid M and Micklitz H 1990 *Applications of the Mössbauer Effect* (Singapore: World Scientific) p 290
- Brand R A 1988 Duisburg University
- Bødker F, Mørup S, Oxborrow C A, Linderøth S, Madsen M B and Niemantsverdriet J W 1992 *J. Phys.: Condens. Matter* 4 6555
- Chien C L, Liou S H, Kofalt D, Wu Yu, Egami T and McGuire T R 1986 *Phys. Rev. B* 33 3247
- Larica C, Baggio-Saitovitch E and Xia S K 1992 *J. Magn. Magn. Mater.* 110 106
- Kataoka N, Sumiyama K and Nakamura Y 1985 *J. Phys. F: Met. Phys.* 15 1405
- Peña Rodríguez V A, Passamani E C, Ellis D and Baggio-Saitovitch E 1995 to be published
- Sielemann R 1992 private communication
- 1993 *Hyp. Int.* 80 1239
- Weeks J R 1963 *NASA Spec. Publ.* 41 21