# Magnetic anisotropy in (110) epitaxial DyFe₂ Laves phase

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Laves phase $DyFe_2$ thin films have been epitaxially grown with [110] as the growth direction. Reflection high-energy electron diffraction patterns confirm the quality of epitaxy and x-ray diffraction measurements evidence that the films are strained compared to the bulk alloy. Mössbauer spectroscopy spectra and Kerr rotation measurements show that the easy magnetization direction varies from [100] at 4.2 K to around [$\bar{2}$41] at 300 K. This is consequently different from the bulk-compound easy axis ($\langle 100 \rangle$ from 4.2 K to room temperature). This effect is new and can be qualitatively understood if we consider the influence of the strains induced by epitaxy on the various energy terms which govern the easy magnetization direction. [S0163-1829(96)51248-8]

## I. INTRODUCTION

The epitaxial strains are known to be an important parameter which may modify the magnetic behavior of thin films compared to the bulk elements.[1] This is particularly crucial for systems containing rare earth (RE) compounds whose anisotropy and magnetoelastic coefficients are usually large (Dy, Tb, Er, . . . ). For example, the epitaxy of RE superlattices or RE thin films leads to the stabilization of the modulated magnetic phase (to low temperature in the Dy/Y system[2,3]) or, at the opposite, to a drastic enhancement of the Curie temperature (from 84 K in bulk dysprosium up to 160 K in the Dy/Lu system).[4] However, no change in the easy magnetization axis has been mentioned in epitaxial pure rare earths, certainly because the anisotropy energy is one order of magnitude larger than the magnetoelastic energy.

With the progress of the epitaxial growth techniques and the recent elaboration of rare-earth–transition-metal (RE-TM) compounds,[5,6] it is now possible to study the effect of the epitaxy on a large variety of systems. Among them, the RE-TM₂ Laves phases constitute a very exciting family because they exhibit giant magnetostrictive properties at room temperature, resulting from the combination of the large anisotropy of rare earth and the strong exchange coupling of transition metals.[7]

In this paper, we show the influence of the epitaxial strains on the easy direction of magnetization in an epitaxially grown 300 Å (110) $DyFe_2$ thin film. The various energy terms which govern the easy magnetization axis in cubic RE-Fe₂ Laves phases are presented in Sec. II. Section III deals with the elaboration and the structural characterization of the epitaxial films. The magnetic anisotropy is investigated by Mössbauer spectroscopy between 4.2 and 300 K (Sec. IV) and by Kerr rotation measurements at room temperature (Sec. V). The results are discussed in the last part.

## II. EASY MAGNETIZATION AXIS IN BULK COMPOUNDS

In the bulk cubic RE-Fe₂ Laves phase compounds (structure $C_{15}$), the easy magnetization axis results from the minimization of the sum of the anisotropy, magnetoelastic, and elastic energies. The anisotropy energy at the lowest order is given by

$$E_{mc} = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2),$$

where $\alpha_i$ are the cosines of the magnetization direction and $K_1$ and $K_2$ are the anisotropy coefficients. The magnetoelastic energy can be expanded as

$$E_{me} = b_0(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) + b_1(\alpha_1^2\varepsilon_{11} + \alpha_2^2\varepsilon_{22} + \alpha_3^2\varepsilon_{33})$$
$$+ b_2(\alpha_1\alpha_2\varepsilon_{12} + \alpha_2\alpha_3\varepsilon_{23} + \alpha_3\alpha_1\varepsilon_{13}),$$

where $\varepsilon_{ij}$ is the strain tensor and $b_0$, $b_1$, and $b_2$ are the magnetoelastic coefficients. $b_1$ and $b_2$ are related to the more usual magnetostrictive coefficients $\lambda_{111}$ and $\lambda_{100}$ by the relations $b_2 = -3\lambda_{111}C_{44}$ and $b_1 = -\frac{3}{2}\lambda_{100}(C_{11} - C_{12})$, where $C_{11}$, $C_{12}$, and $C_{44}$ are the cubic elastic constants. Let us first underline that, in $DyFe_2$, $b_2$ is two orders of magnitude larger than $b_1$. Moreover, $b_2$ is multiplied by a factor 2 when the temperature is lowered from 300 to 4.2 K, whereas $K_1$ is multiplied by a factor 10 in the same temperature range.[7] Furthermore, the elastic energy is

$$E_{el} = \frac{1}{2}C_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + C_{12}(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{22}\varepsilon_{33} + \varepsilon_{33}\varepsilon_{11})$$
$$+ \frac{1}{2}C_{44}(\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2).$$

In the bulk Laves phase compounds and without any external stress, the direction of magnetization is mainly related to the signs and values of both $K_1$ and $K_2$ anisotropy coefficients; this direction depends consequently on the nature of the rare earth atom involved in the compound.[8,9] In the bulk $DyFe_2$ compound,[7] where $K_1$ is positive and $K_2$ negative with $|K_2|/K_1 < 9$, the anisotropy coefficients lead to the $\langle 100 \rangle$ easy magnetization direction, at 4.2 K as well as at 300 K.

The situation is different when the sample is submitted to an external stress, which can occur when a thin film is grown epitaxially on a substrate. If the substrate induces strains in the film, the induced magnetoelastic energy can become large and make the direction of magnetization change.
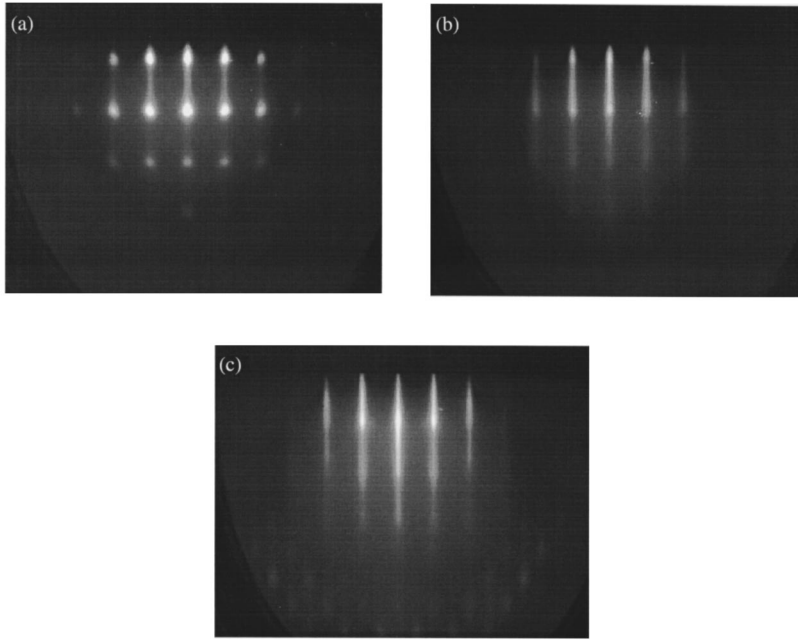
FIG. 1. RHEED patterns obtained during the deposition of (110) $DyFe_2$ on the surface rectangular lattice at 500 °C for different thicknesses: (a) 50 Å, (b) 250 Å, (c) 1000 Å.

## III. PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE SAMPLES

As reported in a previous paper,[10] the samples are prepared by molecular-beam epitaxy in a chamber whose base pressure is typically $4 \times 10^{-11}$ Torr. The substrate is a $(11\bar{2}0)$ sapphire that, prior to evaporation, is outgassed at 800 °C for several hours. Following the process proposed by Kwo, Hong, and Nakahara,[11] the substrate is first covered at 700 °C by a 500-Å niobium buffer. Then a thin layer of iron (15 Å) is deposited at 500 °C. The reflection high-energy electron diffraction (RHEED) pattern is first diffuse, then streaks, characteristic of a rectangular lattice, appear. These lines correspond neither to the bcc iron lattice nor to the bcc niobium one. The parameters of the rectangular mesh (r.m.) at 500 °C are $a_{r.m.} = 7.0 \pm 0.1$ Å and $b_{r.m.} = 4.8 \pm 0.1$ Å.

The epitaxial relationships between the rectangular lattice and niobium are

$$a_{r.m.} \text{ direction} \parallel [001] \text{ Nb and } b_{r.m.} \text{ direction} \parallel [1\bar{1}0]\text{Nb}.$$

This structure is similar to the one already observed on (100) Cu (Ref. 12) and could correspond to the (110) plane of distorted fcc iron. However, at this high temperature, iron and niobium probably interdiffuse and the observed rectangular mesh would then correspond to a Nb-Fe surface alloy.

The $DyFe_2$ is finally grown on the rectangular surface at 500 °C. Cubic $DyFe_2$ is oriented as niobium, and presents the same epitaxial relationships with the rectangular lattice:

$$[001] \text{ DyFe}_2 \parallel a_{r.m.} \text{ direction}$$

and

$$[1\bar{1}0] \text{ DyFe}_2 \parallel b_{r.m.} \text{ direction.}$$

The epitaxy is favored by the match between the parameters of the Laves phase compound and those of the rectangular surface. In the [001] direction the parameter of (110) $DyFe_2$ at 500 °C is $a_{DyFe_2} \approx 7.3$ Å $\approx a_{r.m.}$, and along the $[1\bar{1}0]$ direction the parameter is $a_{DyFe_2}\sqrt{2} \approx 10.3$ Å $\approx 2b_{r.m.}$.

At the early stage of the deposition of the (110) $DyFe_2$ compound, the RHEED patterns exhibit well-defined points showing that the growth mode is tridimensional [Fig. 1(a) for a thickness of 50 Å]. Then the points progressively turn into spotty lines and finally to straight lines typical of a rather flat layer [Figs. 1(b) and 1(c)]. For a thickness $t = 300$ Å, and because of the high deposition temperature, the layer is not yet continuous, but composed of large islands, as it was observed by scanning electron microscopy (SEM). As mentioned above, the RHEED patterns exhibit lines because these islands appear to be flat. Let us also underline that the SEM observations reveal a continuous layer for a 1000-Å-thick film.

The parameters along the growth direction of (100) $DyFe_2$ samples were measured *ex situ* by x-ray diffraction. The specular reflection on the (220) planes of a 300-Å $DyFe_2$ film gives a parameter of 7.29 Å instead of 7.324 Å in the bulk. This lower value indicates the occurrence of a negative $\varepsilon_{12}$ strain in the sample.

## IV. MÖSSBAUER SPECTROSCOPY

The direction of the magnetization was determined by Mössbauer spectroscopy in backscattering mode from 4.2 K to room temperature.

### A. Generalities

On the first hand, Mössbauer spectra depend on the direction of magnetization. In RE-Fe$_2$ compounds, all the Fe sites are chemically equivalent with the same number and the same relative configuration of the neighbors. However, the neighborhoods of the four iron atoms forming a tetrahedra in the Laves phase compounds are oriented in different ways along the crystalline axis of the sample, so that the electric-field gradients acting on the four sites are along the four $\langle 111 \rangle$ equivalent directions.[13] As the direction of the magnetization is the same on the four sites (the coupling between iron atoms is ferromagnetic), the $\theta_i$ angle between the mag-

netization and the local electric-field axis is *a priori* different on the four sites. As a consequence, the quadrupolar effects and the dipolar hyperfine fields are different for the four iron nuclei. For a RE-Fe$_2$ compound, the expected Mössbauer spectrum is then the superposition of four sextuplets whose hyperfine parameters are related to the angular factor $f(\theta_i)$:[14]

$$f(\theta_i) = \frac{3\cos^2\theta_i - 1}{2} \quad (i = 1,4).$$

When the magnetization is along one of the highest symmetry axes, some angular factors are equal and some sextuplets coincide. In particular, when the magnetization is along ⟨100⟩, the four angular factors $f(\theta_i)$ are equal to 0 and the resulting spectrum exhibits one single sextuplet. When the magnetization is along ⟨111⟩, the spectrum is the superposition of two typical components which appear in the ratio 3:1. When the magnetization is along ⟨110⟩, the spectrum is the superposition of two components which appear in the 1:1 ratio. When the magnetization is not along one of the highest symmetry direction, the spectrum is more complex.

On the other hand, the Mössbauer spectroscopy brings information on the orientation of the magnetization in respect to the direction of the incident $\gamma$ beam, which is perpendicular to the plane of the sample. Indeed, the intensities of the six lines of the sextuplet are in the ratio

$$3:X:1:1:X:3 \quad \text{with} \quad X = 4 \times \frac{1 - \langle\cos^2\zeta\rangle}{1 + \langle\cos^2\zeta\rangle}.$$

$\langle\cos^2\zeta\rangle$ is the average of the square of the cosine of the angle $\zeta$ between the magnetization direction and the incident $\gamma$ beam, i.e., the perpendicular to the sample (which in our system is the [110] direction). In particular, $X = 0$ if the magnetization is perpendicular to the sample and $X = 4$ if the magnetization is in the plane of the sample.

## B. Experimental results

In order to get a reasonable counting rate, 300-Å-thick DyFe$_2$ samples were prepared with $^{57}$Fe isotope enriched iron. Measurements were performed at room temperature with a proportional gas flow (He–5% CH$_4$). At lower temperatures, reflection spectra were collected in a homemade cryostat equipped with a circular microchannel plate provided with a central hole.[15]

The Mössbauer spectra collected at 4.2 K and at room temperature for a 300 Å (110) DyFe$_2$ epitaxial film are pictured in Fig. 2. This figure shows clearly an evolution from a simple sextuplet at 4.2 K to a more complex spectrum at room temperature.

The spectrum collected at 4.2 K (Fig. 2) exhibits one unique component, which means that the magnetization is along the ⟨100⟩ directions. The relative intensity of the second and fifth peaks $X = 2.4$ leads to an average $\zeta$ angle of 60° which does not correspond to a ⟨100⟩ direction. If the easy magnetization direction was [001], the magnetization would be in the plane of the sample and $X_{[001]} = 4$; an easy magnetization direction along [100] and [010], which make an angle of 45° with [110], would lead to $X_{[100]} = X_{[010]} = 1.33$. As the experimental value is close to $X = 0.4X_{[001]}$
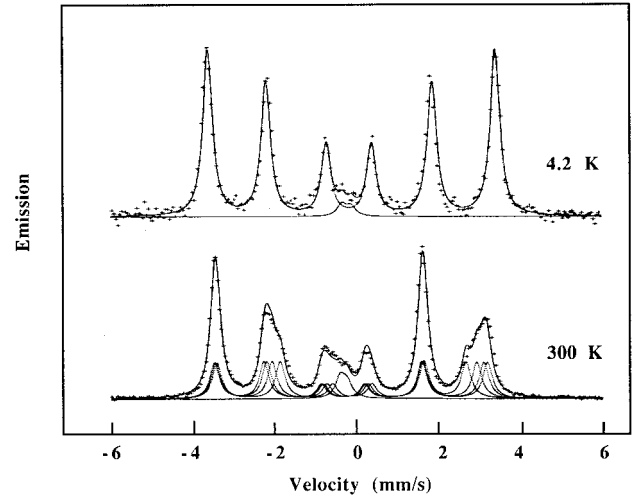


FIG. 2. Mössbauer spectra collected at 4.2 K and at 300 K for a 300-Å-thick (110) DyFe$_2$ epitaxial film.

$+ 0.3X_{[100]} + 0.3X_{[010]}$ and as the spectrum is clearly ⟨100⟩ type, we conclude that the magnetization is in randomly oriented domains (with a slight preference for the in-plane direction). This could be due to the island shape of the film where the demagnetization field does not act as in a continuous film.

At room temperature (Fig. 2), the spectrum is clearly no longer of the ⟨100⟩ type. The easy magnetization direction is not a high-symmetry direction and four sextuplet components are necessary to fit the spectrum. Assuming that the magnetization is along one crystallographic direction, we obtained the best fit for the magnetization along ⟨124⟩, which corresponds to 24 directions in a cubic structure. From the rather high value of $X = 3.1$, it is obvious that the magnetic moments are along the ⟨124⟩ directions close to the plane of the sample, which means that four nonequivalent possibilities still exist: [$\bar{1}$42], [$\bar{2}$41], [$\bar{1}$24], and [124], all simultaneously, or one or two in particular.

A 1000-Å-thick nonenriched DyFe$_2$ film was also studied at room temperature. The Mössbauer spectrum collected with the gas counter showed a result similar to the thinner film.

## V. KERR ROTATION AT ROOM TEMPERATURE

The Kerr rotation angles were measured at room temperature in the longitudinal geometry in the −6-kOe, +6-kOe field range. Different measurements performed with the magnetic field applied along the high-symmetry directions in the plane of the sample ([001], [$\bar{1}$11], and [$\bar{1}$10]) are shown in Fig. 3. It is clear that the magnetic loop collected with the field along the [$\bar{1}$10] and [$\bar{1}$11] directions are the most square. The loop collected with the field along the [001] direction is rather flat and typical of a hard magnetization axis. According to the simple theory of anisotropy in thin films, it would indicate that the easy axis is far from [001] and is closer to the [$\bar{1}$10] direction, where the magnitude of the Kerr rotation is the highest. The direction consistent with Mössbauer spectroscopy would be [$\bar{2}$41]. The measurements performed on a 100-Å-thick film were again very close.
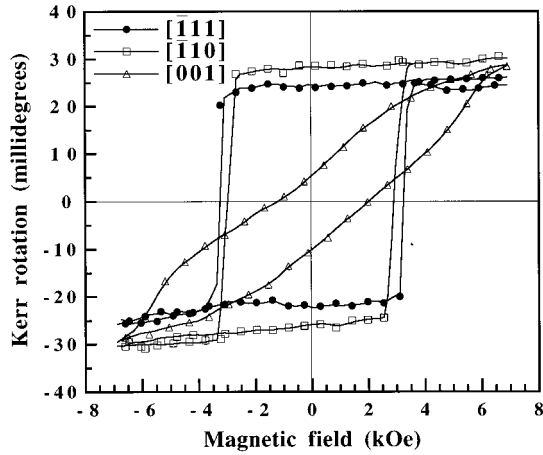
FIG. 3. Kerr rotation measurements performed at 300 K with the magnetic field applied in different directions in the plane of a 300-Å-thick (110) $DyFe_2$ epitaxial film: (filled circles, $[\bar{1}11]$; open squares, $[\bar{1}10]$; triangles, $[001]$).

## VI. INTERPRETATION AND DISCUSSION

The main result of this study is that a 300-Å (110) $DyFe_2$ epitaxial film does not exhibit, like the bulk compound, a $\langle 100 \rangle$ easy magnetization axis at room temperature. The direction $\langle 100 \rangle$ is the easy axis in the film at the low temperature. However, the magnetization in the film departs from this crystallographic direction when the temperature increases to reach a direction which is not a high-symmetry one but which is closer to $\langle 110 \rangle$ directions. In addition it is not close to any $\langle 110 \rangle$ direction but to $[\bar{1}10]$, which is close to the plane of the sample, perpendicular to $[001]$.

Such an effect can be qualitatively explained if we con-sider the energy terms which depend on the cosines $\alpha_i$ in the total energy of a Laves phase film:

$$E = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) + b_2(\alpha_1\alpha_2\varepsilon_{12}).$$

The $b_1$ coefficient has been neglected with respect to $b_2$, and the strains $\varepsilon_{23}$ and $\varepsilon_{31}$ are equal to 0 if, as it could be ex-pected, homogeneous strains occur in the (110) plane of the film. The reduction of the distance between (110) atomic planes, observed by x-ray diffraction, leads to a negative $\varepsilon_{12}$ strain.

In the $DyFe_2$ epitaxial thin film, where $K_1$ is positive and $|K_2|/K_1 < 9$, the first two terms of the previous expression tend to put the magnetization in $\langle 100 \rangle$ directions. $b_2$ and $\varepsilon_{12}$ being negative, the third term tends to put the magnetization along the $[\bar{1}10]$ direction. At low temperature, the ratio $K_1/b_2$ is certainly large enough to maintain the magnetiza-tion in the $\langle 100 \rangle$ directions. When the temperature increases, $K_1$ decreases more rapidly than $b_2$ and the ratio $K_1/b_2$ be-comes smaller: this explains why the magnetization leaves $\langle 100 \rangle$ directions and shifts to the $[\bar{1}10]$ direction in (110) $DyFe_2$ epitaxial films.

In summary, we have demonstrated that the epitaxy modi-fies the easy magnetization axis of thin films of Laves phase compounds. To the best of our knowledge, such an effect has never been observed before. This modification can be quali-tatively understood if we consider the influence of the epi-taxial strains on the energy terms involved in the determina-tion of the easy magnetization axis. This study is currently being extended in two directions: (i) the deposition of other RE-$Fe_2$ compounds which exhibit different anisotropy and magnetoelastic coefficients, and thus present different bulk-easy magnetization axis and (ii) the deposition of RE-$Fe_2$ compounds on another buffer in order to change the induced epitaxial strains.

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