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Magnetically induced quadrupole interactions and anisotropic hyperfine fields at Fe-sites in RFe₂-compounds

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Résumé. — Les raies Mössbauer du ⁵⁷Fe dans HoFe₂ et DyFe₂ présentent une légère asymétrie dans leurs positions et dans leur largeur. L'asymétrie des largeurs de raies suggère que l'aimantation s'écarte de la direction [100], celle des positions peut provenir soit d'interactions quadrupolaires induites magnétiquement soit d'une composante du champ hyperfin normale à la direction d'aimantation. On a donc analysé les spectres suivant deux approches. Dans la première, on suppose que l'interaction quadrupolaire totale est la somme du terme habituel et d'un terme à symétrie axiale induit magnétiquement. Dans la seconde approche, on suppose un tenseur de couplage hyperfin anisotrope. On estime le signe et la grandeur de l'interaction quadrupolaire aussi bien que la grandeur des composantes du tenseur hyperfin. On discute les différents modèles proposés pour expliquer l'origine des champs hyperfins anisotropes.

Abstract. — ⁵⁷Fe Mössbauer studies of HoFe₂ and DyFe₂ at various temperatures exhibit a small but definite asymmetry in the peak positions as well as in the peak widths. The symmetry in the line widths suggests that the magnetization deviates from [100] direction, whereas the asymmetry in the peak positions can arise either due to the existence of magnetically induced quadrupole interactions or due to the presence of an appreciable component of hyperfine field at right angle to the magnetization direction. The observed spectra have, therefore, been analysed in terms of two different approaches. In the first approach the total quadrupole interaction is assumed to consist of an axially symmetric magnetically induced part in addition to the usual term, whereas in the second approach the hyperfine coupling tensor has been assumed to be anisotropic. The sign and magnitude of quadrupole interaction terms as well as the magnitudes of the components of hyperfine coupling tensor have been estimated. Various approaches used earlier to analyse the magnitudes of anisotropic hyperfine fields have been shown to be functionally similar to our second approach of fitting.

For ⁵⁷Fe nuclear excited state an explicit analytical expression has been derived for an axially symmetric quadrupole splitting in terms of the observed peak positions of the nuclear Zeeman pattern.

1. Introduction. — A large number of ⁵⁷Fe Mössbauer investigations have been reported [1-8] on rare earth cubic Laves phase compounds with a general formula (R'_xR''_{1-x})(M'_yM''_{1-y})₂, where R' and R'' are rare earth elements and M' and M'' represent the 3d-elements, mostly Fe or Co. These investigations are mostly related to the estimation of anisotropic hyperfine interactions and spin orientation as a function of temperature and/or composition. In these compounds, the M-atoms occupy crystallographically equivalent sites of trigonal symmetry ($\bar{3}m$) and their symmetry axes are directed along the four $\langle 111 \rangle$ axes. As a result, there are four different local principal efg axes systems for the Fe-atoms (at the M-sites), with the q_{zz} being along their respective three fold rotation axes. Therefore, for an arbitrary direction of magnetization say $[uvw]$, the

observed Mössbauer spectrum should consist of four nuclear Zeeman patterns characterized by four different values of θ , the angle between the principal efg axis and the hyperfine field direction. For special magnetization direction, however, the number of components may be smaller than four. For example, for the magnetization direction (\bar{M}) along any one of the $\langle 100 \rangle$ directions, only a single well defined nuclear Zeeman pattern is observed because all Fe-atoms are characterized by a single value of θ . Similarly, for \bar{M} along any one of the $\langle 111 \rangle$ or $\langle 110 \rangle$ directions two nuclear Zeeman patterns are obtained in the intensity ratio of 3 : 1 and 2 : 2, respectively. This happens because there are two values of θ equal to 0° and 70°32' for Fe-atoms in the ratio of 1 : 3 for \bar{M} along any body diagonal and θ equals 90° and 35°16' for Fe-atoms, in equal pro-

portion, for \bar{M} along any base diagonal, under the assumption that hyperfine field is parallel to magnetization.

From the survey of the large number of papers that have appeared on the Mössbauer investigations of these cubic Laves phase compounds, it is found that, in general, there is an agreement as regards the number and relative intensity of the component nuclear Zeeman patterns, into which a given Mössbauer spectrum is to be resolved. It is also established that for \bar{M} along any of $\langle 111 \rangle$ or $\langle 110 \rangle$ directions, the nuclear hyperfine fields ascribed to the component nuclear Zeeman patterns, originating from crystallographically equivalent Fe-sites, are significantly different due to the existence of anisotropic hyperfine fields. However, for certain systems, there are notable differences in the derived values of hyperfine interaction parameters, particularly as regards the quadrupole interaction parameters. In fact, the very form of the quadrupole interaction, as it appears in the total nuclear hyperfine Hamiltonian, has been a matter of controversy. Some authors [5, 8] have used an additional term, namely the magnetically induced quadrupole interaction while analysing their data. This approach assumes that the net hyperfine field which the nucleus experiences is necessarily parallel to \bar{M} . However, in another approach the direction of the net nuclear hyperfine field is not constrained to be along the magnetization direction. The origin of this deviation of the net hyperfine field direction from \bar{M} , has been a subject of various discussions [2, 4, 7, 9]. From a careful examination of the Mössbauer spectra for most of the systems where \bar{M} is reported to be along [100], we have found that, although, the spectra consist of single sextets but contrary to what is expected for $\theta = 54^\circ 44'$, they are somewhat asymmetric i.e. $S_{56} \neq S_{12}$. Typical examples where this asymmetry is fairly large are the cobalt rich compositions of $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ [4], ^{57}Fe -doped NdCo_2 [5] and DyCo_2 [10] and NdFe_2 and PrFe_2 [11] etc. Further, in some of these systems even the line widths and the intensities of the nuclear Zeeman patterns are clearly found to be asymmetric which suggests that the magnetization direction is not exactly along [100]. In case of HoFe_2 and DyFe_2 which are the subject of present investigations, all authors [2, 6, 12-15], but for Feder (Bukshpan) and Nowik [8], have concluded that in the range of temperature reported in the present paper, magnetization is along [100] direction. In case of HoFe_2 , Rosen *et al.* [16] have found that below 20 K, the \bar{M} is along $[uv0]$. Feder (Bukshpan) and Nowik [8], in a recent paper have concluded that for both HoFe_2 and DyFe_2 , the direction of magnetization is along $[uv0]$ and that the angle (α) which the magnetization direction makes with [100] increases with the increase in temperature.

In the present communication we have shown that for both these compounds, even at 77 K, the

magnetization shows a slight deviation from [100] direction and that the angle α increases with the increase in temperature, in conformity with the finding of Feder (Bukshpan) and Nowik [8]. The experimental Mössbauer spectra of HoFe_2 and DyFe_2 have been analysed in two different modes. In the first mode, we used a fitting procedure similar to that employed by Atzmony *et al.* [5] (procedure I of this reference) and Feder (Bukshpan) and Nowik [8], where in addition to the usual quadrupole interaction term an additional axially symmetric magnetically induced quadrupole term is also incorporated into the nuclear hyperfine Hamiltonian. In the appendix we have derived an explicit analytical expression for the magnetically induced quadrupole splitting in terms of the eigen values of the nuclear excited state which, in turn, can be obtained from the observed peak positions.

In the second mode of fitting the observed Mössbauer spectra have been analysed in terms of anisotropic hyperfine coupling $\tilde{\mathcal{A}}'$ tensor and dipolar fields arising from the external magnetic moments. The equivalence of different formalisms, used earlier to explain the observed anisotropic hyperfine fields, has been brought out in terms of the anisotropy of $\tilde{\mathcal{A}}'$ tensor components.

2. Experimental. — The samples were prepared from high purity metal elements with a slight excess of rare earth component, by arc melting in argon atmosphere. The compacts so formed were annealed in vacuum. The X-ray diffraction showed the formation of single phase compounds. The Mössbauer spectra were recorded using ^{57}Co in Rh as the source and the absorbers contained $\approx 0.25 \text{ mg } ^{57}\text{Fe}/\text{cm}^2$. The high temperature Mössbauer spectra were recorded in oxygen free atmosphere.

3. Results and discussion. — A large number of Mössbauer spectra recorded at 77 K and at 297 K clearly showed that there is a definite asymmetry in the line positions. In addition a slight difference in line widths was also noticed. This was confirmed by fitting these spectra in terms of six completely independent Lorentzians i.e. the peak positions, their half widths and intensities were left as parameters. This showed that the peaks S_1 and S_5 , consistently, had slightly narrower line widths and deeper intensities as compared to S_6 and S_2 , respectively. This clearly establishes that the spins to deviate from the [100] direction even down to 77 K. In order to deduce the exact spin orientation and to estimate the magnitude of other hyperfine interaction parameters, as a function of temperature the spectra were least square fitted as a superposition of two nuclear Zeeman patterns, with equal intensity as mentioned in reference [8]. As pointed out earlier in the first mode of fitting the total quadrupole interaction was assumed to consist of two axially symmetric terms, viz., the (QS) and $(QS)_m$. So that the required nuclear

hyperfine Hamiltonian matrix, to be diagonalized to get the generated spectrum for comparing with the observed one in the fitting computer program, is given by equation (A.3) of the appendix. The two nuclear Zeeman patterns were characterized by a single value of chemical isomeric shift (*IS*), quadrupole splitting (*QS*) and magnetically induced quadrupole splitting (*QS*)_m. The line widths for all the lines were assumed to be same in the program. However, the two hyperfine fields, which were constrained to be along *M*, were treated as independent parameters. So that the value of the angle *θ* which the two hyperfine fields make with their respective principal efg axis, is given by

$$\theta_1 = \cos^{-1} \left(\frac{\cos \alpha + \sin \alpha}{\sqrt{3}} \right) \quad (1)$$

$$\theta_2 = \cos^{-1} \left(\frac{\cos \alpha - \sin \alpha}{\sqrt{3}} \right).$$

Here *α* which gives the direction of magnetization with regard to [100] in the (001) plane, was treated as a fitting parameter to get the values of *θ*₁ and *θ*₂ which enter into the matrix (A.3). The values of various Mössbauer parameters which are given in table I are the averages of at least four observations at each temperature. Typical room temperature spectra of HoFe₂ and DyFe₂ fitted in this manner are shown in figure 1*a* and *c*. From this table it is clear that for both these compounds, although the values of (*QS*)_m is small *≈* + 0.05 mm/s but it is certainly beyond the experimental errors decided by the analysis of several spectra recorded at a single temperature. Similar value of (*QS*)_m has been reported in reference [8] for these compounds. The temperature dependence of (*QS*)_m is, however, not beyond the experimental uncertainty. The table also shows that *α* is non-zero (*≈* 2°) even at 77 K i.e. *M* deviates slightly from [100] direction. Further, the value of *α* is found to increase with the increase in temperature, in conformity with finding of Feder (Bukshpan) and Nowik [8]. We would like to mention that because

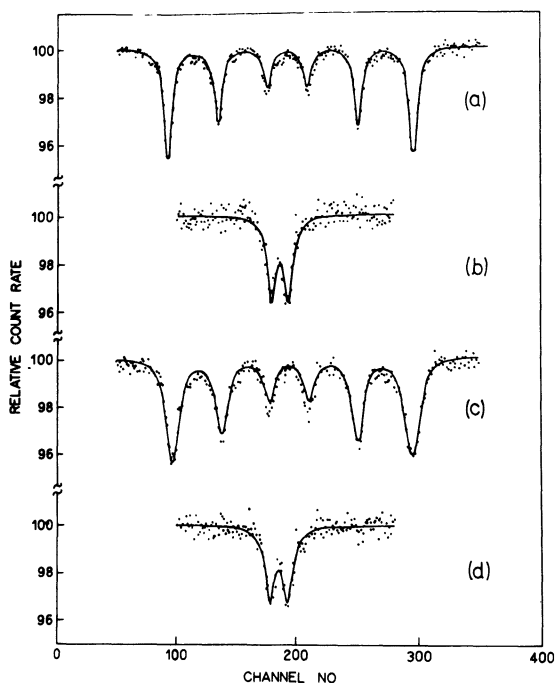


Fig. 1. — Mössbauer spectrum of : a) HoFe₂ at 297 K with respect to ⁵⁷Co(Rh). Zero velocity at 200.66 channels and

1 channel = 0.032 0 mm/s ;

b) HoFe₂ at 650 K with respect to ⁵⁷Co(Pd). Zero velocity at 201.85 channels and 1 channel = 0.034 4 mm/s ; c) DyFe₂ at 297 K with respect to ⁵⁷Co(Rh). Zero velocity at 201.79 channels and 1 channel = 0.034 1 mm/s ; d) DyFe₂ at 690 K with respect to ⁵⁷Co(Pd). Zero velocity at 201.85 channels and

1 channel = 0.034 4 mm/s .

The source was maintained at 297 K for all the experiments.

in this mode of fitting $\cos^2 \theta_1 + \cos^2 \theta_2 = 2/3$ (see eq. (1)), the shift in the peak positions of different lines i.e. $\epsilon' = (QS) \times \left(\frac{3 \cos^2 \theta - 1}{4} \right)$, as a result of the finite value of *α*, will be equal and opposite for the two nuclear Zeeman patterns. Therefore the centre of gravity of different lines is almost unaltered when the magnetization turns from [100] towards

Table I

Compound	Temp. (K)	IS wrt Fe-metal (mm/s)	(QS) (mm/s)	(QS) _m (mm/s)	<i>h</i> ₁ (kOe)	<i>h</i> ₂ (kOe)	Angle <i>α</i> (degrees)
HoFe ₂	77	+ 0.02	- 0.41	+ 0.07	- 214.8	- 221.8	2.5
	297	- 0.11	- 0.43	+ 0.05	- 196.3	- 201.3	2.0
	398	- 0.16	- 0.42	+ 0.05	- 178.5	- 184.1	8.0
	650	- 0.34	- 0.48	—	Paramagnetic	—	—
DyFe ₂	77	+ 0.02	- 0.56	+ 0.06	- 214.0	- 228.0	2.5
	297	- 0.12	- 0.49	+ 0.05	- 201.5	- 212.6	3.0
	424	- 0.19	- 0.59	+ 0.05	- 178.0	- 189.3	8.5
	493	- 0.26	- 0.55	+ 0.07	- 164.0	- 171.4	17.0
	690	- 0.36	- 0.52	—	Paramagnetic	—	—

[$uv0$] direction. Hence, in this case also $(QS)_m$ is approximately equal to $\frac{1}{2}(S_{56} - S_{12})$ of the unresolved pattern. Keeping this in mind we have also calculated $(QS)_m$ from the data of Bowden [2], who have fitted their spectra into a single Zeeman pattern, and the value so obtained is in excellent agreement with our fitted value.

Before we discuss the next approach of fitting we would like to add that the assumption of « eq_m » being axially symmetric with its principal axis along the magnetization direction, may not exactly hold in the present case, particularly at higher tempe-

ratures. Because the magnetization is not directed along any symmetry direction and further closer to T_c the crystal field effects are not negligible as compared to the exchange field.

In the second mode of fitting which is similar to the one used by Meyer *et al.* [7, 17] the observed line shapes are analysed in terms of the anisotropy of the $\tilde{\mathcal{A}}'$ tensor along with the dipolar field arising from external magnetic moments. So that the hyperfine fields corresponding to the two nuclear Zeeman patterns and their relative orientation with regard to their respective principal efg axis are given by

$$\begin{aligned}\bar{h}_1 &= (h_0 \cos \alpha + A \sin \alpha) \bar{i} + (h_0 \sin \alpha + A \cos \alpha) \bar{j} + A(\cos \alpha + \sin \alpha) \bar{k} \\ \bar{h}_2 &= (h_0 \cos \alpha - A \sin \alpha) \bar{i} + (h_0 \sin \alpha - A \cos \alpha) \bar{j} + A(\sin \alpha - \cos \alpha) \bar{k}\end{aligned}\quad (2)$$

$$\begin{aligned}\theta_1 &= \cos^{-1} \left[\frac{(\cos \alpha + \sin \alpha) (h_0 + 2A)}{\sqrt{3} |h_1|} \right] \\ \theta_2 &= \cos^{-1} \left[\frac{(\cos \alpha - \sin \alpha) (h_0 + 2A)}{\sqrt{3} |h_2|} \right]\end{aligned}\quad (3)$$

$$\begin{aligned}|h_1| &= [h_0^2 + 2A^2 + A(A + 2h_0) \sin 2\alpha]^{1/2} \\ |h_2| &= [h_0^2 + 2A^2 - A(A + 2h_0) \sin 2\alpha]^{1/2}.\end{aligned}\quad (4)$$

In the above expressions $\bar{i}, \bar{j}, \bar{k}$ are unit vectors along the crystal axes and the quantities h_0 and A are given by

$$h_0 = \frac{\mathcal{A}'_{\parallel} + \mathcal{A}'_{\perp}}{3} \left| \frac{\mu_{Fe}}{\mu_B} \right| \quad (5)$$

$$A = A_d + \frac{\mathcal{A}'_{\parallel} - \mathcal{A}'_{\perp}}{3} \left| \frac{\mu_{Fe}}{\mu_B} \right| \quad (6)$$

where \mathcal{A}'_{\parallel} and \mathcal{A}'_{\perp} correspond to the components of the hyperfine coupling $\tilde{\mathcal{A}}'$ tensor, parallel and perpendicular to the principal efg axis, respectively and A_d which gives a measure of the dipolar field at the Fe-sites of interest, is given by (2, 7)

$$A_d = \sum_{Fe} \frac{3}{r^5} \mu_{Fe} \pm \sum_{RE} \frac{3}{r^5} \mu_{RE} \quad (7)$$

where the summations extend over both iron and rare earth (RE) sites, and the \pm sign is decided by whether the magnetic ordering is of the antiferromagnetic or ferromagnetic nature.

As regards the computer program, in this mode also IS and QS values are assumed to be identical for both the patterns. Eqs. (3) and (4) give the values of θ_1, θ_2 and the magnitudes of two hyperfine fields in terms of h_0, A and α which were treated as fitting parameters in the hyperfine Hamiltonian matrix. The computer fitted envelopes in this case looked almost similar to the first mode of fitting, with almost equal value of χ^2 in both cases. Separate envelopes for this case have, therefore, not been shown for this fitting. The various Mössbauer parameters obtained from this analysis are given in table II, along with the derived values of the hyperfine fields for the component patterns. A comparison of this table

Table II

Compound	Temp. (K)	IS wrt Fe-metal				Angle α (degrees)	Derived Parameters			
		(mm/s)	(QS) (mm/s)	h_0 (kOe)	A (kOe)		h_1 (kOe)	δ_1 (degrees)	h_2 (kOe)	δ_2 (degrees)
HoFe ₂	77	+ 0.02	- 0.46	- 216.2	20.1	4	- 215.4	7.8	- 220.7	7.1
	297	- 0.11	- 0.43	- 198.8	11.3	4	- 197.9	4.8	- 201.0	4.5
	398	- 0.16	- 0.48	- 180.5	8.9	9	- 178.2	4.1	- 183.6	3.5
	650	- 0.34	- 0.48	—	—	—	Paramagnetic	—	—	—
DyFe ₂	77	+ 0.02	- 0.51	- 220.6	18.2	8	- 217.3	7.2	- 226.8	5.8
	297	- 0.12	- 0.51	- 206.4	12.9	8	- 203.7	5.2	- 210.6	4.5
	424	- 0.19	- 0.55	- 182.9	13.0	12	- 178.7	6.3	- 188.8	4.6
	493	- 0.25	- 0.56	- 167.7	8.1	14	- 164.4	4.2	- 171.7	2.7
	690	- 0.36	- 0.52	—	—	—	Paramagnetic	—	—	—

with table I shows that the fitted IS , QS and h_i values are fairly close to each other. However in the second mode of fitting, the value of α at low temperatures is found to be somewhat larger than for the first mode and its value also increases with the increase in temperature. Further, the value of A is found to be significantly larger than the calculated value of A_d . In order to get an approximate estimate of the anisotropy in $\tilde{\mathcal{A}}'$ tensor components i.e. \mathcal{A}'_{\parallel} and \mathcal{A}'_{\perp} , we have analysed the data of 77 K using the fitted values of h_0 and A along with the calculated values of A_d obtained from the reported magnetic moment values for Fe and RE-atoms. This analysis showed that the magnitude of \mathcal{A}'_{\perp} is significantly larger than that of \mathcal{A}'_{\parallel} as given below

$$\text{HoFe}_2 (77 \text{ K}) \begin{cases} \mathcal{A}'_{\parallel} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \simeq -192 \text{ kOe} \\ \mathcal{A}'_{\perp} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \simeq -228 \text{ kOe} \end{cases}$$

$$\text{DyFe}_2 (77 \text{ K}) \begin{cases} \mathcal{A}'_{\parallel} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \simeq -201 \text{ kOe} \\ \mathcal{A}'_{\perp} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \simeq -231 \text{ kOe} . \end{cases}$$

It may be mentioned that we analysed, in this mode, the reported hyperfine fields of SmFe_2 [18] for the two spin orientation regions and found that the values of $(\mathcal{A}'_{\parallel} - \mathcal{A}'_{\perp})$ is of the same order of magnitude, in spite of the fact that Sm carries a much smaller magnetic moment as compared to Ho and Dy in our compounds. This large difference in \mathcal{A}'_{\parallel} and \mathcal{A}'_{\perp} suggests that the direction of nuclear hyperfine field deviates significantly from that of magnetization. This is equivalent to the nuclear spin tipping mentioned by Bowden [2] and Meyer *et al.* [7]. These deviations for the two patterns for \bar{M} along $[uv0]$ are given by

$$\delta_1 = \cos^{-1} \left[\frac{h_0 + A \sin 2\alpha}{|h_1|} \right];$$

$$\delta_2 = \cos^{-1} \left[\frac{h_0 - A \sin 2\alpha}{|h_2|} \right]$$

and their magnitudes at 77 K are found to be 7.8° and 7.1° for HoFe_2 and 7.2° and 5.8° for DyFe_2 , respectively. It may be mentioned that whenever the direction of magnetization coincides with any of principal efg axes, this formalism implies that the angle of deviation δ is zero.

We would like to mention that we tried to analyse the data in yet another approach in which the effect of $(QS)_m$ is also incorporated, in addition to the anisotropy of hyperfine coupling tensor discussed in the second mode of fitting. However, this analysis did not give consistent results.

In the discussion that follows we bring out the functional similarity between the second approach

(wherein the differences in the hyperfine fields for the crystallographically equivalent Fe-atoms are explained in terms of the anisotropy of the $\tilde{\mathcal{A}}'$ tensor and A_d) with those used by earlier authors. First attempts to explain the differences in the hyperfine field values in RFe_2 compounds was made in terms of enhanced dipolar fields, arising from the external magnetic moments [18-20]. This enhancement factor supposedly arising [19-20] due to the additional conduction electron polarization by the dipolar field, was found to be appreciably different for different systems. For example in case of $(\text{Y}_x\text{Er}_{1-x})\text{Fe}_2$ and $(\text{Y}_x\text{Tb}_{1-x})\text{Fe}_2$ series of compounds, the enhancement factor was found to be $\simeq 1.5$ [20], but for SmFe_2 this factor turns out to be four times higher. In the present approach A of refs. [2, 19] has been replaced by

$$A = \left(A_d + \frac{\mathcal{A}'_{\parallel} - \mathcal{A}'_{\perp}}{3} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \right).$$

This means that the enhancement factor (k) in our approach is equal to

$$k = \left[1 + \frac{\mathcal{A}'_{\parallel} - \mathcal{A}'_{\perp}}{3 A_d} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| \right]. \quad (8)$$

In another model used by Window [21], Billard and Chamberod [22] and by Hesse *et al.* [23] to explain the unusual line shapes of Mössbauer spectra of cubic Fe-Ni alloy systems, the anisotropic hyperfine fields are assumed to be proportional to structure factors S_p , defined by

$$S_p = \sum_p (3 \cos^2 \gamma_i - 1) \quad (9)$$

where the summation extends over the p -near neighbours, γ_i is the angle which the line, joining the i th Fe-near neighbour and the probe Fe-atom, makes with the magnetization direction. We would like to mention that this is basically similar to the approach suggested by Bowden [2] but for the fact that S_p is proportional to the component of dipolar field parallel to \bar{M} , arising from near neighbours only. So that the proportionality factor between S_p and the observed hyperfine field, which appears as a fitting parameter [21-23], is directly related to our k -value in eq. (8).

In yet another approach the anisotropic hyperfine fields have been expressed in terms of an expression of the form [24, 25]

$$h = h_{\text{iso}} + D_{\text{an}} \left(\frac{3 \cos^2 \theta - 1}{2} \right). \quad (10)$$

For RFe_2 compounds (i.e. axially symmetric case) it can be easily shown that in our second approach, the component of hyperfine field parallel to \bar{M} , h_{\parallel} , can be written in the following form

$$h_{\parallel} = h_0 + A(3 \cos^2 \theta - 1) \quad (11)$$

where h_0 and A have already been defined earlier in eqs. (5) and (6) and θ is the angle between the principal efg axis and the magnetization direction. The approximation of considering h_{\parallel} in place of actual fields, for finding the hyperfine field differences, is reasonable for most systems where the anisotropies are not too large. In fact eq. (10) assumes that hyperfine field is parallel to \bar{M} , so that the comparison of eqs. (10) and (11) implies that h_0 represents the isotropic hyperfine field and A equals $1/2 D_{\text{an}}$. It can be easily shown that for a general case, where $\mathcal{A}'_x \neq \mathcal{A}'_y \neq \mathcal{A}'_z$ the expression for h_{\parallel} can be written in the following form

$$h_{\parallel} = C_0 + C_1[(3 \cos^2 \theta - 1) + C_2 \sin^2 \theta \cos 2\varphi] \quad (12)$$

where

$$C_0 = \frac{\mathcal{A}'_x + \mathcal{A}'_y + \mathcal{A}'_z}{3} \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right|$$

$$C_1 = \frac{1}{6} \left[(2\mathcal{A}'_z - \mathcal{A}'_x - \mathcal{A}'_y) \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| + (2A'_{d_z} - A'_{d_x} - A'_{d_y}) \right]$$

$$C_2 = \frac{1}{2C_1} \left[(\mathcal{A}'_x - \mathcal{A}'_y) \left| \frac{\mu_{\text{Fe}}}{\mu_{\text{B}}} \right| + (A'_{d_x} - A'_{d_y}) \right].$$

In the above expression A'_{d_x} etc. are given by

$$A'_{d_x} = \sum_{\text{M}} \left[\frac{3x'^2 - r'^2}{r'^5} \mu_{\text{M}} \right].$$

The summations extend over all magnetic M-atoms and x' , y' , z' refer to the principal efg axes frame.

Thus, in systems where crystallographically equivalent Fe-sites give rise to multiple nuclear Zeeman patterns due to the presence of local principal efg axes systems, the fitting of hyperfine fields in equation of the form given above, \mathcal{A}'_x , \mathcal{A}'_y and \mathcal{A}'_z can be easily found. Although, the above discussion presents functional similarities of different approaches, it is not understood as to how exactly different contributions such as spin dipolar and orbital fields etc. account for the $\tilde{\mathcal{A}}'$ tensor anisotropy.

4. Conclusions. — In the present paper we have analysed the observed asymmetry in the peak positions and peak widths of HoFe_2 and DyFe_2 data, in terms of two different modes : (i) by assuming that the quadrupole interaction consists of two terms, namely the magnetically induced part in addition to the usual term, and (ii) by assuming that the hyperfine coupling $\tilde{\mathcal{A}}'$ is anisotropic. From both the fittings it is found at even at 77 K, \bar{M} deviates slightly from [100] direction in (001) plane and that this deviation increases with increase in temperature, in conformity with the finding of Feder (Bukshpan) and Nowik [8]. Further, it is found that for the present system, on

the basis of the quality of the fitting alone, it is not possible to choose between the two modes of fitting. However, we believe that unlike what has been done in the first mode of fitting it is necessary to include the effect of non-collinearity of hyperfine field and magnetization direction. But the existence or otherwise of $(QS)_{\text{m}}$ could not be decided from the present data, because our attempts, taking both these aspects into account, did not give consistent results. We hope to resolve this aspect by carrying out experiments on certain other systems where the observed asymmetries are reported to be much larger and the system shows temperature and composition dependent spin orientation. An estimation of \mathcal{A}'_{\parallel} and \mathcal{A}'_{\perp} values, in different regions of spin orientation in RFe_2 compounds, should be helpful in deciding this issue.

Appendix

Magnetically Induced Quadrupole Interactions. —

The quadrupole interaction can be manifested even at the cubic site when the probe atom experiences a magnetic field, be it external or that arising due to exchange interactions in the magnetically ordered state. The effect of magnetic field is to create a preferred direction in space which also decides the perturbation of magnetic electronic charge distribution and therefore a non-zero electric field gradient (eq_{m}) is produced even at the cubic sites. In RFe_2 intermetallics the eq_{m} at the Fe-sites has been assumed to be axially symmetric [5, 8] with its principal axis along the Fe-sublattice magnetization. Adding this interaction also to the nuclear hyperfine Hamiltonian described earlier [26], the new Hamiltonian becomes

$$H = H_{\text{m}} + H_{\text{q}} + (H_{\text{q}})_{\text{ind}}$$

$$= -g_{\text{n}} \beta_{\text{n}} h I_z + \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1)]$$

$$+ \frac{e^2 q_{\text{m}} Q}{4I(2I-1)} [3I_z^2 - I(I+1)] \quad (\text{A.1})$$

where H_{m} is the nuclear Zeeman term and H_{q} determines the quadrupole interaction which exists in the absence of exchange field. The principal axes x' , y' and z' of H_{q} are determined by the symmetry around the probe nucleus. Defining the following quantities.

$G = g_{\text{n}} \beta_{\text{n}} h$ (which is the excited state splitting due to H_{m} alone).

$$P = \frac{e^2 q Q}{12}; \quad M = \frac{e^2 q_{\text{m}} Q}{12}$$

$$W_1 = 3P[1 - 3/2 \sin^2 \theta] \quad (\text{A.2})$$

$$W_2 = 3\sqrt{3} P \sin \theta \cos \theta$$

$$W_3 = \frac{3\sqrt{3}}{2} P \sin^2 \theta.$$

We can write down the matrix elements of the Hamiltonian in the manifold of $I = 3/2$ — the ⁵⁷Fe nuclear excited state :

$$\| \mathcal{H} \| = \begin{vmatrix} \frac{3}{2} G + W_1 + 3 M & W_2 & W_3 & 0 \\ W_2 & \frac{1}{2} G - W_1 - 3 M & 0 & W_3 \\ W_3 & 0 & -\frac{1}{2} G - W_1 - 3 M & -W_2 \\ 0 & W_3 & -W_2 & -\frac{3}{2} G + W_1 + 3 M \end{vmatrix} \quad (\text{A.3})$$

Here θ is the angle which the hyperfine (\bar{h}) makes with z' , the principal axis of H_q .

If E_1, E_2, E_3 and E_4 represent the eigen values of this Hamiltonian matrix [3], then for the case of $H_m > H_q$ these can be easily obtained from the observed peak positions S_1, S_2, \dots, S_6 (in the increasing order of energy) of the Mössbauer spectrum, using the following relations :

$$\begin{aligned} E_1 &= -[\frac{1}{4}(S_1 + S_2 + S_5 + S_6) - S_1 - \frac{1}{4}(S_{24} + S_{35})] \\ E_2 &= -[\frac{1}{4}(S_1 + S_2 + S_5 + S_6) - S_2 - \frac{1}{4}(S_{24} + S_{35})] \\ E_3 &= [S_5 - \frac{1}{4}(S_1 + S_2 + S_5 + S_6) - \frac{1}{4}(S_{24} + S_{35})] \\ E_4 &= [S_6 - \frac{1}{4}(S_1 + S_2 + S_5 + S_6) - \frac{1}{4}(S_{24} + S_{35})] \end{aligned} \quad (\text{A.4})$$

where $\frac{1}{4}(S_1 + S_2 + S_5 + S_6)$ determines the centre of gravity of the Mössbauer spectrum and therefore gives the estimate of the chemical isometric shift with reference to the source employed and $\frac{1}{2}(S_{24} + S_{35})$ gives the ground state splitting and therefore the hyperfine field. The value of the excited state splitting G is obtained by multiplying $\frac{1}{2}(S_{24} + S_{35})$ by the ratio of the nuclear g -factors. The above expressions for E_i 's hold for case of $H_m \approx H_q$ also, provided the peak positions S_1, S_2, \dots , etc. are correctly assigned to the appropriate nuclear transitions. Defining

$$a = \prod_{i=1}^4 E_i, \quad b = \sum_{i=1}^4 \frac{1}{E_i} \quad \text{and} \quad c = \sum_{i=1}^4 E_i^2 \quad (\text{A.5})$$

and following the method similar to that of Dabrowski *et al.* [26], we arrive at the following explicit analytical expression for

$$(QS)_m = \frac{1}{2} e^2 q_m Q,$$

$$(QS)_m^2 + 4 W_1(QS)_m - [C - 5 G^2 - (QS)^2] = 0$$

or

$$(QS)_m^2 - \frac{ab}{G^2}(QS)_m + [C - 5 G^2 - (QS)^2] = 0 \quad (\text{A.6})$$

where a, b, c and W_1 are defined in eq. (A.5) and eq. (A.2) and their values can be obtained from the observed peak positions of the Mössbauer spectrum using eq. (A.4). (QS) is equal to $\frac{1}{2} e^2 qQ$ and its value, in general, equals that in the paramagnetic state, if there is no distortion of the crystal lattice at T_N and it shows temperature independent behaviour above T_N . For the systems where \bar{M} is along a cube edge $\theta = 54^\circ 44'$ so that $W_1 = 0$ and eq. (A.6) simplifies to

$$(QS)_m = [C - 5 G^2 - (QS)^2]^{1/2}. \quad (\text{A.7})$$

Dabrowski *et al.* [26] have tabulated expressions for the limiting values of $e^2 qQ$ and θ when

$$H = H_m + H_q.$$

By taking $(H_q)_{\text{ind}}$ also into account, as in eq. (1), we find that the formulations for the limiting values of the above parameters can be retained in the same form as presented in tables I and II of reference [10], provided we replace W_1 by W'_1 such that

$$W'_1 = \left[\frac{ab}{4 G^2} - \frac{1}{2} (QS)_m \right] \quad (\text{A.8})$$

W_1 of the above reference equals $\left(\frac{ab}{4 G^2} \right)$.

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