# Pb–0.5 at. % Fe and Yb–0.5 at. % Fe vapor-quenched films: Location and magnetization of the Fe impurities

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(Received 12 November 1998)

By combining vapor quenching technique at low temperature and *in situ* Mössbauer spectroscopy, we have studied the site occupation and magnetism of Fe in Pb and Yb films, as well as their stability with temperature. $^{57}$Fe Mössbauer spectra at 7 K, for as-prepared Pb–0.5 at. % Fe and Yb–0.5 at. % Fe films, have two paramagnetic components: a singlet, which is attributed to Fe at interstitial sites, and a doublet, assumed to be due to Fe atoms at ''substitutional'' sites, with at least one Fe near neighbor. Mössbauer measurements under an external magnetic field have been performed in as-prepared films and revealed that Fe atoms, associated with the doublet, have a magnetic moment in *both* systems, while those Fe atoms located at interstitial sites have magnetic moments only in the case of Yb films. These results confirm theoretical calculations predicting magnetic moments for interstitial Fe atoms in divalent hosts (Yb) and negligible probability of magnetic Fe atoms in tetravalent hosts (Pb). [S0163-1829(99)07425-1]

## I. INTRODUCTION

Studies of the electronic structure and magnetism of impurities in metals have proved to be fruitful to enhance our knowledge of magnetic materials. However, experiments have been limited to thermally stable systems [i.e., those systems formed by elements which have some solubility in equilibrium phase diagram (EPD)] and theoretical interpretations usually involved phenomenological models. On the other hand, the study of dilute systems can help us to understand the interactions between *d* orbitals, for example, from Fe impurities, with conduction electrons in the solid. In such studies, a fundamental question is the formation of a local magnetic moment at the impurity. Theoretical calculations[1] have shown that Fe atoms can have a magnetic moment if they are located at interstitial sites in monovalent or divalent host metals, while for most of the other hosts, the probability of Fe atoms having a magnetic moment at interstitial sites is negligible.

Recently, developments have been made in studies of diluted impurities in metals: theoretical methods,[1] based on first-principles density functional theory, and experimental techniques,[2] like in-beam Mössbauer spectroscopy (IBMS) and in-beam time differential perturbed angular correlation (IBTDPAC). As is well known, these experimental techniques can be applied to any intermetallic system, even without a solubility region in their EPD, but these experiments are very difficult to perform and require in-beam accelerator facilities. The vapor quenching (VQ) technique with cold substrate (He temperature) can also be used to study such systems, since this method may lead to the formation of alloys of immiscible components, due to the fast quenching rate involved.

Our experimental setup allows the preparation of films using the VQ method at low temperatures to study, by *in situ* Mössbauer spectroscopy, the location of the Fe impurity, its diffusion, and related aging effects. The essential information about the magnetism is based on the Mössbauer spectra of the films obtained, *in situ*, under an external magnetic field necessary to avoid spin-lattice relaxation effects that usually happen in the case of diluted Fe atoms in nonmagnetic hosts, such as Pb and Yb.

Iron/lead (Fe/Pb) and iron/ytterbium (Fe/Yb) are two systems known to be immiscible in the entire concentration range in the EPD, even in the liquid state. Studies of the Fe/Pb system have been reported by Sielemann[3] where they analyzed by IBM the Fe impurities implanted in a Pb host. Their results indicated that the Fe atom goes mainly into interstitial sites, and this information was relevant for the discussion of our previous work,[4] where we demonstrate the solubility of Fe in a Pb host, by VQ. This was made by independent thermal coevaporation of both elements deposited onto a substrate kept at low temperature (20 K). Recently, while we performed our work on Fe in an Yb matrix, Kapoor *et al.*[5] reported IBMS and IBDTPAC studies on Fe impurities in an Yb host,[5] and their experimental results show that Fe atoms have a magnetic moment and occupy substitutional sites (60%) and interstitial site (40%).

The aim of this work is to combine the VQ technique and *in situ* Mössbauer spectroscopy, performed with and without an external magnetic field in the temperature range of 7–300 K, to study the Fe impurities in Pb and Yb hosts as well as their magnetic features. In addition, we will show that our experimental conditions can be useful to study the stability of several Fe species and the diffusion process induced by heating.

## II. EXPERIMENT

Pb–0.5 at. % $^{57}$Fe, Yb–0.5 at. % $^{57}$Fe, and Yb–5 at. % $^{57}$Fe films were prepared in a He cryostat by thermal co-

 

evaporation of iron (90% enriched in $^{57}$Fe) and high-purity Pb (99.99%) and Yb (99.99%) metals from two independent resistively heated Ta crucibles. The deposition was performed onto Kapton subsrates kept at 20 K during the evaporation. Before the deposition, the residual pressure in the cryostat was $9\times10^{-9}$ mbar, and during the depositions, it raised to $7\times10^{-8}$ mbar. Crystal oscillators were used to control the deposition rates and the composition of the films, which have a final thickness of the order of 9000 Å, for the films with Fe composition of 0.5 at.% and 2000 Å for that film with 5 at.% of Fe. The details of the evaporation setup have been given elsewhere.[6] This setup is especially suitable for the present study because it allows *in situ* measurements, thus avoiding the oxidation of the Pb and Yb metal films. No x-ray diffraction analysis was performed since the films were easily oxidized, even at the deposition place, at pressures above $10^{-4}$ mbar in the case of Pb films and at ambient pressure in case of Yb films.

The films were analyzed by *in situ* Mössbauer spectroscopy in the transmission geometry, in the temperature range 7–300 K, using 50 mCi $^{57}$Co:*Rh* source moving in sinusoidal mode. The film surface was tilted with an angle of 45° with respect to the $\gamma$-ray direction, a geometry defined by our experimental conditions.[6] The source and absorber were kept at the same temperature during the measurements. The evaporator-cryostat setup has a superconducting magnet, which was used for the measurements with external magnetic fields ($B_{ex}$). In these experiments, the fields are parallel to the $\gamma$-ray direction. The usual time of measurement of each spectrum varied from 20 to 72 h, depending on the broadening induced by the $B_{ex}$.

The low-Fe-concentration Mössbauer spectra of both films with zero external field were analyzed using two components. For the experiments performed with an external field, the Mössbauer spectra were fitted using a random spatial electric field gradient for a fixed external magnetic field, in the case of the component with quadrupole splitting (QS). The center shift (CS) values are given relative to an $\alpha$-Fe absorber at room temperature (RT).

## III. RESULTS AND DISCUSSION

### A. Sites assignment and diffusion effects

The temperature dependence of the Mössbauer spectra for the Pb–0.5 at.% Fe film is shown in Fig. 1. The spectrum at 7 K has two paramagnetic components: a singlet, with CS $=0.53(3)$ mm/s and linewidth ($\Gamma$) of 0.50(2) mm/s, which is the main contribution at this temperature (around 85% of the total area) and a doublet with CS$=0.33(3)$ mm/s and QS $=0.67(3)$ mm/s.

The CS value of the singlet is very close to the one found by Sielemann[3] with IBMS, involving sophisticated preparation and measurement techniques. Thus, since the IBMS method allows the implantation of isolated Fe atoms at interstitial sites in a Pb host, we may claim that our VQ technique is also able to locate Fe atoms at interstitial sites. The other subspectrum (doublet) observed in our experiments has been already discussed in our previous work,[4] being attributed to Fe atoms at substitutional lattice sites. The nonzero electric field gradient was attributed to the presence of Fe or a defect nearby. However, we need to consider also the possibility

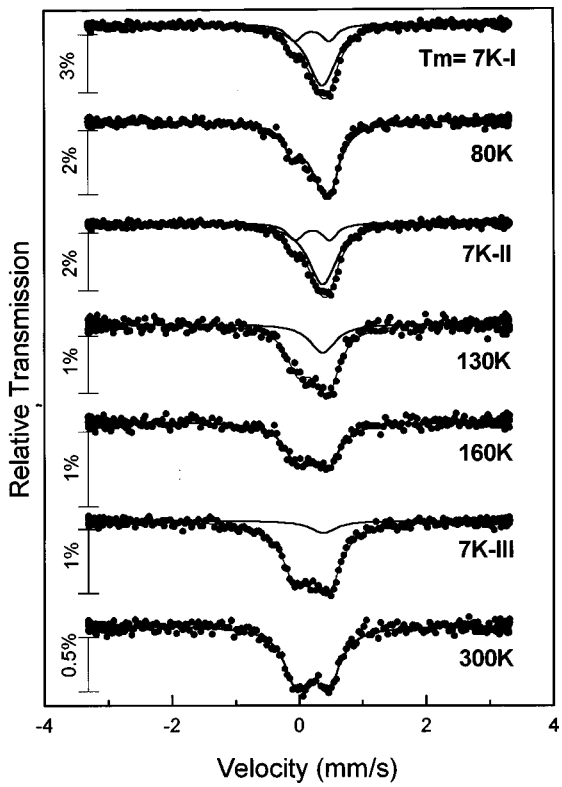


FIG. 1. Temperature dependence of the $^{57}$Fe Mössbauer spectra of the Pb–0.5 at.% $^{57}$Fe film.

that the doublet can be due to small Fe clusters in the Pb host. Most studies are necessary in order to decide among the two above possibilities for the formation of the doublet component.

From the temperature dependence of the Mössbauer spectra (Fig. 1), it is clear that the area of the doublet increases at expense of the singlet as the temperature is raised. The singlet seems to have disappeared at 190 K; however, it can be seen again (with lower intensity) after cooling down the film to 7 K. This behavior can be understood if we consider that Fe atoms in the cubic configuration in a Pb host have a Debye temperature lower than the one corresponding to the doublet. At 300 K, the spectrum displays again only the doublet. Figure 2 shows the behavior of relative area of each subspectrum versus temperature, illustrating the annealing process that occurred in the Pb–0.5 at.% Fe film, as described above.

At this point, we would like to stress that the assignment of a singlet to Fe at interstitial cubic configurations was based on the diffusion process, clearly observed in the temperature-dependent measurements, and on the similarity of its hyperfine parameters with the results of the implantation technique.[3] On the other hand, the assignment of a doublet was based on the temperature variation of the Mössbauer spectra being attributed to substitutional Fe with another Fe atom or a defect located nearby.

In Fig. 3 we show the temperature variation of the $^{57}$Fe Mössbauer spectra of the Yb film with 5 at.% of Fe. The Mössbauer spectrum obtained at 7 K is analyzed with three paramagnetic components: one singlet with CS$=-0.25(4)$ mm/s and $\Gamma=0.30(3)$ mm/s, speaking for a highly symmetric environment, and two doublets: doublet 1 with CS

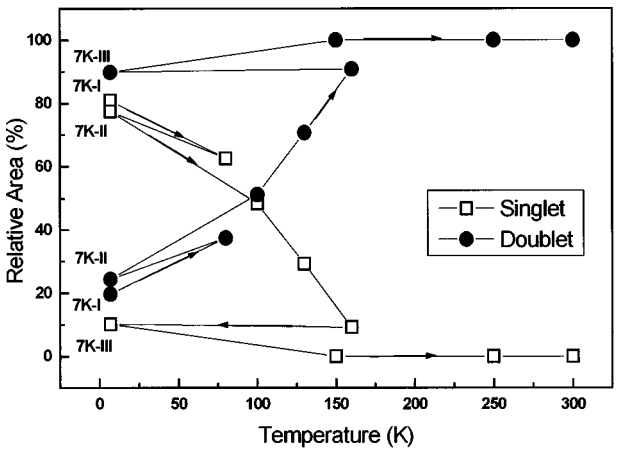


FIG. 2. Temperature variation of the relative area for the paramagnetic components observed in the Mössbauer spectra of the Pb–0.5 at. % Fe film. The arrows indicate the temperature cycles.

$=-0.05(3)$ mm/s and QS$=0.49(2)$ mm/s and doublet 2 with CS$=0.20(6)$ mm/s and QS$=1.0(2)$ m/s. The relative area of doublet 2 at 7 K, for as-prepared films is small (around 10%) compared to the other components. The spectra obtained at higher temperatures indicate that the area of doublet 2 increases mainly at the expense of the singlet, while the relative fraction of doublet 1 apparently remains nearly constant throughout all the temperature range, within our experimental resolution and fitting precision. At 110 K, almost only the doublets 1 and 2 are observed in the spectrum. The singlet

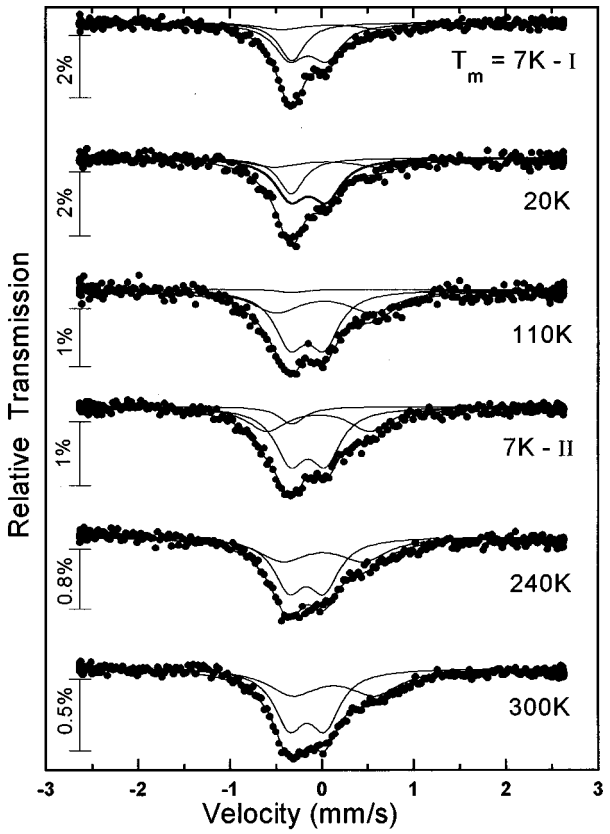


FIG. 3. Temperature dependence of $^{57}$Fe Mössbauer spectra of the Yb–5 at. % $^{57}$Fe film.

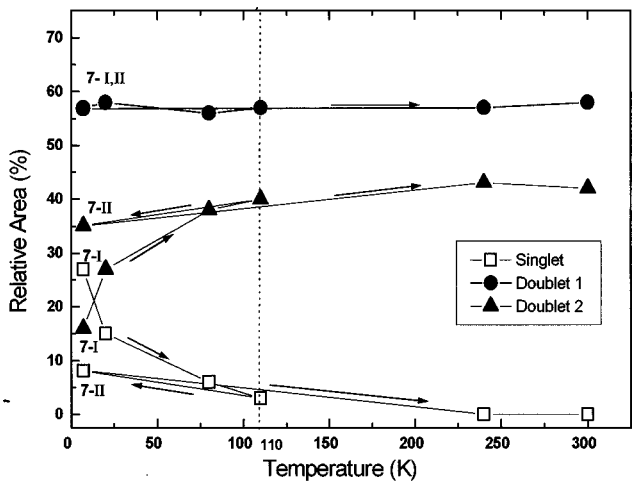


FIG. 4. Temperature variation of the relative area for the paramagnetic components observed in the Mössbauer spectra of the Yb–5 at. % $^{57}$Fe film. The arrows indicate the temperature cycles.

area is partially recovered by cooling down the film to 7 K, and we concluded that the behavior at 110 K is determined by two facts: (a) the Debye temperature of Fe atoms in a cubic configuration in a Yb host is smaller than the two other components (doublets 1 and 2), and (b) there was a partial transformation of the singlet to the doublet. By further raising the temperature to 300 K, the spectrum again displays only the doublets. In Fig. 4, the variation of the relative areas of each component with temperature illustrates the behavior of the Mössbauer spectra mentioned above and gives us a better understanding of the annealing process of Fe in Yb films. This behavior is similar to Fe in Pb films, allowing us to conclude that Fe atoms at interstitial sites, in both systems, have a low Debye temperatures and they diffuse easily, leading to the formation of doublets.

In order to understand the origin of the doublet 2 and to study the magnetic properties of different Fe species in a Yb host, we have prepared another sample with lower Fe concentration (0.5 at. %). The results are displayed in Fig. 5, showing that the spectrum at 7 K has two paramagnetic components, a singlet and a doublet 1; both components have been already found in the previous films with 5 at. % of Fe, while the spectrum at 300 K displays the doublet 1 with about 97% of relative area and a small fraction of the singlet still persists at this temperature. Therefore, the behavior of the Mössbauer spectra with temperature depends on the Fe concentration. For a film with 0.5 at. % Fe, the singlet is transformed into a doublet 1 with increasing temperature, while for a film with 5 at. % Fe the singlet transforms to a doublet 2, and the doublet 1 seems to keep constant relative intensity. This may be an artifact due to the broader linewidth of doublet 2, which disturbs the definition of doublet 1. On the other hand, it is expected that in a film with higher Fe content (5 at. %), the probability of having Fe nearest neighbors is higher and we may correlate doublet 2 with Fe clusters. The formation of such clusters will occur easily for a film with 5 at. % than 0.5 at. % of Fe. This may explain why there is no observable contribution of doublet 2 in the Mössbauer spectra of Yb film with 0.5 at. % of Fe.

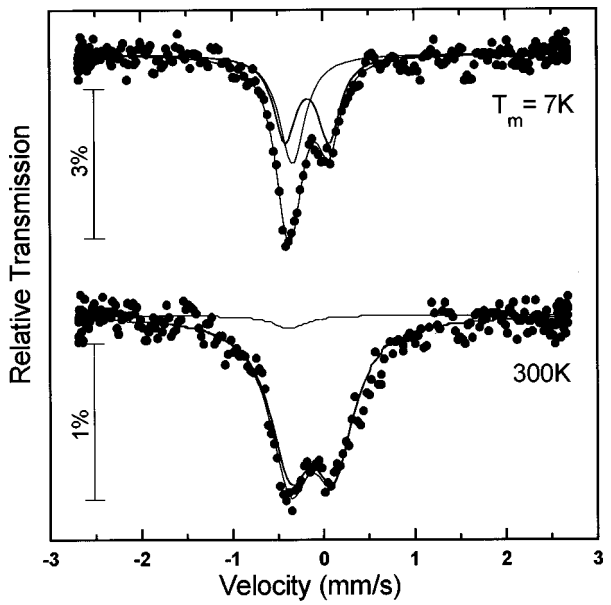


FIG. 5. $^{57}$Fe Mössbauer spectra of the Yb–0.5 at. % $^{57}$Fe film obtained at 7 and 300 K.

To identify the components observed in the Mössbauer spectra of Fe in Yb film, we follow two known ideas: (1) Fe atoms located at interstitial sites undergo a fast diffusion process,[3] and (2) CS values of Fe in metals show a quite good systematic trend for substitutional and for interstitial sites.[3] For an interstitial site, there is strong increase in *s*-electron density and, therefore, a more negative CS can be expected, due to a reduced volume of the Fe Wigner-Seitz cell. Thus the singlet is considered to be due to interstitial Fe atoms and the doublet 1 to Fe at substitutional positions. From the temperature dependence of the Mössbauer spectra of Yb–0.5 at. % Fe, it is possible to attribute the doublet 2 to small Fe clusters with more than one Fe near neighbor, but leading to a nonmagnetic subspectrum, even at low temperatures. Our interpretation, as outlined above, is different from the one recently given by Kapoor *et al.*[5] In their work, Coulomb-excited $^{57}$Fe atoms were recoil implanted into Yb foils, and the Mössbauer emission spectrum looks very similar to ours. However, the Mössbauer spectra have been analyzed in a different way, i.e., with two single lines: one line has the same CS as our singlet, and another line corresponds to the right line of the doublet 1. The fitting procedure adopted here, with one single line and one doublet, is based on the occurrence of the diffusion process and on the shape of the Mössbauer spectra under applied magnetic fields, as will be shown in the next section.

In case of Fe in Pb systems, only the fast diffusion process was used to justify the assignment of Fe to interstitial sites, since the CS of this component does not follow the systematic behavior of metallic hosts. More theoretical calculations must be performed to clarify the discrepancy in the CS behavior of each component for $^{57}$Fe in Pb system.

Finally, we would like to comment on the electric field gradient that appears at the substitutional Fe atoms in our Pb and Yb films. Since both metals have a fcc crystalline structure, a zero electric field gradient would be expected for Fe at substitutional and interstitial sites. However, the doublet in the Pb film and doublet 1 in Yb film are clear evidence of a nonzero electric field gradient. In principle, it can be induced by the presence of one Fe near neighbor in the lattice sites or to a local distortion, which means defects of the lattice induced by our sample preparation method. Therefore, the Fe at substitutional sites formed with our technique have features distinct from the one obtained by implantation, the main reason for that being a higher probability of having two near-neighbor Fe atoms in our case, whose origin comes from the fast diffusion process that occurs for interstitial Fe configurations, even during deposition at low temperatures.

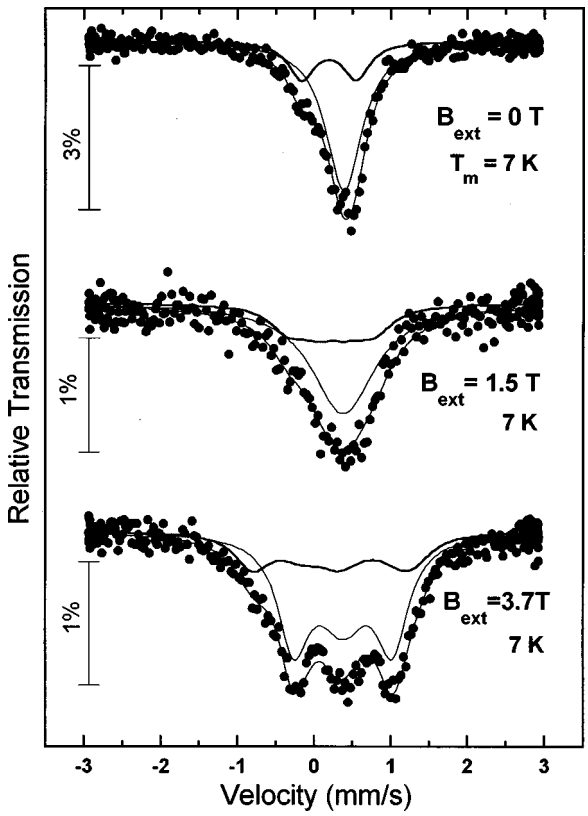


FIG. 6. $^{57}$Fe Mössbauer spectra of the Pb–0.5 at. % $^{57}$Fe film recorded at 7 K without and with external magnetic fields ($B_{ex}$), as indicated in the figure.

### B. Magnetic moment of the Fe species

In order to study the formation of the magnetic moments of different Fe species in both systems, i.e., Fe in Pb and Fe in Yb, we have performed *in situ* Mössbauer measurements at 7 K under external magnetic fields. The $B_{ex}$ has been applied to avoid spin-lattice relaxation, but with the magnitude used in our measurements no saturation condition was achieved.

The spectra at low temperature (7 K) as a function of $B_{ex}$ are shown in Fig. 6 for the Pb film containing 0.5 at. % of Fe. For the experiment performed at 1.5 and 3.7 T, the Mössbauer spectra were fitted considering the two subspectra at zero field, using a pure magnetic interaction for the singlet and a random distribution of the direction of $V_{zz}$ (main component of electric field gradient tensor) relative to the direction of $B_{ex}$ for doublet with the same value for the electric quadrupole interaction parameter ($\Delta E_Q$) taken for the zero-

TABLE I. Hyperfine parameters obtained from the Mössbauer spectra of the Pb–0.5 at.% $^{57}$Fe film for different external magnetic fields values. The center shift (CS) values are relative to $\alpha$-Fe at 300 K.

| Doublet | $B_{ex}=0$ T | $B_{ex}=1.5$ T | $B_{ex}=3.7$ T |
|---|---|---|---|
| CS (mm/s) | 0.33 (3) | 0.33 (6) | 0.33 (3) |
| $\Delta E_Q$ (mm/s) | 0.67 (3) | 0.68 (2) | 0.68 (3) |
| $\Gamma$ (mm/s) | 0.46 (2) | 0.50 (7) | 0.54 (7) |
| $B_{eff}$ (T) | | 1.9 (1) | 5.0 (4) |
| Singlet | $B_{ex}=0$ T | $B_{ex}=1.5$ T | $B_{ex}=3.7$ T |
| CS (mm/s) | 0.53 (3) | 0.52 (3) | 0.53 (3) |
| $\Gamma$ (mm/s) | 0.50 (2) | 0.52 (3) | 0.52 (3) |
| $B_{eff}$(T) | | 1.6 (2) | 3.8(2) |

field case. Table I summarizes the results of the hyperfine parameters obtained from the fitting procedure as described above for Fe in Pb film.

The observed effective magnetic hyperfine field $B_{eff}$ at the Fe nucleus is given by $B_{eff}=B_{hf}+B_{ex}$. From our analysis, we conclude that the Fe species corresponding to the singlet has $B_{eff}$ values close to the applied external fields, which means that the Fe atoms in this cubic configuration in a Pb host do not have a magnetic moment. However, the Fe atoms associated with the quadrupolar component (doublet) display a $B_{eff}$ value larger than the applied field and consequently has its own magnetic moment. The sign of the magnetic hyperfine field ($B_{hf}$) and the magnitude of the Fe moments were not determined, since the saturation of the magnetic moments could not be achieved in our experimental conditions. Therefore, as was predicted by the theory,[3] the interstitial Fe atoms at a tetravalent host, i.e., Pb host, do not have a magnetic moment.

Figure 7 displays the Mössbauer spectra of the Yb film with 0.5 at. % of Fe at 7 K under different external magnetic fields. For the experiment performed at 1.8 and 3.7 T, the Mössbauer spectra were analyzed as in the case of Pb film containing 0.5 at. % of Fe: using a pure magnetic interaction for the singlet and a random distribution of the direction of $V_{zz}$ relative to the direction of $B_{ex}$ for doublet 1. Table II summarizes the results of the hyperfine parameters obtained from the fitting procedure as describe above for Fe in Yb film.

The observed magnetic hyperfine field $B_{eff}$ at Fe nuclei at two sites is also given by $B_{eff}=B_{hf}+B_{ex}$. From our observation that $|B_{eff}|<B_{ex}=1.8$ and 3.7 T at both sites (see Table II), we can conclude that $B_{hf}<0$ for Fe in both sites in Yb film. Part of this result does not agree with Ref. 5: by measuring the spin rotation of Fe implanted in Yb metal, it was shown there that $B_{hf}$ is negative for interstitial Fe sites, but positive for the substitutional one. In order to understand this different magnetic response, we have to conclude that our concept of a ''substitutional'' site and the one mentioned in Ref. 5 are distinct, as is also indicated by the different values of Cs and $\Delta E_Q$.

It is important to emphasize that the values of the magnetic hyperfine field at interstitial Fe sites in Yb film leads us to conclude that Fe atoms have magnetic moments, as predicted by theoretical calculations.[1] The formation of magnetic moments of Fe atoms at interstitial sites is not common, and it happens only in a few hosts.[7]

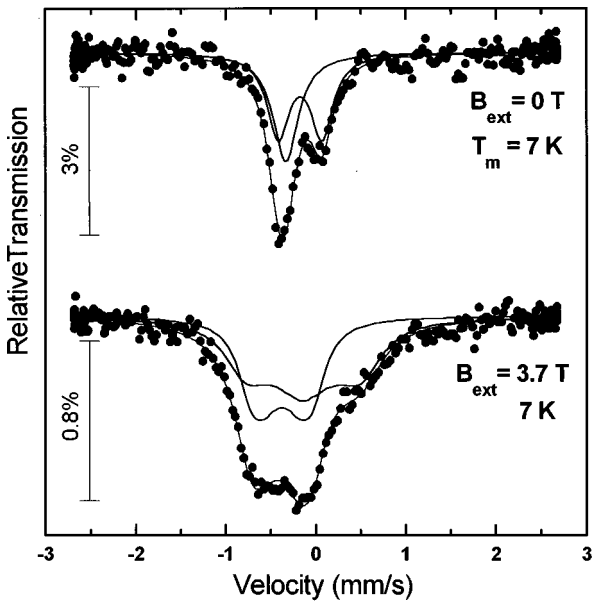


FIG. 7. $^{57}$Fe Mössbauer spectra of the Yb–0.5 at. % $^{57}$Fe film obtained at 7 K, without and with an applied external magnetic fields of 3.7 T.

## IV. CONCLUSION

Comparing our results to those obtained by the implantation technique, it is possible to conclude that interstitial Fe atoms in Pb and Yb hosts have similar electronic configurations independent of the preparation method. Moreover, interstitial Fe atoms in nonequilibrium alloys like Pb and Yb have similar behavior relative to the diffusion process. However, the neighborhood of Fe atoms in substitutional sites depends on the preparation method because by the VQ method a quadrupolar interaction is found which may be attributed to the presence of one near-neighbor Fe atom or a defect around Fe atoms, which was not observed by the implantation method.

From our results, we have demonstrated that the vapor

TABLE II. Hyperfine parameters obtained from the Mössbauer spectra of the Yb–0.5 at.% $^{57}$Fe film for different external magnetic fields values. The center shift (CS) values are relative to $\alpha$-Fe at 300 K.

| Doublet 1 | $B_{ex}=0$ T | $B_{ex}=1.8$ T | $B_{ex}=3.7$ T |
|---|---|---|---|
| CS (mm/s) | −0.05 (3) | −0.04 (3) | −0.03 (2) |
| $\Delta E_Q$ (mm/s) | 0.49 (2) | 0.49 (2) | 0.49 (2) |
| $\Gamma$ (mm/s) | 0.36 (2) | 0.46 (1) | 0.56 (7) |
| $B_{eff}$ (T) | | 1.6 (2) | 2.6 (4) |
| Singlet | $B_{ex}=0$ T | $B_{ex}=1.8$ T | $B_{ex}=3.7$ T |
| CS (mm/s) | −0.25 (4) | −0.27 (3) | −0.26 (3) |
| $\Gamma$ (mm/s) | 0.30 (4) | 0.31 (4) | 0.33 (3) |
| $B_{eff}$ (T) | | 0.8 (2) | 2.2 (2) |

quenching technique can be used to prepare diluted Fe in most metallic hosts, as already demonstrated in our previous work of Fe diluted in rare-earth quenched films.[8]

Moreover, the Mössbauer spectra, for both systems, show that Fe atoms located at interstitial sites have low Debye temperatures compared to those located at substitutional sites.

With measurements under external magnetic fields, it was possible to establish that substitutional Fe in Pb and Yb films obtained by the VQ method have their own magnetic moments. However, as predicted theoretically, Fe in interstitial sites in a divalent Yb host has its own magnetic moment, while in a tetravalent Pb host it does not.

## ACKNOWLEDGMENTS

We thank Dr. Klinger M. B. Alves for reading the manuscript. We also acknowledge financial support from CNPq-MCT Grant No. 9110154/95-30 and FAPERJ.

[1] S. Frota-Pessoa, Hyperfine Interact. **97/98**, 41 (1996).
[2] W. D. Brewer, S. Hauf, D. Jones, S. Frotta-Pessoa, J. Kapoor, Yi Li, A. Metz, and D. Riegel, Phys. Rev. B **51**, 12 595 (1995).
[3] R. Sielemann, Hyperfine Interact. **80**, 1239 (1993).
[4] E. C. Passamani, E. Baggio-Saitovitch, S. K. Xia, and C. Larcia, J. Phys. F **7**, 8437 (1995).
[5] 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-Pessoa, Phys. Rev. Lett. **78**, 1279 (1997).
[6] E. Baggio-Saitovitch, J. Terra, and F. J. Litterst, Phys. Rev. B **39**, 6403 (1989).
[7] D. Riegel and K. D. Gross, Physica B **163**, 678 (1990); D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, Phys. Rev. Lett. **61**, 2129 (1988); D. Riegel, L. Büermann, K. D. Gross, M. Luszik-Bhadra, and S. N. Mishra, *ibid.* **62**, 316 (1989).
[8] E. C. Passamani, E. Baggio-Saitovitch, and H. Micklitz, Phys. Rev. B **55**, 12 382 (1997).