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MÖSSBAUER STUDIES OF $R(\text{FeCo})_2$ LAVES PHASES

by

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ABSTRACT

Magnetic hyperfine field and isomer shift measurements in $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ intermetallic compounds are reported, and the changes in these quantities with concentration are related to changes in the d-moment and in the lattice parameter. The origin of the ^{57}Fe hyperfine fields and the proportionality between field and magnetic moment are discussed using a simple model. The Mössbauer spectra of the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds show that the direction of magnetization changes from $\langle 111 \rangle$ axis (in YFe_2) to $\langle 101 \rangle$ in the samples with $x \geq 0.17$.

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I - INTRODUCTION

The structural and magnetic properties of the rare-earth-transition metal intermetallic compounds are the subject of a growing interest stimulated by the recent development of permanent magnets based on the RCo_5 compounds; the reader should refer to the review by Taylor (1971)¹ for the literature.

The 3d transition metals form a large series of intermetallic compounds with the rare-earths, including many cubic Laves phases (MgCu₂-type) of formula RT_2 (where R = rare-earth or yttrium). The RFe_2 cubic Laves phases display in some instances complete solid solubility with the corresponding RCo_2 compound of the same crystal structure. Several of these ternary systems have been investigated by Mansey and co-workers (Mansey et al. 1968)², e.g. $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Er}(\text{Fe}_{1-x}\text{Co}_x)_2$.

II - EXPERIMENTAL DETAILS

In this work we present some Mössbauer measurements of the ^{57}Fe hyperfine (hf) interaction in the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ systems. The compounds were prepared by melting the pure elements in an arc furnace; the resulting buttons were crushed either under dry acetone or in an argon atmosphere. The samples showed the correct crystalline structure when examined by X-ray diffraction. The measurements were made at 78°K, and the experimental spectra computer-fitted to a set of six Lorentzian lines (for the holmium system) and two sets of six lines (for the yttrium system). Each six-line pattern was assumed to be composed of three doublets (two lines of same intensity, e.g. lines 1 and 6, or 2 and 5); the relative intensities of the doublets was left free. The positions of the lines were constrained

to give the splitting of the ^{57}Fe ground state ($I = 1/2$) and the splittings of the excited state ($I = 3/2$); the excited state splittings were then fitted to the Hamiltonian

$$\mathcal{H} = -g_N \mu_N I_z H + \frac{e^2 q Q}{4I(2I-1)} (3I_z^2 - I(I+1)) \frac{3 \cos^2 \theta - 1}{2}$$

From a least-squares fit to the corresponding secular equations we could obtain separately the value of the electric quadrupole interaction parameter $e^2 q Q$ and of the angular factor $(3 \cos^2 \theta - 1)/2$. This procedure is necessary when we want to compare systems that magnetize along different crystal axes, and consequently have different values of θ (at least different angular factors affecting the lattice contribution to the electric field gradient (EFG)).

The experimental measurements on the absorbers with a higher concentration of cobalt were much more difficult to perform since the probability of atomic absorption of the gamma ray increased with cobalt concentration; this was particularly serious in view of the high atomic number of the rare-earth constituents of the compounds.

The values of the isomer shifts given in Table I are referred to a $^{57}\text{Co}(\text{Pd})$ source at room temperature; the shift of the source was $-0.440 \pm 0.002 \text{ mm s}^{-1}$ relative to sodium nitroprusside, and $+0.175 \pm 0.004 \text{ mm s}^{-1}$ relative to pure (4N8) iron foil.

III - MAGNETIC STRUCTURE OF THE COMPOUNDS

Magnetization measurements on intermetallic compounds containing gadolinium (Nesbitt et al. 1959)³ gave the first evidence of anti-parallel

coupling of magnetic moments of the rare-earth metal and of the transition metal. Other studies showed that the two moments are parallel when R is a light rare-earth, in such a way that the spins of the rare-earth and of the transition metal are always anti-parallel.

The directions of easy magnetization can be determined from Mössbauer measurements: the presence of two superposed six-line patterns in the ^{57}Fe spectra of TmFe_2 and ZrFe_2 led Wertheim and co-workers (Wertheim et al. 1964)⁴ to infer that these compounds magnetize along a $\langle 111 \rangle$ direction. When the magnetization lies along this axis, which coincides with a threefold axis of the tetrahedron of iron atoms, the iron sites are not all equivalent; in site I the axial lattice EFG forms an angle of approximately 70° with the direction of magnetization, and in site II the angle is 0° . Also the hyperfine field at the nuclei in site I is different from the field in site II; this difference is of the order of the ionic dipole fields (Bowden et al. 1968)⁵. Of the four atoms in each tetrahedron, one occupies a site of type II, and the other three, sites of type I: consequently the two six-line patterns forming the Mössbauer spectrum have an intensity ratio of approximately 3:1. The fact that the ^{57}Fe Mössbauer spectra of the isostructural compounds HoFe_2 and DyFe_2 show only six lines is due to the circumstance (Bowden et al. 1968)⁵ that these systems magnetize along a $\langle 001 \rangle$ direction, which results in all Fe atoms being magnetically equivalent. Another possibility which can arise is magnetization along a $\langle 101 \rangle$ axis: now there are two sites with equal population, but $\theta_{\text{I}} = 35^\circ 16'$ and $\theta_{\text{II}} = 90^\circ$ (this appears to be the case in the compound LuFe_2 (Guimarães 1971))⁶.

The direction of magnetization in the RFe_2 compounds is essentially determined (Bowden 1967, Bowden et al. 1968)^{7,5} by the rare-earth anisotropy,

since the transition metal has practically all its orbital moment quenched. When R is an S-state ion, as in GdFe_2 , this rule does not apply, since the anisotropies of the transition metal and the rare-earth metal may become comparable. It is consequently more difficult to predict the directions of magnetization in these cases. When R does not carry a moment, as in LuFe_2 , the direction of magnetization is determined by the anisotropy of the transition metal ion (within this "ionic" model).

In the $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds the magnetization remained parallel to a $\langle 001 \rangle$ direction at every concentration examined ($x = 0, 0.2, 0.4, 0.6, 0.8$) since the holmium anisotropy dominates that associated to the transition metal. The direction of magnetization in the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ series, however, changed with the addition of cobalt: YFe_2 magnetizes along a $\langle 111 \rangle$ direction but the other solid solutions with $x > 0.17$ all magnetize along a $\langle 101 \rangle$ direction. This conclusion was reached from the intensities of the lines and splittings given by the computer fits; it can be verified by careful visual inspection of the experimental data that the two superposed spectra for the alloys containing cobalt have approximately the same intensity, contrasting with the ratio of about 3:1 in YFe_2 (Fig. 1). A similar change is observed in the binary FeCo alloys (b.c.c structure) (Hall 1960)⁸; the ordered alloys change from a $\langle 100 \rangle$ direction in iron to a $\langle 111 \rangle$ direction when the Fe concentration is reduced to 50%.

IV - HYPERFINE INTERACTIONS

The magnetic susceptibilities of $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ have been measured by Abel and Craig (1968)⁹ and by Piercy and Taylor (1968)¹⁰ and the solid solutions found to be ferromagnetic, with Curie temperatures ranging from 555°K

to 305°K (with $1 > x > 0$). Since the samples used in our measurements have T_c 's varying from 555°K to 635°K, the degree of magnetic saturation at 78°K was practically the same for all Y compounds; this is also reasonable in relation to our $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ samples, with Néel temperatures in the range 400-600°K. The curves for the total magnetic moment and Curie temperatures as a function of composition display maxima occurring approximately at the compound $\text{Y}(\text{Fe}_{0.6}\text{Co}_{0.4})_2$. This behaviour was explained by the above authors in terms of a rigid band model, in the same way as the magnetic moments in the binary transition metal systems (in the Slater-Pauling diagram) may be analysed. The curve for T_c against concentration in $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ does not exhibit a maximum (Slanicka et al. 1971)¹¹; the same is true of the total magnetic moment in the series. The flatness in the curve of magnetic moment versus x is probably due to a cancellation between a small rise due to filling of the d-band and a decrease in Ho moment with concentration. Our Mössbauer measurements (Fig. 2) show that the ^{57}Fe hyperfine fields in $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ (Table I) have maxima at about the same concentration, at $x \sim 0.4$.

The iron hf fields are opposed to the total transition metal moment; this has been established, by applying large ($\sim 30\text{kOe}$) external magnetic fields, in the case of ZrFe_2 (Wertheim et al. 1964), DyFe_2 and HoFe_2 (Guimarães 1971)⁶.

V - DISCUSSION

In the pseudo-binary systems of the form $\text{R}(\text{Fe}_{1-x}\text{Co}_x)_2$ the ^{57}Fe hyperfine interaction changes with concentration x because each cobalt atom adds an extra electron to the band, filling the spin up and spin down d

sub-bands: since the s band is practically flat, its contribution is independent of concentration. The highest magnetic moment is reached for $x \sim 0.4$, i.e. when we have 0.8 cobalt atoms per formula unit. The variation in hyperfine field from YFe_2 to $\text{Y}(\text{Fe}_{0.66}\text{Co}_{0.34})_2$ is approximately 30 kOe; this can be related to the change in the d magnetization (m^d), which affects directly the core-polarization field, and indirectly (by polarizing the s band), the contact field.

The total hyperfine field can be written (Campbell 1969)¹²

$$H = -\alpha_{\text{core}}^d m^d + A(Z) m^s \quad (5-1)$$

Since the s magnetization is induced through s-d hybridization, we put (Gomes et al. 1972)¹³ $m^s = -\alpha_{\text{sd}} m^d$ with $\alpha_{\text{sd}} > 0$, and consequently

$$H = -(\alpha_{\text{core}}^d + A(Z)\alpha_{\text{sd}})m^d \text{ and } m = m^d + m^s = (1 - \alpha_{\text{sd}})m^d$$

The hyperfine field is then proportional to the total band magnetization m ; this proportionality is actually verified from the total hyperfine fields in the yttrium compounds at 78°K using the respective moments per Fe atom (Piercy and Taylor 1968)¹⁰ (Table I). The mean ratio, excluding the value for the $\text{Y}(\text{Fe}_{0.3}\text{Co}_{0.7})_2$ sample due to its larger experimental uncertainty, is

$$\frac{H}{m} = -\frac{(\alpha_{\text{core}}^d + A(Z)\alpha_{\text{sd}})}{(1 - \alpha_{\text{sd}})} \approx -155 \text{ kOe}/\mu_B$$

Using $\alpha_{\text{core}}^d \approx 50 \text{ kOe}/\mu_B$ and $A(Z) = 1.78 \times 10^3 \text{ kOe}/\mu_B$ (Campbell 1969)¹² it follows that the mixing factor α_{sd} is approximately 0.05; the s and d magnetizations per iron atom in YFe_2 are $m^s \approx -0.1\mu_B$ and $m^d \approx 1.5\mu_B$.

The iron hf fields in the $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ series have another contri-

bution arising from the polarization of the band electrons due to the localized holmium spin. This term has the same sign of the two contributions given in (5-1) as can be seen from the fact that the ^{57}Fe hf fields in the RFe_2 tend to increase in absolute value with the rare-earth de Gennes factor (Fig. 3). In this figure we have used our unpublished results for the hf fields averaged (with weights 3:1, or 1:1) over the two sites; the procedure of averaging is justified whenever one wants to correlate hf field data with the mean magnetization m or with rare-earth spin.

It is interesting to compare the magnetic properties of the isostructural compound series $\text{Zr}(\text{Fe}_{1-x}\text{Co}_x)_2$ with the systems presently under consideration. Zirconium has a "valence" of about 4, and consequently the band in ZrFe_2 has one electron more, and the d magnetization (from the results with $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ is near a maximum; this explains why diluting ZrFe_2 with ZrV_2 (in the series $\text{Zr}(\text{Fe}_{1-x}\text{V}_x)_2$) decreases the total magnetic moment (Kanematsu 1968)¹⁴. The maximum magnetic moment of the band in both systems would be identical if the band structure was the same; the Fe moment in ZrFe_2 is $1.62\mu_B$ (Piegger and Craig 1963)¹⁵, and this is quite near the moment* in $\text{Y}(\text{Fe}_{0.66}\text{Co}_{0.34})_2$, of $1.57\mu_B$ (Piercy and Taylor 1968)¹⁰. We would therefore expect in the $\text{R}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds the same variation of ^{57}Fe hf field with concentration when R does not carry a magnetic moment; when R has a moment, the hf fields depend on the spin of the lanthanide 4f shell (Fig. 3).

* The slight disagreement may be partly due to deviations in stoichiometry in the compound; this is suggested by the studies of magnetization versus Fe concentration (Brückner et al. 1968)¹⁸.

The electric quadrupole interactions do not show a significant variation with concentration in either series (Table I). The isomer shifts were expected to go through a maximum with concentration, since the maximum in d magnetization produces a positive contribution due to the shielding of the s electrons. The experimental shifts increase (become less negative) in the $R(\text{Fe}_{1-x}\text{Co}_x)_2$ when x increases from zero, but the presence of a maximum could not be established unambiguously (Fig.4). Plotting our isomer shift results obtained in several $R\text{Fe}_2$ compounds at 78°K versus the corresponding (room temperature) lattice parameters from the compilation by Nevitt (1963)¹⁶, a linear correlation is evident (Fig.5); other measurements (Nevitt et al. 1964)¹⁷ show the same dependence at 300°K and 800°K , and this suggests that differences in Debye temperature of the compounds may not be relevant. Even the compound CeFe_2 , where cerium is "tetravalent", does not deviate much from the main trend.

Using the lattice parameters given by Piercy and Taylor (1968)¹⁰ for the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds and our isomer shift data we do not find a linear correlation. Comparing the variation in lattice parameter in the $R\text{Fe}_2$ compounds, where we change from one lanthanide to another, and the equivalent variation along the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ series, it appears that:

- a) the change in size of the rare-earth ion (the "lanthanide contraction") induces an accommodation of the Fe atom, and we may in this case speak of a size effect in the ^{57}Fe isomer shift*;

* The expansion or contraction of the A and B atoms to approach the ideal ratio of $R_A/R_B = 1.225$ in a cubic AB_2 Laves phase is well known (e.g. Dwight 1961)¹⁹.

- b) the variation in lattice parameter in a series of $R(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds with concentration has a different origin, the changes in electronic structure being of such character that they do not affect in the same proportion the isomer shifts and the equilibrium lattice parameters.

VI - ACKNOWLEDGEMENTS

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TABLE I Hyperfine parameters* and magnetic structure of the $Y(Fe_{1-x}Co_x)_2$ and $Ho(Fe_{1-x}Co_x)_2$ intermetallic compounds at 78°K.

<u>COMPOUND</u>	<u>\bar{H} (kOe)</u>	<u>$\overline{e^2qQ}$ (mm s⁻¹)</u>	<u>I.S._{pd} (mm s⁻¹)</u>	<u>Direction of magnetization</u>	<u>\bar{H}/m (kOe/μ_B)</u>
YFe ₂	218±1.5	1.11±0.1	- 0.148±0.006	<111>	156
Y(Fe _{0.835} Co _{0.165}) ₂	230±3.5	1.5 ±0.4	- 0.142±0.008	<101>	148
Y(Fe _{0.615} Co _{0.335}) ₂	241±7	1.8±0.3	- 0.128±0.006	<101>	154
Y(Fe _{0.49} Co _{0.51}) ₂	242±6	1.3±1.6	- 0.137±0.01	<101>	161
Y(Fe _{0.295} Co _{0.705}) ₂	233±8	0.8±1.1	- 0.17 ±0.03	<101>	183
HoFe ₂	221±1.5	1.1 ±0.1	- 0.163±0.004	<001>	
Ho(Fe _{0.8} Co _{0.2}) ₂	240±2	1.06±0.1	- 0.144±0.002	<001>	
Ho(Fe _{0.6} Co _{0.4}) ₂	245±3	1.22±0.17	- 0.143±0.009	<001>	
Ho(Fe _{0.4} Co _{0.6}) ₂	232±3.5	1.14±0.23	- 0.143±0.012	<001>	
Ho(Fe _{0.2} Co _{0.8}) ₂	214±8	1.4 ±2	- 0.149±0.03	<001>	

* The hf fields and quadrupole parameters in the Y series are the mean values for the sites I and II.

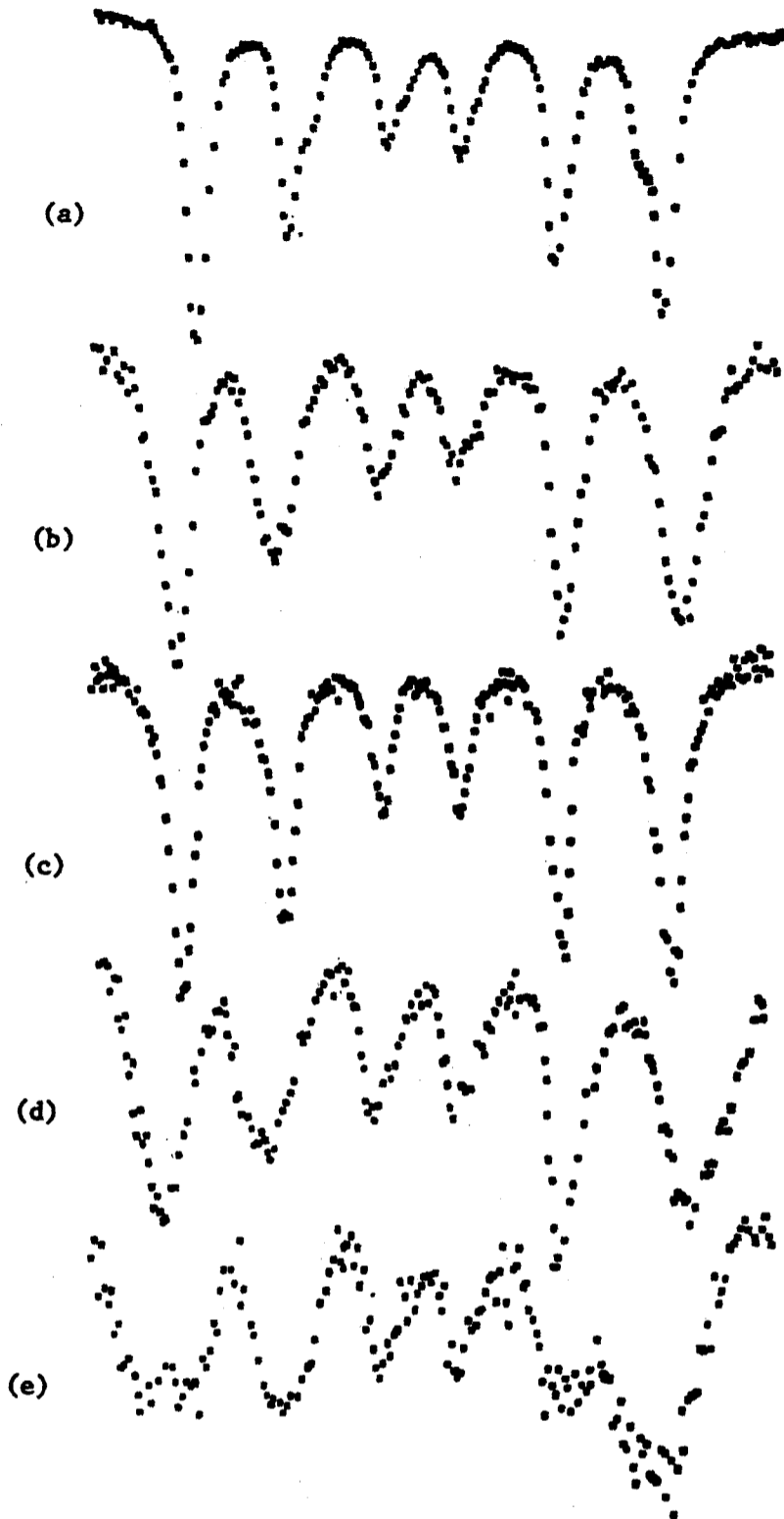


Fig. 1 - Mössbauer spectra of a) YFe_2 , b) $\text{Y}(\text{Fe}_{0.835}\text{Co}_{0.165})_2$, c) $\text{Y}(\text{Fe}_{0.615}\text{Co}_{0.335})_2$, d) $\text{Y}(\text{Fe}_{0.49}\text{Co}_{0.51})_2$, and e) $\text{Y}(\text{Fe}_{0.295}\text{Co}_{0.705})_2$ obtained at 78°K .

The horizontal and vertical scales differ from one spectrum to the other; the vertical scale is such that the largest peak in each spectrum corresponds to a) 8.16%, b) 3.38%, c) 2.80%, d) 1.80%, and e) 0.71%.

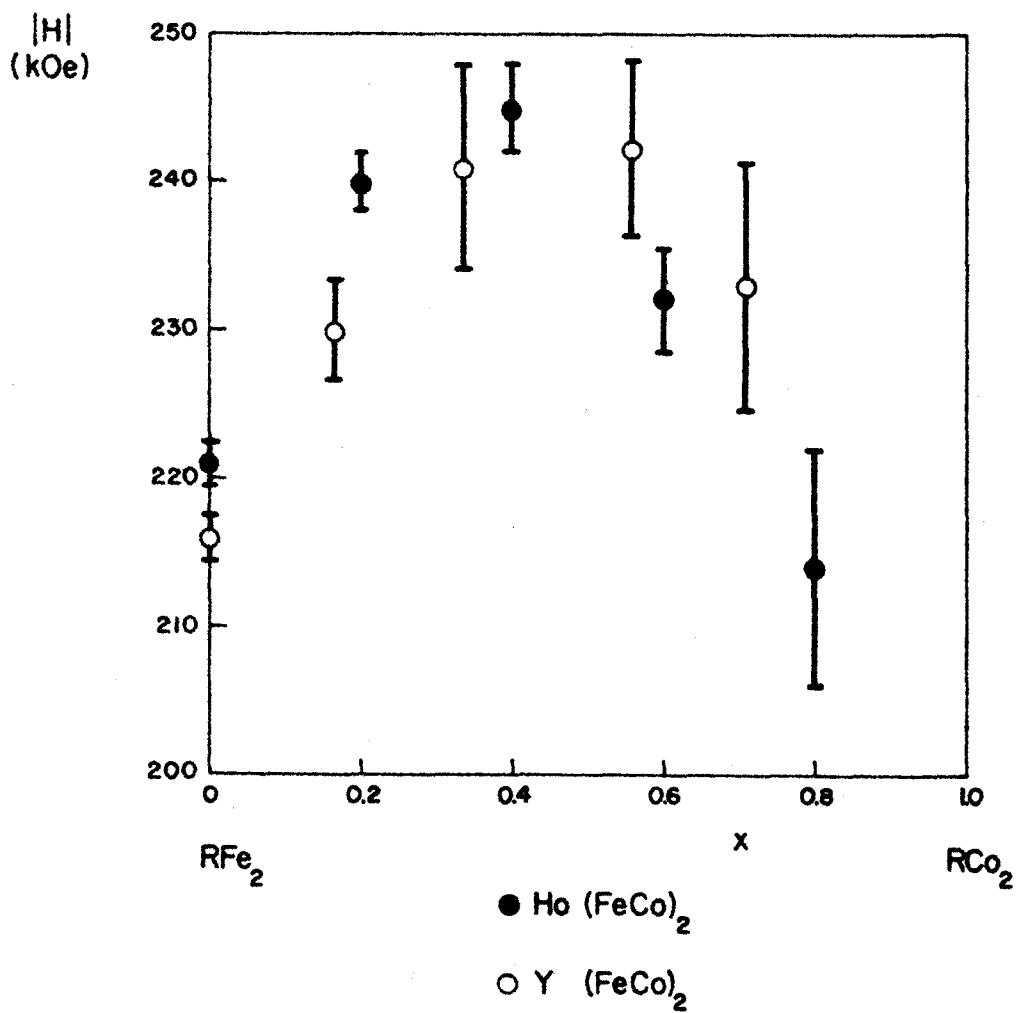


Fig. 2 - Variation of the iron hyperfine fields in $Y(Fe_{1-x}Co_x)_2$ and $Ho(Fe_{1-x}Co_x)_2$ with cobalt concentration ($T = 78^\circ K$).

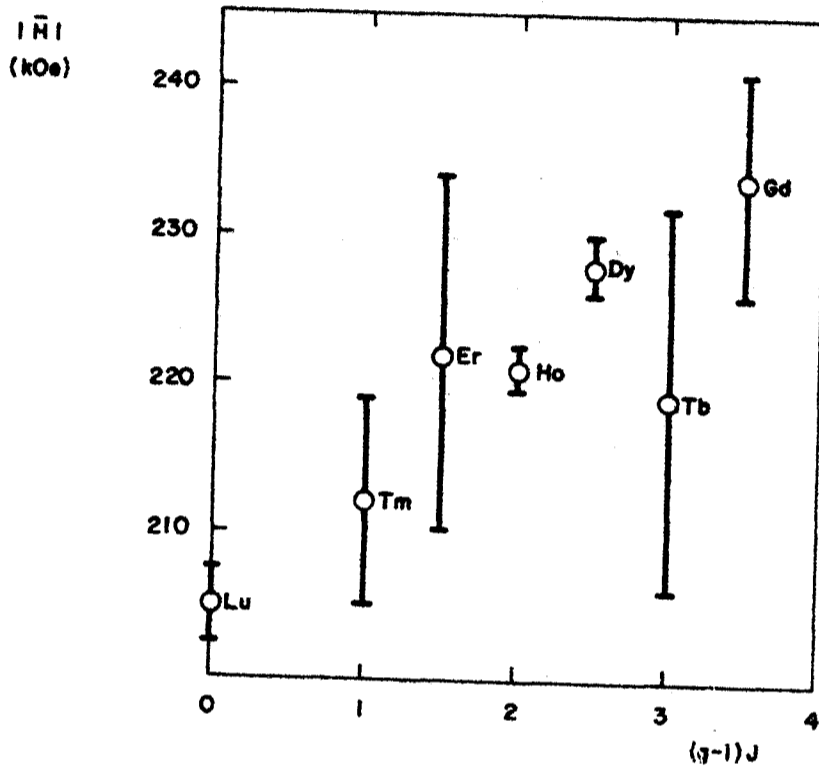


Fig. 3 - ^{57}Fe hyperfine fields in the RFe_2 Laves phases at $T=78^\circ\text{K}$ (averaged over the two iron sites) against rare-earth de Gennes factor; the value for TmFe_2 (4.2°K) is from Wertheim et al. (1964)⁴.

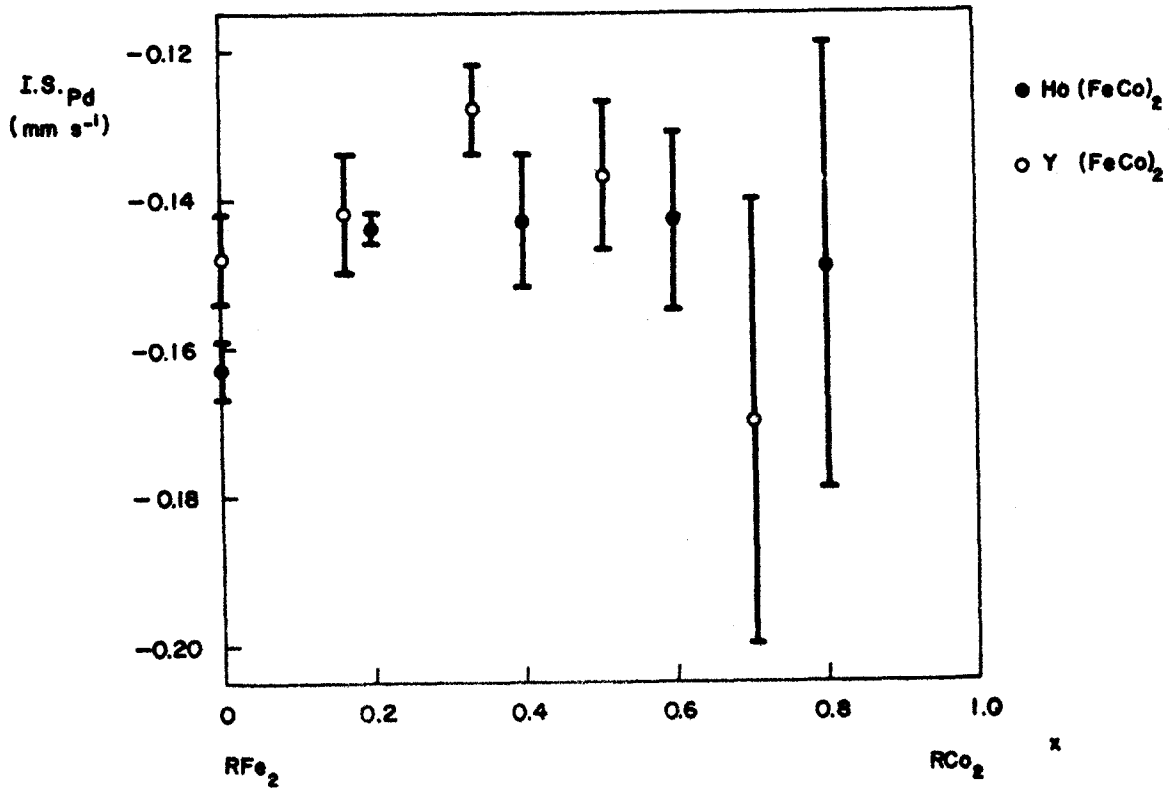


Fig. 4 - Variation of the ^{57}Fe isomer shifts with cobalt concentration in the $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Ho}(\text{Fe}_{1-x}\text{Co}_x)_2$ compounds ($T = 78^\circ\text{K}$).

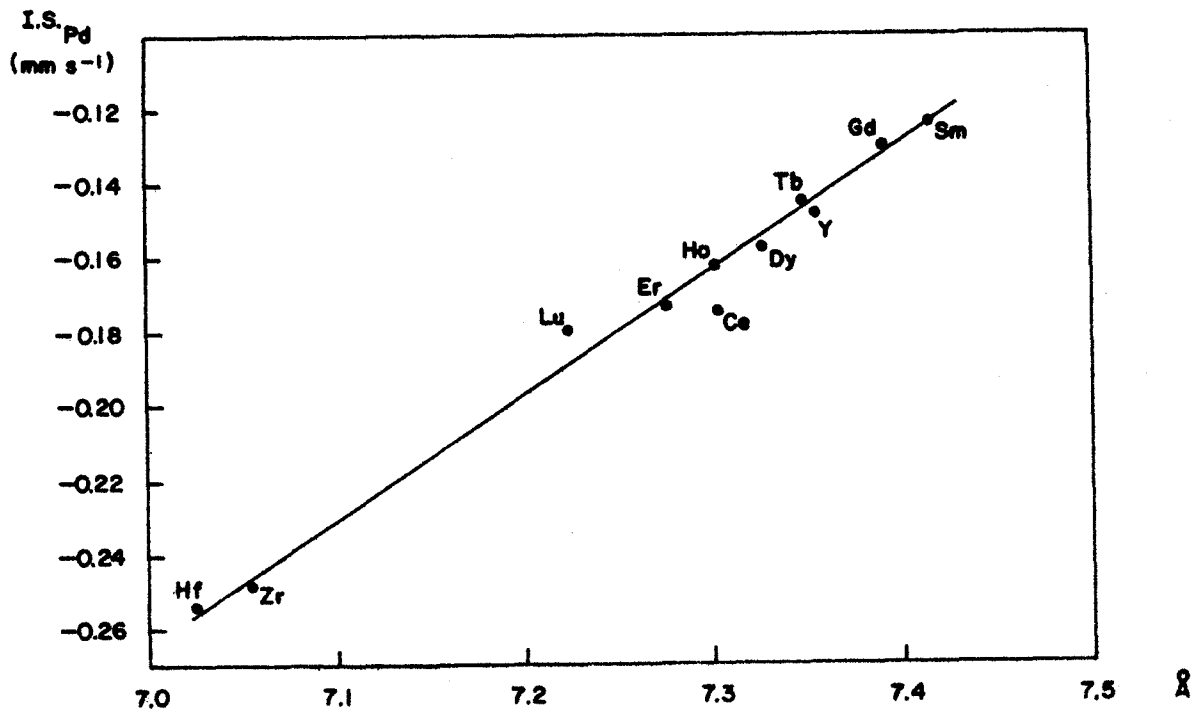


Fig. 5 - ^{57}Fe isomer shifts for the RFe_2 compounds at 78°K versus lattice parameters (room temperature values).

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