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Iron nano-clusters in ytterbium films: a ^{57}Fe Mössbauer spectroscopic study

C. Rojas-Ayala · W. T. Herrera · I. S. Dinóla · M. Kraken · E. C. Passamani · E. Baggio-Saitovitch · F. J. Litterst

Abstract We have performed a Mössbauer study on iron clusters that are formed in ytterbium films prepared by vapor co-deposition onto kapton substrates kept at room temperature. The film thicknesses were chosen in a range between 2.5 and 2.8 μm. XRD of the films reveals a mixture of fcc- and hcp-like ytterbium. Iron concentrations were between 0.3 and 5 at %. All samples reveal hyperfine spectra attributed to only two types of iron clusters with well defined hyperfine parameters. The clusters are supposed to be formed at boundaries of hcp- and fcc-like grains. In addition there is found a small contribution from monomeric iron. Spectra taken at 4.2 K reveal a complex distribution of magnetic hyperfine fields. The dynamic origin of the spectral shape is supported by susceptibility data revealing spin-freezing at temperatures below ca. 10 K. This proves that the iron clusters have sizes on the order of nm.

Keywords Mössbauer spectroscopy · Iron nano-clusters · Ytterbium films · Vapor deposition · Spin-freezing

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C. Rojas-Ayala (✉) · W. T. Herrera · I. S. Dinóla · E. Baggio-Saitovitch · F. J. Litterst
Centro Brasileiro de Pesquisas Físicas,
Rua Dr. Xavier Sigaud 150, 22290-180, Rio de Janeiro, RJ, Brazil
e-mail: chachi@cbpf.br

C. Rojas-Ayala
Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos,
P.O. Box 14-149, Lima 14, Lima, Peru

M. Kraken · F. J. Litterst
Institut für Physik der Kondensierten Materie, Technische Universität Braunschweig,
38106 Braunschweig, Germany

E. C. Passamani
Departamento de Física, Universidade Federal do Espírito Santo,
29075-910, Vitória, ES, Brazil

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1 Introduction

Dilute magnetic impurities with concentrations ranging from parts-per-million up to parts-per-hundred in non-magnetic metallic matrices have been intensively studied in the past for investigating, firstly, the site occupation of the impurities and its influence on magnetism, and secondly, Kondo effect and competing spin-glassy behavior [1–3]. Based on this previous work, we have started some years ago investigations on the formation of iron nanoclusters in non-magnetic metallic hosts with low solubility among impurity and host elements [4, 5].

Earlier Mössbauer studies on iron in ytterbium [6, 7] had initially been devoted to investigate the preferential site occupation of Fe and its relation to magnetism. Further going investigations deal with the formation of magnetic Fe-clusters by diffusion of Fe atoms [8, 9]. The presence of iron magnetic moments in isolated sites and clusters could be shown. However, Mössbauer spectra are complex [8, 9], showing a superposition of several components, and a satisfying interpretation could not yet be presented. The main aim of the present work is to contribute to a better systematics and to propose some new simple assignments to spectral components for dilute Fe in Yb films prepared by deposition onto substrates kept at room temperature.

2 Experimental details

Iron-doped Yb films were prepared by vapor co-deposition of high purity Fe (95 % enriched in ^{57}Fe) and Yb with nominal compositions between 0.3 and 5.0 at. % of Fe. The sample preparation procedure and the evaporation details have been described previously [5, 9].

Depositions were performed onto Kapton substrates mounted tilted 45^o relative to the metal vapor flux direction. The substrate temperature was kept at 290 K. The base pressure in the deposition chamber was 2×10^{-8} mbar, increasing to 2×10^{-7} mbar during the evaporation. The deposition rate was monitored using piezo-crystals and typical values were 2–7 Å/s for Yb and 0.02 Å/s for Fe. The total film thicknesses were typically 2.5 to 2.8 μm.

Samples were characterized by X-ray diffraction (XRD) and ^{57}Fe transmission Mössbauer spectroscopy. We used a standard type Mössbauer spectrometer with sinusoidal velocity sweep. Low temperature Mössbauer experiments have been performed in a variable-temperature ^{4}He cryostat. The ^{57}Co/Rh source and the Mössbauer absorbers were kept at the same temperatures. X-ray diffraction measurements were performed on a Rigaku Miniflex using Cu -Kα radiation.

3 Results and discussion

From XRD we find that all of our films possess a mixture of fcc- and hcp-like Yb phases with a ratio of fcc:hcp of about 3:2. This result agrees with a recently reported one obtained for an undoped Yb film [10], which also suggests that the fcc-like Yb phase is dominant. We propose that the structure of our films is consisting of fcc-domains surrounded by an interconnecting hcp phase. A detailed consideration of the influence of the mixture of structural phases of the films on the formation of

specific clusters taking into account the very sensitive Martensitic transition between hcp and fcc Yb [11, 12] will be given elsewhere. The XRD Bragg peaks of both crystalline ytterbium phases of our iron-doped films reveal significant broadening, indicating the formation of small grains. Using the Scherrer relation, we estimate mean grain sizes of the fcc-like Yb of about 25 nm; this is very close to previously obtained values for Fe/Yb films [9]. From the relative intensities of Bragg peaks there are indications for varying degrees of texture of the ytterbium films.

RT Mössbauer absorption spectra of Yb films with different iron concentrations are shown in Fig. 1. All samples reveal paramagnetic behavior. These spectra were fitted using a superposition of three components: one single absorption line labeled S and two doublets (D1, D2). For all films studied, these components have very similar hyperfine parameters. From our fits there are no indications for an asymmetry in areas between the two lines of each doublet. This means, there is no preferred orientation of the electric field gradient, despite the XRD data of the films reveal some texture. From this we conclude that the doublet spectra D1 and D2 should be attributed to aggregates or clusters that are not affected by the texture of the ytterbium matrix.

The variation of the relative spectral areas for the three components is presented in Fig. 2. Whereas the relative spectral area for the D1-component slightly increases with iron concentration, the area for the D2-component slightly decreases. The area for the S-component remains constant within experimental error.

The introduction of the singlet (S) in the fitting procedure is based on results obtained earlier from films deposited at low substrate temperatures [8]. For these films this component dominates the Mössbauer spectra. Its spectral fraction is reduced when increasing the temperature of the films and instead there is found an increase of the area of doublet D1 [8]. But even after annealing the films up to 300 K some spectral contribution of the single line S remains present. We attribute S to iron monomers in interstitial sites of fcc-Yb [8, 9]. The negative isomer shift (see Fig. 3b) indicates that the electron density is high in comparison to metallic iron, which can be understood to result from a charge transfer from ytterbium host atoms. Since Yb, being a rare-earth element, is highly electropositive and iron is highly electronegative, the latter tends to acquire electrons from the ytterbium atoms. This behavior is in good agreement with earlier work [6, 7].

The isomer shift of the D1-component is higher than the isomer shift of the monomers (S), indicating different surroundings with higher number of iron neighbors. However, its low value of quadrupole splitting (see Fig. 3a) may suggest an almost cubic arrangement. We attribute D1 to iron clusters formed upon Fe atomic diffusion during the deposition process (respectively during annealing after low temperature deposition due to diffusion of monomers) at grain boundaries of the fcc-like Yb phase, where the growth of clusters is supposed to be favorable.

The doublet D2 has a bigger value of quadrupole splitting (see Fig. 3a), which indicates a surrounding with lower symmetry. We attribute D2 to very small iron aggregates (dimers, trimers, etc) formed mainly at hcp-like grain boundaries.

4.2 K Mössbauer spectra of the iron doped ytterbium films prepared at RT are plotted in Fig. 4. While for low Fe-concentrations (< 3.5 at. %), superparamagnetic contributions dominate the spectra even at 4.2 K, the spectra for high Fe-contents display a broad magnetic component. The complex spectral shapes found for all concentrations are supposed to be influenced by fluctuations of the magnetic cluster moments on a time scale comparable to nuclear Larmor precession.

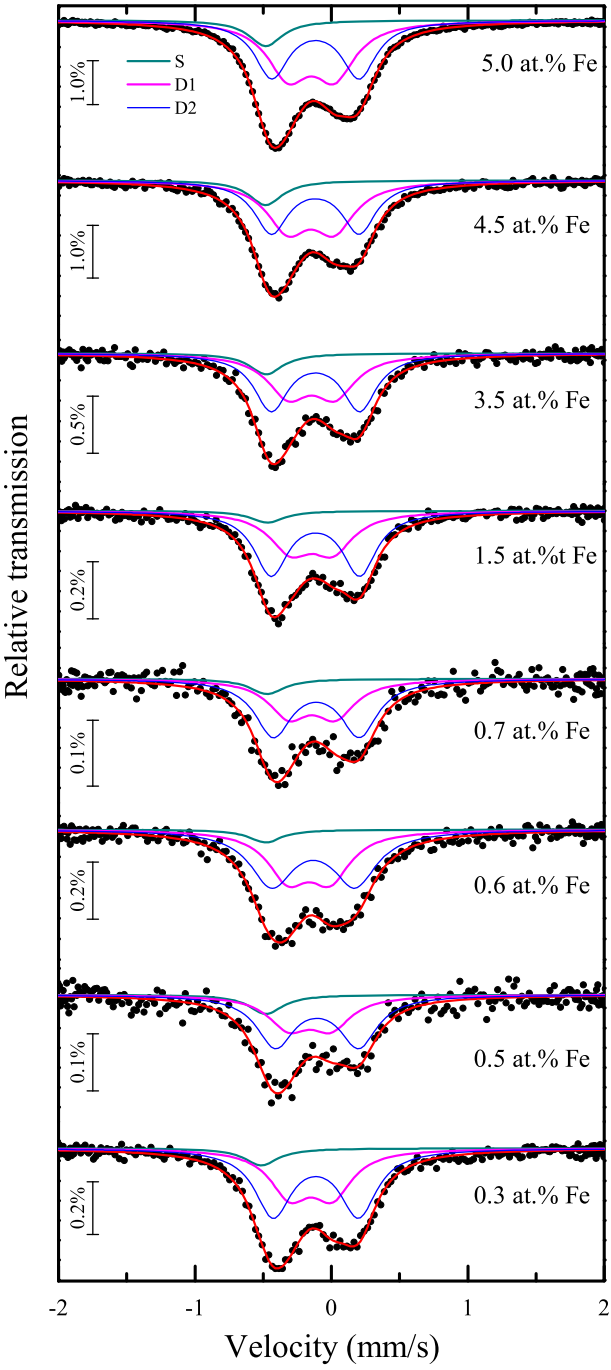

Fig. 1 Room temperature ^{57}Fe Mössbauer absorption spectra of ytterbium films with different iron concentrations

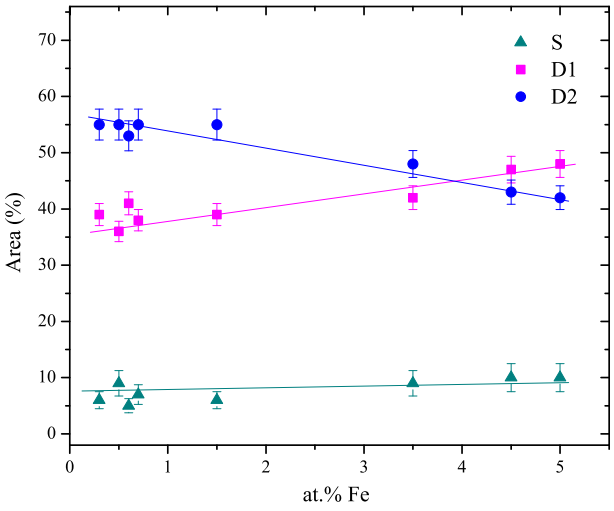

Fig. 2 Variation of relative spectral area of S, D1 and D2 as a function of iron concentration in iron doped ytterbium films deposited at RT

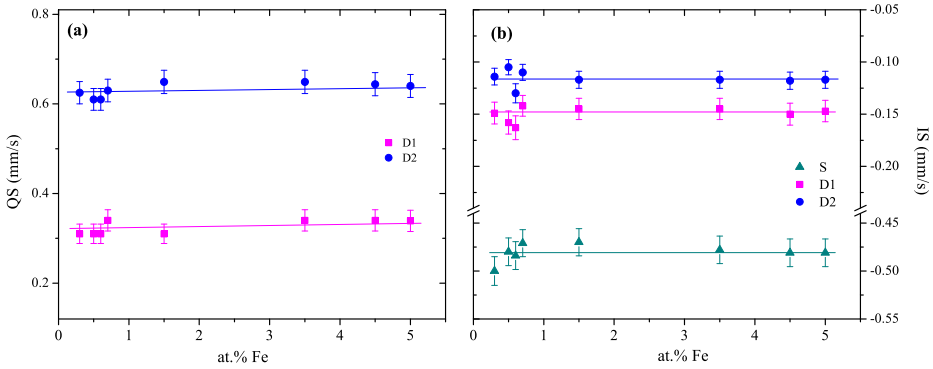

Fig. 3 Hyperfine parameters for iron doped ytterbium films prepared at RT. **a** Quadrupole splitting, QS, and **b** isomer shift, IS. Values of IS are relative to the ^{57}Co/Rh source at RT

We have omitted here a rigorous dynamic fit to the complex spectral shapes. The drawn fit lines in Fig. 4 come from a simplistic static magnetic hyperfine field distribution, which is certainly inadequate for the low iron concentrations and therefore should serve only as a guide to the eye. It should be noted that according to the hyperfine parameters there are no indications for the presence of clusters of metallic iron or iron oxides.

The increased concentration of clusters for samples with 4.5 at. % and 5.0 at. % Fe leads to considerable slowing-down of fluctuations and an increase of magnetic interactions between clusters. As consequence nearly static distributions of magnetic hyperfine fields are found. This freezing of cluster dynamics is in agreement with dc magnetic susceptibility revealing spin-glassy behavior below about 10 K for these Fe concentrations, whereas for lower concentrations there are no indications for spin-freezing down to 4.2 K. From this we conclude that the iron clusters in our samples must have sizes on the order of few nanometers.

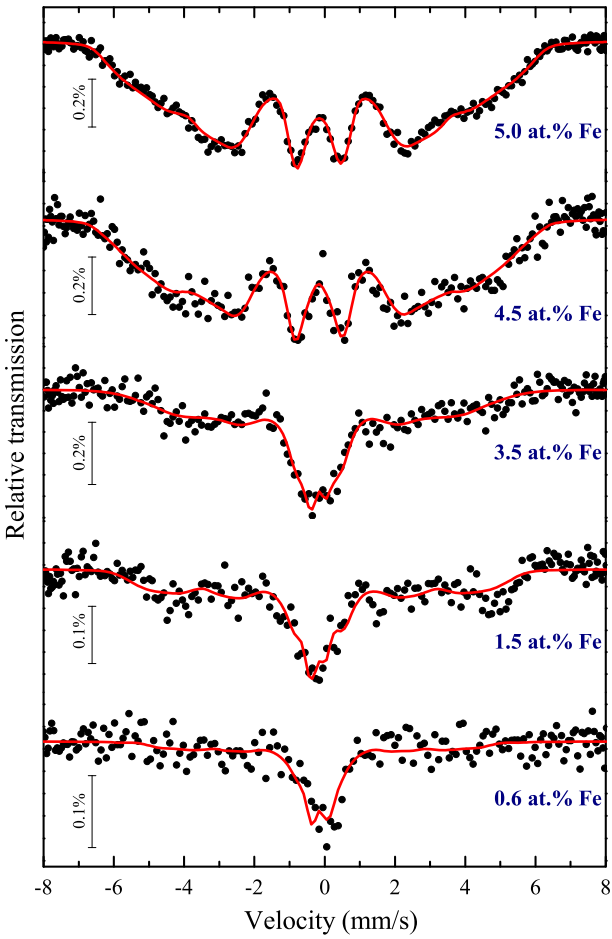

Fig. 4 ^{57}Fe Mössbauer absorption spectra of ytterbium films with different iron concentrations taken at 4.2 K

The superparamagnetic fraction visible in the spectra for lowest iron concentrations is dominated by doublet D2, i.e. the spectral area of doublet D1 is mainly comprised in the broad magnetically split background. The clusters associated with D1 should therefore be bigger than those associated with D2.

A detailed interpretation of these spectra, taking into account dynamic magnetic fluctuations including cluster-cluster interactions and a comparison of the dynamical behavior with that derived from susceptibility data, will be presented elsewhere.

4 Summary

We have shown by Mössbauer spectroscopy that two types of iron clusters are formed in ytterbium films prepared by vapor co-deposition onto kapton substrates kept at room temperature. The films possess a mixture of fcc- and hcp-like ytterbium. In contrast to earlier studies [8, 9], which have shown that the formation of iron clusters is strongly dependent on film thickness, preparation and annealing conditions, we took

special care of nearly identical conditions of preparation. The film thicknesses were chosen in a narrow range between 2.5 and 2.8 μm. Iron concentrations were between 0.3 and 5 at %. All samples reveal hyperfine spectra attributed to only two types of iron clusters with well defined hyperfine parameters. The clusters are supposed to be formed at boundaries of hcp- and fcc-like grains. In addition there is found a small contribution from monomeric iron.

Spectra taken at 4.2 K reveal a complex distribution of magnetic hyperfine fields. The spectral shape is clearly influenced both by inhomogeneous broadening and relaxation effects. The dynamic origin of the spectral shape is supported by susceptibility data revealing spin-freezing at temperatures below ca. 10 K. This also proves that the iron clusters possess sizes on the order of nm.

Additional experiments, as systematic magnetization measurements and Mössbauer spectroscopy under external magnetic field, will be presented elsewhere.

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