# Magnetic anisotropy and hyperfine interactions in $CeFe_2$ , $GdFe_2$ , and $LuFe_2$

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Mössbauer-effect measurements on <sup>57</sup>Fe have been carried out on the cubic Laves compounds CeFe<sub>2</sub>, GdFe<sub>2</sub>, and LuFe<sub>2</sub> between 80 and 300 K. The analysis of the Mössbauer spectra allowed the determination of the easy axes of magnetization  $\vec{n}$  in these compounds. In CeFe<sub>2</sub>,  $\vec{n}$  is parallel to the [100] direction up to 150 K; it then becomes of type [*uuw*] with an angle of inclination with respect to the [100]axis of 20°. Just below the Curie temperature at 230 K, this angle increases to 30°. In GdFe<sub>2</sub>,  $\vec{n}$  is parallel to the [100] direction at 80 and 300 K. In LuFe<sub>2</sub>,  $\vec{n}$  is of [*uuw*] type at 80 and 300 K. In terms of the phenomenological treatment of the magnetic anisotropy, the presence of an [*uuw*] type of easy axis of magnetization indicates that the bulk magnetic-anisotropy constant  $K_3$  is of the same order of magnitude as  $K_1$  and  $K_2$ . The hyperfine parameters of the three compounds are reported and discussed.

#### INTRODUCTION

Mössbauer-effect measurements on the 14.4keV transition of <sup>57</sup>Fe have been successfully used in order to determine magnetic-anisotropy properties of binary  $(RFe_2)^1$  and ternary  $(R_x^1R_{1-x}^2Fe_2)^{2,3}$ cubic rare-earth (R)-iron Laves compounds. In these compounds the number and type of inequivalent iron sites depends on the direction of the easy axis of magnetization with respect to the cubiccell axes. The easy axis of magnetization, its temperature and composition dependence (in ternary compounds) was deduced from the analysis of the Mössbauer spectra. The observed magnetic-anisotropy properties of the heavy rare-earth (R = Tb,Dy, Ho, Er, and Tm) Laves compounds were in good agreement with the predictions of the singleion model. For this group of compounds, the major part of the magnetic anisotropy is due to the interaction of the rare-earth ion with the crystalline field. Other minor sources of magnetic anisotropy are those arising from the magnetic anisotropy of the iron sublattice and from the possible anisotropy of the exchange interactions. Besides the above-mentioned Laves phases, several other isostructural RFe<sub>2</sub> compounds, i.e., SmFe<sub>2</sub>, CeFe<sub>2</sub>, LuFe<sub>2</sub>, and also YFe<sub>2</sub> exist. The singleion model either cannot be applied to these compounds or, if applied, breaks down. In SmFe<sub>2</sub> Mössbauer-effect studies revealed a peculiar behavior with a spin reorientation taking place over a wide temperature interval.<sup>4,5</sup> The presence of the spin reorientation and several other features present in SmFe<sub>2</sub>, cannot be accounted for by a simple single-ion model and are inconsistent with the results deduced from the study of the heavy rare-earth-iron Laves compounds.

 $CeFe_2$  has been subject to several magnetic and Mössbauer-effect studies. Wertheim and Wer-

nick's<sup>6</sup> sample probably contained foreign phases. Their reported Curie temperature, 878 K, has not been corroborated by later studies. Magnetometric measurements by Farrel and Wallace<sup>7</sup> and by Buschow and van Wieringen<sup>8</sup> showed that the Curie temperature of CeFe<sub>2</sub> was 235 and 230 K, respectively. Buschow and van Wieringen also carried out some Mössbauer-effect studies on CeFe<sub>2</sub> but did not draw any conclusions concerning its magnetic anisotropy. Bowden *et al.*<sup>1</sup> reported a complex Mössbauer spectrum, while according to Guimaraes, <sup>9</sup> CeFe<sub>2</sub> has an [100] easy axis of magnetization.

The rare-earth ion in  $GdFe_2$  is in an S state: magnetic anisotropy will therefore not be due to its interaction with the crystal field but to the secondary sources of magnetic anisotropy, that have been previously mentioned. Bowden *et al.*<sup>1</sup> reported a complex Mössbauer spectrum which could not be interpreted in terms of a well-defined axis of magnetization parallel to one of the cubic axes of symmetry.

Only the iron ions carry magnetic moments in  $YFe_2$  and  $LuFe_2$ . Mössbauer spectra of  $YFe_2$  indicate that [111] is the easy axis of magnetization. This conclusion was verified by hyperfine-field studies of  $R_xY_{1-x}Fe_2$  compounds.<sup>10</sup> In  $LuFe_2$  Guimaraes<sup>9</sup> reported an [110] easy axis of magnetization; the experimental spectra upon which this conclusion is based are however not unambiguous.

It thus appears that the magnetic anisotropy of the  $RFe_2$  compounds, which have their easy axis of magnetization determined by factors, other than those due to interactions of the rare-earth ion with the crystal field, cannot be given a consistent explanation. The purpose of the present work was to carry out a detailed Mössbauer-effect study of this class of compounds in order to gain

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	<i>T</i> (K)	CeFe <sub>2</sub>	GdFe <sub>2</sub>	$LuFe_2$
Lattice parameters (Å)	300	$\textbf{7.3010} \pm \textbf{5}$	$\textbf{7.3875} \pm \textbf{5}$	$\textbf{7.2330} \pm \textbf{5}$
Isomer shift (mm/sec)	$\begin{cases} 80\\ 300 \end{cases}$	$\begin{array}{c} -\ 0.\ 19 \pm \ 0.\ 02 \\ -\ 0.\ 27 \pm \ 0.\ 02 \end{array}$	$\begin{array}{c} -\ 0.16 \pm \ 0.02 \\ -\ 0.31 \pm \ 0.02 \end{array}$	$\begin{array}{c} -\ 0.14 \pm \ 0.02 \\ -\ 0.30 \pm \ 0.02 \end{array}$
Quadrupole constant $\frac{1}{4}  aq  Q  (mm/sec)$	${80 \\ 300}$	$\begin{array}{c} -\ 0.32 \pm \ 0.02 \\ -\ 0.31 \pm \ 0.02 \end{array}$	$\begin{array}{c} -\ 0.\ 27 \pm \ 0.\ 02 \\ -\ 0.\ 26 \pm \ 0.\ 02 \end{array}$	$\begin{array}{c} - \ 0.31 \pm \ 0.02 \\ - \ 0.27 \pm \ 0.02 \end{array}$
Magnetic hyperfine field (kG)	{80 300	156 ± 1	$\begin{array}{c} 225.6 \pm 1 \\ 216.8 \pm 1 \end{array}$	$\begin{array}{c} 214.6 \pm 1 \\ 184.7 \pm 1 \end{array}$

TABLE I. Lattice parameters and hyperfine constants of CeFe<sub>2</sub>, CdFe<sub>2</sub>, and LuFe<sub>2</sub>.

more insight into their magnetic-anisotropy behavior. Special attention was given to phase identification in the samples, since it seemed that some of the previously obtained spurious results could be attributed to faulty sample preparation.

### **EXPERIMENTAL DETAILS**

The Laves compounds were prepared by arc melting 99.9%-pure rare-earth metals with 99.99% iron under a purified-argon atmosphere. In all instances the relative amount of the rare-earth metals was in excess of the stoichiometric composition by (5-15)%. This was found necessary in order to (i) compensate for the loss of the rareearth metals during melting as a result of their relatively high vapor pressure and (ii) ensure that the final rare-earth content was higher than that corresponding to the  $RFe_2$  composition. In all rare-earth-iron binary systems, the Laves phases are the intermetallic compounds with the highest rare-earth content. Since the solubility of iron in the rare-earth metals is negligible, RFe<sub>2</sub> was the only iron-containing phase present in the samples. The arc-melted buttons were wrapped in tantalum foils and vacuum annealed in sealed quartz capsules. The  $CeFe_2$  sample was annealed at 500  $^{\circ}C$ for three weeks: the GdFe<sub>2</sub> and LuFe<sub>2</sub> samples were annealed at 900 °C for 1 week.

Debye-Scherrer diffraction photographs were taken from powder samples obtained by crushing the annealed buttons under alcohol. The lattice parameters were determined using the Nelson-Riley extrapolation method. The results (Table I) for CeFe<sub>2</sub> and GdFe<sub>2</sub> are in good agreement with the previously published lattice parameters of these compounds. In the case of LuFe<sub>2</sub> there is a slight discrepancy between the measured lattice parameter and the only previously reported value of Kripyakevich *et al.*<sup>11</sup> (7.217 Å). All samples were examined metallographically, phases other than  $RFe_2$ , which amounted to less than 5%, were identified by electron microprobe analysis, as being primary rare-earth metals.

The possibility of the presence of a range of composition over which the  $RFe_2$  compounds exist,

was looked for in the Gd-Fe system. Lattice parameter and electron microprobe analysis of twophased samples of compositions bracketing that corresponding to GdFe<sub>2</sub>, showed it to be a line compound. Similar conclusions concerning CeFe<sub>2</sub> were reached by Buschow and van Wieringen.<sup>8</sup>

A constant-acceleration Mössbauer spectrometer was used with a nitrogen-flow cryostat. The temperature was stabilized within 0.2 K, but the estimated accuracy in its determination is 1 K. A 15mC: Pd: <sup>57</sup>Co source was employed. The spectrometer was periodically calibrated with an enriched  $Fe_2O_3$  absorber.

## FITTING PROCEDURE OF THE MÖSSBAUER SPECTRA

The interpretation of the Mössbauer spectra depends to a large extent of the fitting procedure employed. This fitting method will therefore be discussed in some details.

The number of magnetically inequivalent iron sites in the rare-earth-iron RFe<sub>2</sub> Laves compounds depends on the direction of the magnetization n, with respect to the cubic-cell axes. The axes of local symmetry at the iron sites are parallel to the  $4\langle 111 \rangle$  directions. These sites are magnetically equivalent or inequivalent, depending on whether the angles between  $\vec{n}$  and the axes of local symmetry are equal or not. Thus when  $\vec{n}$  is parallel to the [100] direction, all sites are equivalent; when  $\vec{n}$  is parallel to the [110] or [111] direction, there are two inequivalent iron sites with population ratios 2:2 and 3:1, respectively. In the more general case, with  $\vec{n}$  contained within the (110) plane but not parallel to a major axis of symmetry that is of direction type [uuw], there are three inequivalent iron sites with population ratio 2:1:1. Finally with n pointing in an arbitrary direction, the four iron sites may all become inequivalent.

The hyperfine interactions differ at the inequivalent iron sites for two reasons: (i) The total hyperfine splitting at the nuclei depends on the angle between the effective hyperfine magnetic field and the axis of the quadrupole interaction, which is parallel to the axis of local symmetry, i.e., the  $\langle 111 \rangle$ directions. (ii) The contribution of the magnetic



FIG. 1. Calculated magnetic dipolar contributions to inequivalent iron sites in  $CeFe_2$  as function of  $\cos \Theta$ .  $\Theta$  is the angle between  $\overline{n}$  the direction of magnetization and the [100] axis. The direction of magnetization  $\overline{n}$  is assumed to be of type [*uuw*], i.e., contained in the (110) plane. The three curves *a*, *b*, and *c* correspond to dipolar contributions at sites with relative population 2:1:1.

dipolar fields also depends on the same angle. This dipolar contribution  $\vec{D}$ , can be expressed in the form<sup>1</sup>

$$\vec{\mathbf{D}}(\vec{\mathbf{r}}_i) = (1/a_0^3) \left[ \mu^{\mathbf{F} \bullet \mathbf{S}^{\mathbf{F} \bullet}}(\vec{\mathbf{r}}_1) + \mu^{\mathbf{R} \mathbf{S}^{\mathbf{R}}}(\vec{\mathbf{r}}_i) \right],$$

where  $a_0$  is the lattice parameter,  $\mu^{F\bullet}$  and  $\mu^R$  are the magnitudes of the magnetic moments, and  $\vec{S}^{Fe}$ and  $\vec{S}^{R}$  are lattice summations over the iron and rare-earth sublattice, respectively. The lattice summations depend on the crystal structure, the lattice site  $\vec{r}_i$ , and the directions of the individual moments. A detailed study of the dipolar contributions to the hyperfine field has been carried out in  $R_x Y_{1-x} Fe_2$  (R = Tb, Er)<sup>10</sup> and  $Sm Fe_2^5$  compounds. The results showed that the experimentally observed differences between the hyperfine fields at the inequivalent iron sites were proportional, rather than equal, to the calculated differences, assuming dipolar contributions. In the heavy rare-earth-iron Laves compounds the proportionality factor  $\alpha$  was found to be  $1 < \alpha < 2$ . This proportionality factor is assumed to be due to polarization effects induced by the dipolar field. The values of the calculated dipolar fields, in CeFe2, at the three inequivalent iron sites, when  $\vec{n}$  is contained within the (110) plane, as function of the angle  $\Theta$  between  $\vec{n}$  and the [100] direction, are shown in Fig. 1. In the course of the calculation Ce was assumed to be diamagnetic, the value of  $\mu^{F*}$  was  $1.19\mu_B$ , and  $a_0$ = 7.301 Å.

In order to fit the various experimental Mössbauer spectra obtained, a least-squares-fit computer program, that took account of the abovementioned points, was used. Thus the spectra were assumed to be a superposition of one, two, or three six-line Mössbauer patterns depending on the direction assumed for  $\vec{n}$ . All inequivalent iron sites were assumed to possess the same isomer shift and quadrupole interaction constant  $\frac{1}{4}eqQ$ , and to differ in the value of the magnetic hyperfinefield constant  $g_0\mu_N \vec{H}_i$ . When three inequivalent sites were assumed to be present ( $\vec{n}$  of type [uuw]), the relative values of  $H_i$  (i=1, 2, 3) were constrained to follow the dependence of the dipolar fields on  $\Theta$  as calculated theoretically (Fig. 1).

Thus if the magnetic dipolar contribution at site *i* is given by  $f_i(\Theta)$  (Fig. 1), the magnetic hyperfine interaction at this site can be expressed by

$$g_0 \mu_N H_i = g_0 \mu_N H_{av} + \alpha f_i(\Theta), \quad i = 1, 2, 3$$

where  $H_{\rm av}$ , the average magnetic hyperfine field at the inequivalent iron sites, and  $\alpha$ , the proportionality factor, constitute the two free parameters connected with the magnetic hyperfine interaction. As  $\mu^{\rm Fe}$  was assumed constant in all calculations in Fig. 1,  $\alpha$  contains its temperature dependence.

The Hamiltonian for each site was calculated taking into account the angle between the axis of local symmetry and  $\vec{n}$  the direction of magnetization, assuming implicitly that the effective magnetic hyperfine field was parallel to  $\vec{n}$ . The program diagonalized the Hamiltonian in order to calculate the absorption-line positions and intensities, given by proper sums of products of the eigenvectors of the excited and ground states with the appropriate Clebsch-Gordan coefficients. All absorption lines were assumed to possess a Lorentzian shape and as an additional free parameter, the same width at half-maximum.

Usual statistical criteria and in particular the weighted sum of the squares of the residuals<sup>12</sup> were employed in order to evaluate and compare the goodness of fit resulting from the use of different initial assumptions.

#### **RESULTS AND DISCUSSION**

#### CeFe<sub>2</sub>

A cursory, preliminary study of the temperature dependence of the Mössbauer spectra of  $CeFe_2$ revealed the presence of features which could not be given a simple explanation. Up to about 150 K, the Mössbauer spectra were easily interpretable; the simple six-line pattern with the 3:2:1 intensity ratio, indicated the presence of one single iron site which corresponds to an [100] easy axis of magnetization [Fig. 2(a)]. Above 230 K, the Curie temperature, the observed absorption doublet is characteristic of an iron ion in an electric field



FIG. 2. Mössbauer spectra of CeFe<sub>2</sub>: a at 150 K, b at 231 K. Spectrum a is a simple six-line pattern corresponding to an [100] axis of magnetization.

gradient [Fig. 2(b)]. Between 150 and 230 K this simple picture broke down. In this temperature range, in addition to the decreasing magnetic hyperfine fields with increasing temperature, the Mössbauer patterns lost the appearance characteristic of the presence of one iron site. The clue to the interpretation of the complex Mössbauer spectra in this temperature interval, originated in a previous study<sup>5</sup> of the spin reorientation of  $SmFe_2$  from the [110] to the [111] easy axis of magnetization. In that case, the spin reorientation takes place over a wide temperature interval in which the axis of magnetization is of type [uuw], that is departs from the major axes of symmetry of the cubic system and rotates continuously within the  $(1\overline{1}0)$  plane. The presence of an [uuw] type of easy axis of magnetization gives rise, as previously mentioned, to three inequivalent iron sites with a 2:1:1 population ratio, in the C15 (MgCu<sub>2</sub>) structure.

By analogy with the SmFe<sub>2</sub> case, trials were made to fit the CeFe<sub>2</sub> Mössbauer spectra in the 150-230-K temperature interval, assuming that  $\vec{n}$ was of [*uuw*] type. The angle  $\Theta$  (actually cos $\Theta$ ) between the direction of  $\vec{n}$  and the [100] axis was left as a free parameter. These trials were successful as can be seen in Fig. 3. The full line through the experimental points represents the least-squares fit using the above described procedure. In several instances the best fit that was obtained, assuming an [100] easy axis of magnetization, is also shown (dashed lines) in Fig. 3. The improved fit based on the assumption that  $\vec{n}$  ceased to be parallel to the [100] direction and was of type [*uuw*] is convincingly illustrated in the spectrum taken at 220 K (Fig. 3).

The angle of inclination  $\Theta$ , between  $\overline{n}$  and the [110] direction, as obtained from the least-squares computer fit, is plotted as function of temperature in Fig. 4. The values of  $\Theta$  stayed within the range  $18^{\circ} \le \Theta \le 30^{\circ}$ . The errors accompanying these results are relatively large. This is due to two reasons: (i) In this range a small variation of  $\cos\Theta$  corresponds to a large change in  $\Theta$ ; (ii) the dependence of the spectra on the angle arose mainly through the quadrupole interactions which are relatively smooth temperature dependence is obtained with



FIG. 3. Mössbauer spectra of  $CeFe_2$ . All spectra were analyzed assuming an (uuw) type of axis of magnetization (full line through the experimental points). The three low-temperature spectra were also analyzed assuming an [100] type of direction of magnetization (dashed line).



FIG. 4. Temperature dependence of the angle of inclination  $\Theta$  between the direction of the [uuw] type of axis of magnetization and the [100] axis, in CeFe<sub>2</sub>.

a tendency for  $\Theta$  to increase just below the Curie temperature to about 30°. Noteworthy is the discontinuous jump of  $\theta$  at about 150 K from 0° to 20°.

The temperature dependence of the isomer shift of <sup>57</sup>Fe in CeFe<sub>2</sub>, with respect to a Pd: Co source is shown in Fig. 5. Previous studies of other  $RFe_2$  compounds<sup>3</sup> have indicated a similar increasingly negative isomer shift with increasing temperature. The quadrupole constant  $\frac{1}{4}eqQ = -0.32$  $\pm 0.02$  mm/sec at 80 K. This value is similar to that observed in the other heavy rare-earth  $RFe_2$ compounds and shows no significant change with temperature.

The magnetic hyperfine fields at the iron nucleus at 80 K was  $H = 156 \pm 2$  kG. This value is much lower than the values observed in the other  $RFe_2$ compounds which extend from 209 kG for YFe<sub>2</sub> to 225 kG for GdFe<sub>2</sub>. The lower value of the magnetic hyperfine field in CeFe<sub>2</sub> is associated with the reduced magnetic moment of the iron ions  $(1.2\mu_B)$  as



FIG. 5. Isomer shift of  ${}^{57}$ Fe in CeFe<sub>2</sub> with respect to a Pd : Co source as function of temperature.



FIG. 6. Reduced magnetic hyperfine field  $H/H_{\rm av}$  (0) in CeFe<sub>2</sub> as function of the reduced temperature T/Tc, Tc =230K. In the 150-230-K termpeture range,  $H_{\rm av}$  was calculated by taking weighted average of  $H_i$  on the three inequivalent sites.

compared to 1.7 $\mu_B$  in other RFe<sub>2</sub> compounds) and with the lower magnetic-ordering temperature (230 K as compared to 500-700 K in other RFe<sub>2</sub> compounds). These decreased values have been interpreted as being due to the transfer of the single 4*f* electron of Ce to the conduction band, increasing the occupancy of the Fe 3*d* band. The validity of this interpretation is corroborated by the reduced lattice parameter of CeFe<sub>2</sub>, characteristic of tetravalent Ce compounds. Thus CeFe<sub>2</sub> is a simple ferromagnet, its magnetization behavior<sup>7,8</sup> as well as its reduced magnetic hyperfine field follow approximately the molecular-field theory with a  $J = \frac{1}{2}$  Brillouin function (Fig. 6).

The transfer of the 4f electron of Ce into the conduction band reduces the number of vacant 3dstates of the iron ions. A similar situation arises in the isostructural CeCo2 and CeNi2 compounds, which are strong Pauli paramagnets, whereas the the other  $RCo_2$  and  $RNi_2$  compounds with trivalent rare-earth atoms are magnetically ordered at low temperatures. The filling of the vacant 3d states of the iron ions in CeFe2 affects also its magneticanisotropy behavior, which, in this case, is due to Fe-Fe interactions only. The isostructural compound YFe<sub>2</sub> is also a ferromagnet with only a slightly larger lattice parameter than that of  $CeFe_2$ . The easy axis of magnetization of YFe2 is in the [111] direction whereas that of  $CeFe_2$  is in the [100] direction up to 150 K. The departure of the axis of magnetization above 150 K from the [100] axis of symmetry is a puzzling feature, which has already been observed in connection with the spin reorientation in SmFe<sub>2</sub>.<sup>5</sup> In that case it was suggested that



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FIG. 7. Limits of regions with defferent easy axes of magnetization in the  $K_1/K_3$  plane, where  $K_1$ ,  $K_2$ , and  $K_3$  are the bulk anisotropy constants. For values of  $K_1/K_3$  and  $K_2/K_3$  lying within the ABC triangular region, the easy axis of magnetization is of type [uuw] with  $0^\circ < \Theta < 90^\circ$ . The heavy arrow represents the possible projection of the motion of  $E_a$  (anisotropy energy) of CeFe<sub>2</sub> in the  $K_1, K_2, K_3$  space on the plane of the diagram, as function of temperature.

the deviation of  $\vec{n}$  from a direction parallel to a major axis of symmetry, might be due to the loss of cubic symmetry. This possibility appeared plausible in the case of SmFe<sub>2</sub>. The magnetostrictive effects in this compound are among the highest ever measured<sup>13</sup> and might lead to a non-negligible departure from the cubic symmetry. Strong magnetostrictive effects are connected to the high magnetic anisotropy, which in SmFe<sub>2</sub> results from the large crystal-field interaction with the Sm<sup>\*3</sup> ion. This would certainly not be the case for diamagnetic  $Ce^{+4}$ . The magnetic anisotropy in  $CeFe_2$ is exclusively due to that of the iron sublattice and, contrary to the magnetic anisotropy induced by crystal-field interactions with rare-earth ions, cannot be given, at the present stage of knowledge, a treatment based on first principles. It can be given however, a phenomenological treatment to show that the presence of an axis of magnetization nonparallel to major axes of cubic symmetry need not be excluded in the case of cubic materials.

In the phenomenological treatment, the magnetic anisotropy energy  $E_a$  is expressed in terms of a series expansion of the direction cosines  $\alpha_i$  of the direction of the axis of magnetization  $\vec{n}$  relative to the cubic crystal axes:

$$E_a = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) .$$

In general only the  $K_1$  and  $K_2$  terms (up to the sixth power of the direction cosines) are retained in the series expansion. In that case it can be easily shown that the only extrema for  $E_a$  are those corresponding to values of  $\alpha_i$  associated with one of the major axes of symmetry in the cubic system, namely, the [100], [110], or [111] directions. Inclusion in the series expansion of the eighth-power term,  $K_3(\alpha_1^4 \alpha_2^4 + \alpha_2^4 \alpha_3^4 + \alpha_3^4 \alpha_1^4)$  changes this situation. Differentiation of  $E_a$  with respect to the angles  $(\cos^{-1}\alpha_i)$  reveals the existence of  $E_a$  minima for directions of magnetization of a general type [uuw]for certain values of the bulk magnetic-anisotropy constants  $K_1$ ,  $K_2$ , and  $K_3$ . The results are summarized in the diagram plotted in the  $K_1/K_3$ ,  $K_2/K_3$ plane shown in Fig. 7. All points situated in the region ABC correspond to minima of  $E_a$  for axes of magnetization of type [uuw], with values of  $\Theta$ lying between the 0° ([110] direction) and 54.4° ([111] direction). Some lines of constant  $\Theta$ , within the ABC region have also been plotted.

The values of the bulk magnetic-anisotropy constants  $K_1$ ,  $K_2$ , and  $K_3$  are usually strongly temperture dependent. The value of  $E_a$  represented by the position of a point in the diagram of Fig. 7, executes as function of temperature a complicated motion. In the course of this motion,  $E_a$  of CeFe<sub>2</sub> crosses at about 150 K the boundary between the [100] and the *ABC* regions. The experimentally observed discontinuous jump of  $\Theta$  from 0° to 20°, suggests that the projection of the motion of  $E_a$  in the  $K_1$ ,  $K_2$ ,  $K_3$  space on the  $K_1/K_3$ ,  $K_2/K_3$  plane can be described by the heavy arrow (Fig. 7). A more extended discussion of the details of Fig. 7 and of its implications will be presented elsewhere.

# $GdFe_2$

The Mössbauer spectra of the 14.4-keV transition of  $^{57}$ Fe, taken at 80 and 300 K showed the presence of a single iron site, corresponding to an [100] easy axis of magnetization (see Fig. 8). These results differ from those obtained by Bowden *et al.*<sup>1</sup> who reported a complex Mössbauer spectrum. The careful check of the single-phase nature of the sample used in this study strengthens the validity of the present conclusions.

The isomer shift and the quadrupole constant of  ${}^{57}$ Fe, obtained by the best-fit program, are similar to those in the other heavy rare-earth-iron Laves compounds. The magnetic hyperfine field at 80 K, H = 225.6 kG is the largest measured in any RFe<sub>2</sub> compound at this temperature. According to Guimaraes and Bunbury<sup>14</sup> and Dariel *et al.*<sup>10</sup> the hyperfine field at the iron nucleus in the RFe<sub>2</sub> compounds can be expressed in the form

$$H = H_0 + a(g - 1)J$$

where  $H_0$  is a constant through the whole  $RFe_2$ series (with the exception of  $CeFe_2$ ), reflects the Fe-Fe interaction and arises through the core polarization of the iron electrons. The second term reflects the influence of the moment of the rareearth neighbors on the iron nucleus and arises



FIG. 8. Mössbauer spectrum of  $GdFe_2$  at 80 K. The fitted solid line corresponds to the assumption of an [100] easy axis of magnetization.

probably through conduction-electron polarization. Conduction-electron polarization causes a hyperfine field at the iron nucleus directly, through contact interaction, and indirectly, through core polarization. From the study of  $\text{Er}_x Y_{1-x} \text{Fe}_2$  and  $\text{Th}_x Y_{1-x} \text{Fe}_2$  compounds, Dariel *et al.*<sup>10</sup> deduced the values of  $H_0 = 210$  kG and a = 4.3 kG per unit spin (*a* is a constant, its value reported in Ref. 10 is in error). Using these values for Gd with (g - 1)J= 3.5, one obtains H = 225 kG, in excellent agreement with the measured value.

Since  $Gd^{*3}$  is an S-state ion, it does not interact with the crystal field. Thus, the magnetic anisotropy in  $GdFe_2$  must be attributed to the magnetic anisotropy of the iron sublattice and/or to the Gd-Fe and Gd-Gd exchange interactions. It is an accepted view<sup>15,16</sup> that the Gd-Gd exchange interaction is an indirect one via conduction electrons and that it is appreciably weaker than either the Fe-Gd or the Fe-Fe interactions. Mössbauer studies indicate, directly in  $YFe_2$ ,<sup>1</sup> and indirectly in heavy rare-earth ternary  $R_x^1R_{1-x}^2Fe_2$  compounds,<sup>3</sup> that the anisotropy of the Fe-Fe interactions is of an [111] type. By elimination therefore, on the basis of the present results obtained in GdFe<sub>2</sub>, one is led to conclude that the anisotropy of the Gd-Fe exchange interaction is of an [100] type and large enough to outweigh the effects of the Fe-Fe interaction.

### LuFe<sub>2</sub>

The Mössbauer spectra of  $LuFe_2$  at 80 and 300 K are complex and could not be analyzed assuming  $\vec{n}$  to be parallel to one of the major axes of symmetry. A significant improvement of the statistical criteria, used to evaluate the goodness of fit, was achieved when trials were made in a manner similar to that employed in the analysis of CeFe<sub>2</sub> above



FIG. 9. Mössbauer spectrum of  $LuFe_2$  at 300 K. The fitted solid line corresponds to the assumption of a [uuw] type axis of magnetization. The value of the angle  $\Theta$  deduced from the fitting analysis is 20°.

150 K. In Fig. 9 the solid line represents the results of the analysis assuming  $\mathbf{n}$  to be of type [uuw]. In this case the computer fit yielded a value of  $\Theta$ , used as a free parameter, of 20°. This method of analysis did not increase the number of free parameters above the number used in an [110] or [111] type of analysis. Thus the appreciable reduction by a factor of 2, of the value of the weighted squared residuals, represents a real improvement of the fitting procedure and not merely a statistical artifact.

The magnetic hyperfine field at the iron nucleus in LuFe<sub>2</sub> at 80 K is 214.6 kG. This value is higher than the expected one on the basis of the  $H = H_0$ + a(g-1)J expression. Both Y and Lu have J = 0, and therefore one expects in both cases  $H = H_0$ . The difference in the value for YFe<sub>2</sub> (H = 209 kG) and the value found in LuFe<sub>2</sub> may perhaps be attributed to interatomic distance effects. The lattice parameter of LuFe<sub>2</sub> is, as a result of the lanthanide contraction, the smallest of all  $RFe_2$ compounds.

### CONCLUSIONS

This Mössbauer-effect study was successful insofar as it allowed the determination of the magnetic anisotropy behavior of CeFe<sub>2</sub>, GdFe<sub>2</sub>, and to a lesser extent of LuFe<sub>2</sub>. Unlike the case of the heavy

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rare-earth-iron Laves compounds, no systematic explanation can be given to the anisotropy behavior of the presently studied compounds. The microscopic sources of magnetic anisotropy are associated with crystal-field effects of the iron sublattice and, possibly, with the anisotropic exchange interactions in the case of GdFe<sub>2</sub>. The appearance of an [uuw] type axis of easy magnetization indicates that  $K_3$  in the phenomenological power expansion of the magnetocrystalline anisotropy energy, is of the same order of magnitude as the  $K_1$  and  $K_2$  terms. The rare-earth 4f single-ion interaction with the crystal field accounts only for the presence of  $K_1$  and  $K_2$  (fourth- and sixth-power cosine terms).  $K_3$  is therefore due to the anisotropy induced by the transition-metal sublattice. A similar behavior (appreciable  $K_3$  term), has been observed in the course of a careful analysis of the magnetic anisotropy of nickel metal.<sup>17</sup>

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