^{57}Fe diluted in a Ag film prepared by vapor quenching: Nanostructure formation and magnetic behavior

M. A. Morales,[1] E. C. Passamani,[2] and E. Baggio-Saitovitch[1]

[1]*Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, 22290-180, RJ, Brazil*
[2]*Universidade Federal do Espírito Santo, Departamento de Física, Vitória, 29060-900, ES, Brazil*

^{57}Fe diluted in Ag film has been prepared by vapor quenching onto a kapton substrate kept at 16 K. Mössbauer spectroscopy (MS), under 1.5 and 3.7 T applied fields, and temperature-dependent, *in situ* and *ex situ*, measurements have been performed to investigate the site occupation and magnetism of Fe atoms, thermal stability of the Fe species, and Fe cluster formation. *In situ* ^{57}Fe MS for the as-prepared film, measured at 10 K indicates that 74% of Fe atoms are randomly distributed at substitutional sites in fcc Ag matrix (Fe monomer), 20% are associated with Fe dimers, and the remaining Fe atoms form a fcc Fe phase. MS under applied field indicates that each Fe phase has its own magnetic moment. Temperature-dependent MS shows that the Fe monomers and Fe dimers diffuse, forming fcc-like Fe clusters probably distributed at the grain boundaries of the Ag matrix. The fcc Fe phase with particle sizes at about 20 Å is completely transformed to bcc like phase at high temperature. An *ex situ* MS experiment, at 4.2 K without an external field, shows that the magnetic moment of the Fe monomer is frozen by exchange magnetic coupling or by dipolar interactions created by the large Fe clusters present in the annealed film.

I. INTRODUCTION

Knowledge of the magnetic properties of Fe clusters is of great importance due to their basic scientific and technological interest. Fcc Fe precipitated in a Cu matrix or epitaxially grown onto a Cu surface has been reported to show ferromagnetic (FM) or antiferromagnetic (AF) order, depending on the preparation method and the lattice parameters.[1−3] The magnetic moment and hyperfine field were calculated for Co and Fe clusters embedded in fcc Ag host:[4] for the biggest cluster (Fe$_{43}$) considered, the magnetic moment has an average value of $2.88\mu_B$ and the calculated hyperfine field at an Fe isolated impurity (monomer) is in disagreement with the experimental value.[5] The physical properties of Fe clusters are very sensitive to the distribution and structure of crystallite size, and it is rather difficult to control those factors during the precipitation that take place in the aging process of Fe-rich supersaturated alloys. This control can be achieved in the very-low-Fe-concentration regime, which was chosen in this work. Thus we expect to get more details about the formation process and magnetic properties of Fe clusters by combining *in situ* ^{57}Fe Mössbauer spectroscopy (MS) with vapor deposition at low temperatures.

Fe and Ag elements are known to form an immiscible system in the extremes of the composition range, i.e., in the solid as well as in the liquid state.[6] Thus the supersaturated Fe/Ag alloys can only be prepared out of equilibrium using implantation,[7,8] mechanical alloying,[9] or deposition techniques.[10,11] Larica *et al.*[10] have prepared supersaturated Ag$_{1-x}$Fe$_x$ ($17 < x < 80$ at. %) films, with the substrate kept at 20 K, in the same He-cryostat evaporator used in the present work and their result showed that all the films have a fcc-like structure with very small grain sizes, for less than 56 at. % of Fe. Peng *et al.*[11] have studied Ag$_{1-x}$Fe$_x$ ($5 < x < 21$ at. %) films prepared by electron-beam coevaporation, with the va-

por quenched onto a glass substrate kept at 77 K. From transmission electron microscopy and magnetotransport measurements they proposed a granular structure of Fe for the as-prepared films and estimated particle sizes varying from 4 to 17 Å with a giant magnetoresistence of 50%, for the film with 5 at. % of Fe. Kahl and Krebs[12] produced Fe-Ag single-phase bcc alloys, using a pulsed laser deposition technique, onto substrates kept at 150 K with iron concentration varying from 60 to 100 at. %. The process of the bcc Fe clustering initiates around 450 K. However, to our knowledge there is so far no report about how the Fe clusters are formed in the supersaturated Fe/Ag thin films in the very diluted Fe regime.

Diluted Fe impurities in Ag host have been prepared by implantation technique, at room temperature,[7,8] with the implantation dose varying from 1×10^{15} to 5×10^{16} ions/cm^2 (average Fe concentration from 0.25 to 8.7 at. %).[6] MS for alloys with the lowest implantation dose shows 82% of Fe at substitutional sites (Fe monomer) and 18% of Fe atoms as Fe dimers.[6] Temperature-dependent MS indicates the formation of bcc Fe clusters for annealing temperatures above room temperature.

Recently,[13] we have shown that the combination of the vapor quenching (VQ) method onto a low-temperature substrate, with MS under applied magnetic field can give information about the localization and magnetic state of Fe impurities in metallic Yb and Pb hosts. This information has been compared with results obtained for Fe atoms implanted in the same matrices.[14] The results for as-quenched film are in agreement with respect to the site occupation (Fe at substitutional and interstitial sites), however with different relative volume fractions. We have also discussed the effect of atomic diffusion,[13] which occurs even at low temperatures, due to the large number of defects in the crystalline grains as well as a large relative fraction of grain boundary regions.

In the present work, the vapor quenching technique, with the substrate kept at 16 K, is combined with *in situ* MS, under applied magnetic fields, in order to study the localization and magnetic state for diluted ^{57}Fe atoms in Ag film. Moreover, *in situ* and *ex situ* temperature-dependent MS measurements have been done to investigate thermal stability of the Fe phases and the atomic diffusion process at temperatures above 16 K, in order to understand the mechanism of Fe cluster formation.

II. EXPERIMENT

^{57}Fe:Ag (Ag–1.0 at. % ^{57}Fe) thin-film alloy was prepared by vapor quenching method in a He cryostat by thermal co-evaporation of iron (98% enriched in ^{57}Fe) and high-purity Ag (99.999%) metal, from two independent resistively heated Ta ovens. The vapors were deposited onto a Kapton substrates kept at 16 K. Deposition rates for Ag and Fe were, respectively, 1.0 and 0.01 Å/s (these rates were determined with piezoelectric quartz crystal operating at 5 MHz). The residual base pressure was about 5×10^{-9} mbar, increasing up to 3×10^{-8} mbar during the deposition. The ^{57}Fe:Ag film has a nominal thickness of about 4000 Å.

Our experimental set up[15] is especially suitable for *in situ* MS studies in external magnetic fields. The *in situ* MS measurements were performed with a 25 mCi ^{57}Co:Rh source moving in the sinusoidal mode. During the *in situ* MS experiments source and absorber are kept at the same temperature. In the case of MS in an applied magnetic field, the γ rays are parallel to the external field direction. Two other cryostats for low-temperature measurements were used. *Ex situ* high-temperature MS experiments have been done in a Mössbauer furnace under a residual pressure of about 10^{-6} mbar. During *ex situ* high-temperature Mössbauer measurements, the ^{57}Co source was kept at room temperature, while the absorber temperature was varied from room temperature to 480 K. This upper temperature limit was selected to prevent damage of the Kapton substrate. The center shift (CS) values of each Fe component in the present paper are given relative to α-Fe, at room temperature. In the *in situ* experiment the misleading information regarding annealing effect related with f factors of different components is avoided by taking the MS at lowest temperature after annealing the film at high temperature.

III. RESULTS AND DISCUSSION

A. Magnetism of Fe phases in as-quenched ^{57}Fe:Ag film

Figure 1 displays *in situ* 10 K Mössbauer spectra for as-quenched ^{57}Fe:Ag film, measured in different external magnetic fields ($B_{\text{ext}} = 0$, 1.5, and 3.7 T). The best fit for the MS, without applied field, was obtained with three paramagnetic components: two singlet, labeled S1 and S2, and one doublet labeled D1. The main contribution to the MS comes from S1 subspectrum with 74% of the relative absorption area (RAA), followed by the D1 subspectrum with 20%, and finally the contribution of S2 subspectrum of 6% of RAA. According with results reported by Longworth and Rain[7] and by Marest *et al.*,[8] in ^{57}Fe:Ag samples prepared by implanta-

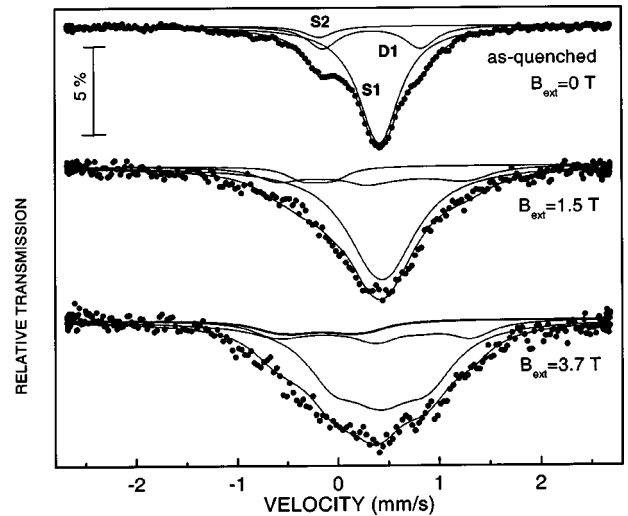FIG. 1. *In situ* ^{57}Fe Mössbauer spectra of as-quenched ^{57}Fe:Ag film, measured at 10 K without and under external magnetic fields ($B_{\text{ext}} = 1.5$ and 3.7 T).

tion method with similar ^{57}Fe concentration, one may associate the S1 subspectrum with Fe randomly distributed at substitutional Ag matrix site (Fe monomer) and the D1 subspectrum to Fe dimers. The volume fraction of Fe monomers (S1 subspectrum) is significantly higher than the 50% obtained by Longworth and Rain,[7] but lower than the 82% reported by Marest *et al.*[8] The assignment for the S2 subspectrum will be discussed below, after the presentation of the temperature-dependent and applied field Mössbauer measurements.

Since we are dealing with very diluted Fe concentration, no magnetic order can be established even at low temperature, therefore in order to get information about the magnetism of the Fe phases formed in as-quenched ^{57}Fe:Ag film, we have performed MS measurements at 10 K with two different external magnetic fields (B_{ext}) and their MS are also shown in Fig. 1. These MS are composed of broad absorption lines, indicating that in these phases, Fe atoms do not have well-defined magnetic orientations. Thus these MS are fitted with the same three subspectra found in Fig. 1(a), now with the additional magnetic field. The hyperfine parameters of the Fe phases, obtained from the fits of the MS taken at 10 K under two different external magnetic fields, are displayed in Table I.

As can be seen in Table I the effective hyperfine magnetic fields (B_{eff}) found for the Fe monomer (S1) are smaller than the external magnetic field (B_{ext}) values, indicating that the Fe atoms in this configuration have a negative B_{hf}. Furthermore, the B_{hf} values of the Fe monomer fit into the systematic observed by Steiner and Hüfner,[16] for diluted ^{57}Co impurities (10 ppm) in an Ag matrix, prepared by electroplating and measured at similar external fields. It is important to mention that in their MS experiments the magnetic saturation regime of the Fe magnetic moment was only obtained for temperatures below of 4.2 K and external fields above 5 T, a condition that cannot be reached in our *in situ* measurements. Thus, based on the results of Steiner and Hüfner,[16] one may assume that the Fe in the monomer phase shows a spin-lattice relaxation effect at 10 K and under an external field of 3.7 T.

TABLE I. Hyperfine parameters of each Fe phase, obtained from the fits of the 10 K Mössbauer spectra of the [57]Fe:Ag film measured under external magnetic fields.

B_{ext}	S1 (Fe monomers)					D1 (Fe dimers)						S2 (fcc Fe clusters)				
	CS	Γ	B_{eff}	B_{hf}	RAA	CS	Γ	QS	B_{eff}	B_{hf}	RAA	CS	Γ	B_{eff}	B_{hf}	RAA
(T)	(mm/s)		(T)		(%)	(mm/s)			(T)		(%)	(mm/s)		(T)		(%)
1.5	0.52	0.7	1.0(2)	−0.5(2)	71	0.45	0.5	1.0	3.4(2)	1.9(2)	22	−0.09	0.4	1.2(2)	−0.3(2)	7
3.7	0.52	0.7	2.9(2)	−0.8(2)	71	0.45	0.4	1.0	3.9(2)	0.2(2)	22	−0.09	0.4	3.0(2)	−0.7(2)	7

Analyzing the B_{eff} values of the D1 phase, shown also in Table I, it can be concluded that Fe ions in this case have their own magnetic moments. To be more confident in our analysis we have performed MS experiment, under field and at high velocity scale, and found no evidence of any magnetic component with B_{eff} values higher than those observed for D1 Fe species. From the absence of large B_{hf} component in MS one may infer that the D1 Fe specie is related to small Fe clusters, with superparamagnetic behavior.

On the other hand, it is difficult to define the magnetic features for the S2 component due to the small relative fraction, which may lead to ambiguous results. However, since at low temperature and under applied field we have not observed the magnetic split of this component one may speculate that the S2 Fe species could be due to Fe clusters in an AF state or having a fast magnetic relaxation process. As will be discussed below, based on S2 hyperfine values and the temperature-dependent measurement one may suggest that the S2 Fe specie is related to small fcc Fe clusters.

B. Localization and thermal stability of Fe phases

1. In situ Mössbauer results

Figure 2 shows the *in situ* temperature-dependent MS of the [57]Fe:Ag film. The first thermal cycle was done from 10 to 200 K, with steps of 50 K, keeping the film during 24 h, at each temperature. In this figure it can be seen that the RAA, of the S2 and D1 subspectra, increases with the temperature, at expenses of the RAA of the S1 subspectrum (see also Table II). After having been kept at 200 K, the film was cooled again down to 10 K and a new MS was recorded. Comparing the Mössbauer results at 10 K of the as-quenched and thermal treated film, one may conclude that the RAA of S1 subspectrum changed after the annealing having narrower line, an effect that can be associated with structural relaxation, in particular a reduction of the number of defects in the vicinity of the Fe monomer. Moreover, the D1 and S2 subspectra increase their relative volume fractions due to an atomic diffusion process that has taken place during the annealing. No Fe magnetic subspectrum has been detected in the 10 K MS after the annealing up to 200 K. The absence of a magnetic component can be due to the small size of the clusters of each Fe phase ($S2$ and $D1$), being in the superparamagnetic regime at 10 K.

Now we would like to discuss in more detail the $S2$ subspectrum. First of all, it has CS hyperfine parameters close to that of γ-Fe[2]. Second, it is also important to recall that this phase, obtained from the diffusion process in a fcc
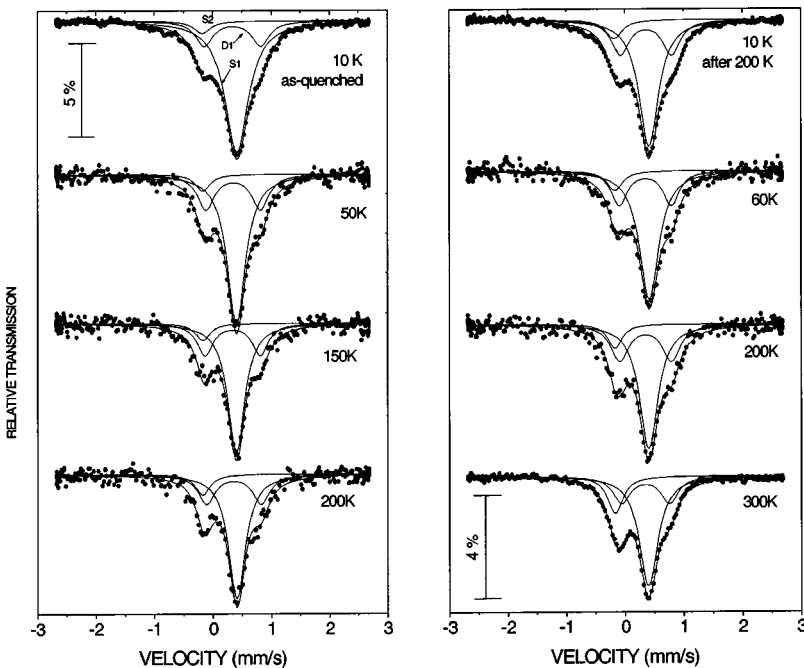

FIG. 2. *In situ* [57]Fe Mössbauer spectra of [57]Fe:Ag film recorded at different temperatures.

TABLE II. Hyperfine parameters of each Fe phase, obtained from the fits of *in situ* temperature-dependent Mössbauer spectra of ^{57}Fe:*Ag* film.

T (K)	$S1$ (Fe monomers)			$D1$ (Fe dimers)				$S2$ (fcc Fe clusters)		
	CS	Γ	RAA (%)	CS	QS	Γ	RRA (%)	CS	Γ	RAA (%)
	(mm/s)			(mm/s)				(mm/s)		
10	0.51	0.49	74	0.51	0.97	0.36	20	−0.09	0.34	6
50	0.51	0.38	66	0.45	0.93	0.35	28	−0.08	0.30	6
150	0.51	0.37	64	0.44	0.94	0.33	29	−0.08	0.30	7
200	0.52	0.36	62	0.45	0.94	0.35	33	−0.07	0.33	9
10	0.52	0.40	61	0.45	0.87	0.35	31	−0.09	0.35	8
60	0.52	0.40	64	0.45	0.86	0.33	28	−0.07	0.33	8
200	0.51	0.37	58	0.45	0.86	0.37	33	−0.07	0.31	9
300	0.51	0.37	58	0.45	0.81	0.36	26	−0.05	0.32	16

Ag matrix, does not display large B_{eff} values for MS under an external field. Therefore, it seems to be reasonable to attribute the $S2$ subspectrum to small Fe clusters in fcc-like phases.

Back to the temperature dependence measurements, we can still say that, due to the absence of magnetic spectra at 10 K, the Fe clusters ($S2$ and $D1$ subspectra), obtained after annealing up to 200 K, are very small in size and with blocking temperatures (T_B) lower than 10 K. A new thermal cycle, from 10 to 300 K, was done and the Mössbauer results are also shown on right-hand side of Fig. 2. At 300 K, the RAA of the $S2$ subspectrum (see Table II) has a relative increase, compared to the data obtained at 10 K, while the $S1$ and $D1$ subspectra reduced their RAA. From the behavior of the RAA of each Fe phase, one can suggest that the formation of fcc Fe clusters is due to the atomic diffusion process which starts when the Fe monomer ($S1$) moves near to the Fe dimer configuration ($D1$), leading to Fe clusters of the fcc-Fe-like phase ($S2$ subspectrum).

2. Ex situ Mössbauer results

In Fig. 3 we can compare at 300 K *in situ* (a) and *ex situ* (b) MS, this one taken 3 days after (a). There are small differences revealed in the analysis of both spectra related with the increase of RAA for $D1$ in the *ex situ* spectrum, variation of CS from −0.09 to −0.05 mm/s for the $S2$ subspectrum and a decrease of QS from 1.0 to 0.9 mm/s for the $D1$ Fe specie. This suggests that the Fe spectra are already modified, and we name them "$S2$" and $D2$. The differences in the hyperfine parameters of the $S2$ and $D1$ subspectra, between *in situ* and *ex situ* experiments, are strong indication for continuing atomic diffusion at room temperature (RT).

In order to study the magnetic behavior and to understand the changes observed in the *ex situ MS at 300* K, we have recorded a new MS at 4.2 K in another cryostat, which allows us to keep the source and absorber at the same temperature. The 4.2 K MS is complex and was fitted with the same RAA obtained at 300 K. Thus the data shown in Fig. 4 reveal a B_{hf} for the Fe monomer ($S1$) of about 3.5 (3) T. This result can be due to a slowing down of Fe magnetic relaxation caused by magnetic exchange and/or dipole interactions of

the monomer with a nearest-neighbor Fe.

The $D2$ subspectrum has a B_{hf} value of 15 T and ε of 0.5 mm/s (ε is a parameter used for unknown θ, the angle between B_{hf} and V_{zz}), while the "$S2$" subspectrum displays a broad magnetic hyperfine field distribution component, having a B_{hf} maximum value of 35 T. No Fe oxide phases are observed. The magnetic splitting of $D2$ and "$S2$" subspectra may be an indication that the blocking temperatures of Fe particles are around 4.2 K, since at 10 K they do not split. Another possibility could be that Fe particles are larger in the *ex situ* measurement and therefore have higher blocking temperatures.

The results described above, for low temperature *ex situ* MS experiment, can be understood as follows: (1) the $D2$ subspectrum is due to bigger iron aggregates, consisting of Fe trimers or larger Fe clusters, but without stabilizing fcc-like Fe clusters: (2) the "$S2$" subspectrum, which is associated with a broad magnetic hyperfine field component, has at least three magnetic peaks in the distribution curve (shown in
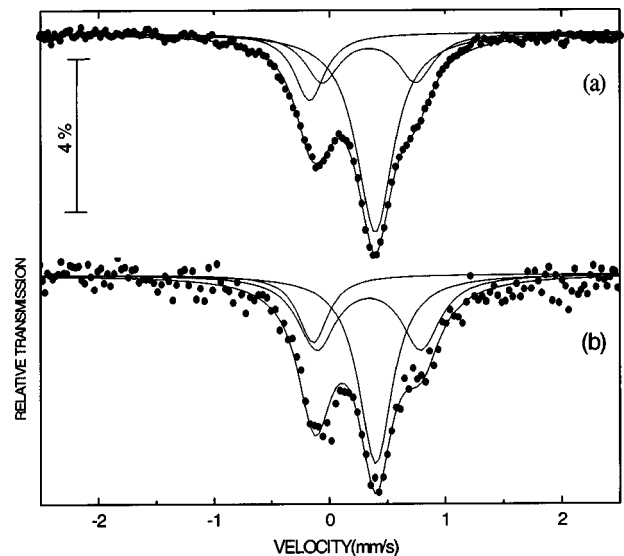

FIG. 3. ^{57}Fe Mössbauer spectra of ^{57}Fe:*Ag* film recorded at 300 K: (a) *in situ*, (b) *ex situ* recorded 3 days after the *in situ* measurement at 300 K.
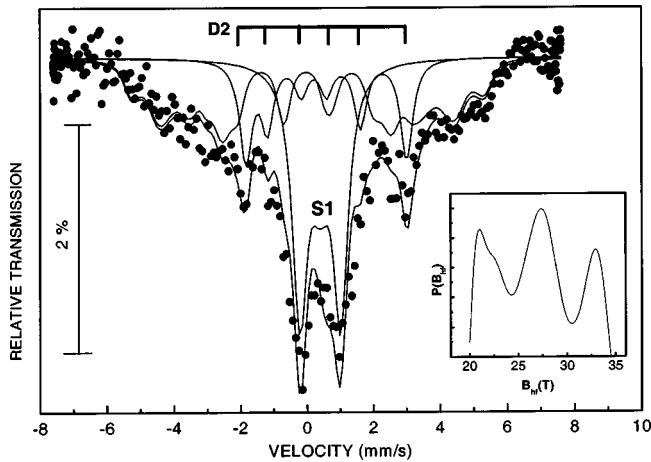
FIG. 4. *Ex situ* ^{57}Fe Mössbauer spectrum of ^{57}Fe:*Ag* film recorded at 4.2 K, the inset shows the B_{hf} distribution.

the inset of Fig. 4) that can be attributed to fcc-like and bcc-like Fe phases; and (3) the Fe monomer ($S1$) becomes magnetically ordered at 4.2 K, due to dipolar and/or exchange magnetic interactions with neighboring Fe clusters.

In order to address the formation of bcc-like Fe clusters, as reported by Longworth and Rain[7] in implanted samples annealed above room temperature, *ex situ* MS experiments were performed from 340 K up to 480 K. As can be seen from the Mössbauer results, shown in Fig. 5, the diffusion process does not reach the saturation regime, since the absorption line close to the peak position of "$S2$" subspectrum increases with temperature.

The 300 K MS obtained after annealing up to 480 K displays an absorption line close to 0.0 mm/s. This new singlet
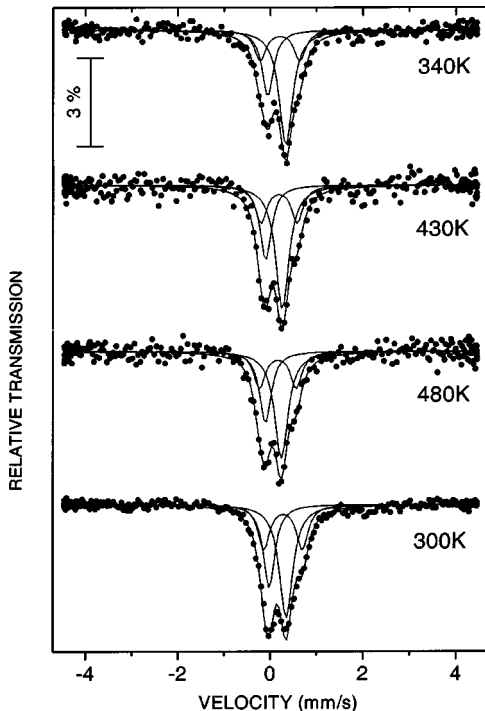

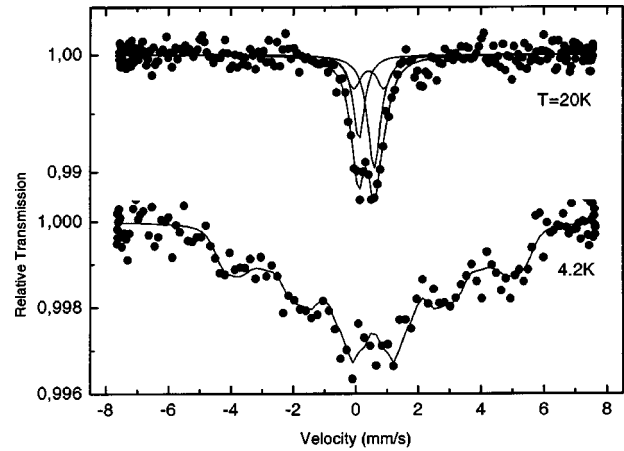FIG. 5. *Ex situ* ^{57}Fe Mössbauer spectra of ^{57}Fe:*Ag* film recorded at different temperatures.

FIG. 6. *Ex situ* ^{57}Fe Mössbauer spectrum of ^{57}Fe:*Ag* film recorded at 20 and 4.2 K.

($S3$ subspectrum) has CS = 0.04 mm/s and Γ = 0.30 mm/s and can be attributed to bcc-like Fe clusters. This smaller linewidth (after annealing at 480 K) indicates that the bcc-like Fe phase is well defined. Therefore, the fcc-like Fe phase seems to be absent.

Low-temperature MS measurements for the film, which was annealed at 480 K, were taken in a third different cryostat, which allows temperature variation with the ^{57}Co source at RT. The spectra at 20 and 4.2 K are displayed in Fig. 6 and a broad sextet, which is typical for Fe particles in the magnetic relaxation regime, can be seen at 4.2 K. At 20 K only Fe phases in the paramagnetic state are present, indicating that the bcc Fe cluster (based on CS values) has blocking temperatures lower than 20 K. Thus, by using the results of the blocking temperature of bcc Fe clusters, obtained by susceptibility measurements,[17] we can suggest that the bcc Fe particle sizes are smaller than 20 Å.

Summarizing, in the as-quenched ^{57}Fe:*Ag* film, Fe monomer ($S1$), has a main contribution (74%), followed by Fe dimers ($D1$), and a small relative volume fraction of fcc Fe clusters ($S2$). The last two phases ($D1$ and $S2$) may be distributed at the interfaces of Ag grains. After annealing, the Fe-monomer and Fe-dimer species diffuse, increasing the relative volume fraction of fcc Fe clusters. Finally, the atomic diffusion process leads to an increase of the fcc Fe cluster size, yielding bcc Fe clusters, mainly after *ex situ* annealing at high temperatures (480 K). The Fe particles with less than 20 Å, formed by the diffusion process, have the bulk bcc Fe structure as indicated by the CS values.

IV. CONCLUSION

Combining VQ technique and MS under applied fields, we have studied thin films of diluted ^{57}Fe in an Ag matrix. The as-quenched film displays a large fraction of isolated Fe atoms distributed randomly in the Ag matrix, named here Fe monomers. The proportion of this phase in the present work is larger than the one reported by Longworth and Rain[7] for Fe implanted in an Ag matrix. The Fe monomer displays similar magnetic behavior as diluted Fe in an Ag matrix pre-

pared by ^{57}Co electroplating.[16] On the other hand, the MS under external magnetic fields have shown that each Fe phase has its own magnetic moment and displays unsaturated magnetic behavior. The *in situ* annealing process (up to 300 K) shows that atomic diffusion from isolated Fe atoms and Fe dimers induces initially the formation of fcc Fe clusters. The bcc Fe clusters are obtained only after annealing further the film at high temperatures. Low-temperature MS measurements shows that the fcc Fe and bcc Fe clusters, obtained at 300 K, are magnetically ordered at 4.2 K and that these clusters induce a B_{hf} at the Fe-monomer site by slowing down the relaxation. Finally, the annealing at 480 K leads to an enhancement of the formation of bcc Fe clusters, with estimated upper particle sizes of 20 Å.

[1] W. A. A. Macedo and W. Keune, Phys. Rev. Lett. **61**, 475 (1988).

[2] W. Keune, T. Ezawa, W. A. A. Macedo, U. Glos, K. P. Schletz, and U. Kirschbaum, Physica B **161**, 269 (1989).

[3] D. Guenzburger and D. E. Ellis, Phys. Rev. B **51**, 12 519 (1995).

[4] R. N. Nogueira and H. M. Petrilli, Phys. Rev. B **60**, 4120 (1999).

[5] T. A. Kitchens and R. D. Taylor, Phys. Rev. B **9**, 344 (1974).

[6] F. A. Shunk, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1969), 2nd suppl.

[7] G. Longworth and J. Rain, J. Phys. F: Met. Phys. **5**, 993 (1978).

[8] G. Marest, H. Jaffrezic, J. Stanek, and H. Binczycka, Nucl. Instrum. Methods Phys. Res. B **80−81**, 357 (1993).

[9] J. A. Gomez, S. K. Xia, E. C. Passamani, B. Giordanengo, and E. M. Baggio-Saitovitch, J. Magn. Magn. Mater. **223**, 112 (2001).

[10] C. Larica, E. M. Baggio-Saitovitch, and S. K. Xia, J. Magn. Magn. Mater. **110**, 106 (1992).

[11] C. Peng, S. Zhang, G. Li, and D. Dai, J. Appl. Phys. **76**, 998 (1994).

[12] Sören Kahl and Hans-Ulrich Krebs, Phys. Rev. B **63**, 172103 (2001).

[13] E. C. Passamani, M. A. Morales, and E. Baggio-Saitovitch, Phys. Rev. B **60**, 1111 (1999).

[14] J. Kapoor, D. Riegel, Yi Li, C. Polaczyk, J. Andres, F. Mezei, R. Sielemann, Y. Yoshida, W. D. Brewer, L. A. Mello, and S. Frota-Pessôa, Phys. Rev. Lett. **78**, 1279 (1997).

[15] E. Baggio-Saitovitch, J. Terra, and F. J. Litterst, Phys. Rev. B **39**, 6403 (1989).

[16] P. Steiner and S. Hüfner, Phys. Rev. B **12**, 842 (1975).

[17] Jian-Qing Wang and Gang Xiao, Phys. Rev. B **49**, 3982 (1994).