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► **To cite this version:**

L. Niesen, H. Wit. HYPERFINE INTERACTIONS OF RARE EARTH IONS SUBSTITUTIONALLY IMPLANTED IN IRON AND NICKEL. *Journal de Physique Colloques*, 1976, 37 (C6), pp.C6-639-C6-642. 10.1051/jphyscol:19766133 . jpa-00216648

**HAL Id: jpa-00216648**

**<https://hal.science/jpa-00216648>**

Submitted on 4 Feb 2008

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## HYPERFINE INTERACTIONS OF RARE EARTH IONS SUBSTITUTIONALLY IMPLANTED IN IRON AND NICKEL

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**Résumé.** — L'effet Mössbauer dans  $^{161}\text{Dy}$  (25,7 keV),  $^{166}\text{Er}$  (80,6 keV) et  $^{169}\text{Tm}$  (8,4 keV) a été utilisé pour étudier l'interaction hyperfine de cette fraction des ions terre rare qui a été implantée en substitution dans des matrices de fer et de nickel. Pour la majorité des systèmes les résultats donnent des valeurs fidèles pour le champ magnétique d'échange opérant au spin 4f. En outre, on a obtenu pour la première fois des résultats concernant le signe et la grandeur des potentiels de l'ordre quatre et six du champ cristallin électrique cubique en position d'un ion terre rare dans une matrice ferromagnétique.

**Abstract.** — The Mössbauer effect of  $^{161}\text{Dy}$  (25.7 keV),  $^{166}\text{Er}$  (80.6 keV) and  $^{169}\text{Tm}$  (8.4 keV) has been used to study the hyperfine interaction of the fraction of rare earth ions that are substitutionally implanted in iron and nickel. From the measurements reliable values for the magnetic exchange field  $B_{\text{exch}}$  acting on the 4f spin have been derived for most impurity-host combinations. For the first time, information was obtained about sign and magnitude of the fourth and sixth rank potential of the cubic crystalline electric field for a rare earth ion in a ferromagnetic host.

Mössbauer spectroscopy on rare earth isotopes implanted in iron and nickel has been shown to be a valuable tool for studying the hyperfine interaction of rare earth impurities in a ferromagnetic cubic host [1-4]. Roughly one half of the implanted ions appear to end up in substitutional lattice positions, as is witnessed also by channeling and PAC measurements [5-7]. The purpose of this paper is to investigate the hyperfine interaction of the substitutional fraction as found in our Mössbauer measurements on  $^{161}\text{Dy}$ ,  $^{166}\text{Er}$  and  $^{169}\text{Tm}$ , and to obtain information about the impurity-host exchange interaction and on the cubic crystalline electric field (CEF) acting on the rare earth electron spin.

The cubic CEF can be written as [8, 9] :

$$H_{\text{CEF}} = A_4 \langle r^4 \rangle \beta_J(O_4^0 + 5 O_4^4) + A_6 \langle r^6 \rangle \gamma_J(O_6^0 - 21 O_6^4) \quad (1)$$

whereby the quantization axis is chosen along the (1, 0, 0) direction of the crystal.  $\langle r^4 \rangle$  and  $\langle r^6 \rangle$  are radial integrals, and the  $O_n^m$  are spherical tensor operators.

Theoretical estimates for the coefficients  $A_4$  and  $A_6$  can be found, for instance, from a point charge calculation, but here  $C_4 \equiv A_4 \langle r^4 \rangle$  and  $C_6 \equiv A_6 \langle r^6 \rangle$  will be considered as parameters to be determined by experiment.

For numerical purposes (1) can be written as [9] :

$$H_{\text{CEF}} = W \left[ \frac{x}{F(4)} (O_4^0 + 5 O_4^4) + \frac{1 - |x|}{F(6)} (O_6^0 - 21 O_6^4) \right] \quad (2)$$

where  $F(4)$  and  $F(6)$  are multiplicative factors given in [8, 9].

The exchange interaction between the 4f spin and the polarized host electrons will be treated in the molecular field approximation :

$$H_{\text{exch}} = \mu_B \mathbf{B}_{\text{exch}} \cdot \mathbf{S}_{4f} = (g_J - 1) \mu_B \cdot \mathbf{B}_{\text{exch}} \cdot \mathbf{J} \quad (3)$$

In polycrystalline material and in the absence of an external field the exchange field will be oriented along the easy axis of magnetization. Taking this as the quantization axis, both interactions can be combined. In the case of Fe, which has a bcc structure, with the (1, 0, 0) direction as the easy axis, this yields.

$$H = W \left[ \frac{x}{F(4)} (O_4^0 + 5 O_4^4) + \frac{1 - |x|}{F(6)} (O_6^0 - 21 O_6^4) + 2 y J_z \right] \quad (4)$$

In the case of Ni, which has a fcc structure, with the (1, 1, 1) direction as the easy axis, we get

$$H = W \left[ \frac{x}{F(4)} \left( -\frac{2}{3} O_4^0 - \frac{40}{3} \sqrt{2} O_4^3 \right) + \frac{1 - |x|}{F(6)} \times \left( \frac{16}{9} O_6^0 - \frac{140}{9} \sqrt{2} O_6^3 + \frac{154}{9} O_6^6 \right) + 2 y J_z \right] \quad (5)$$

where  $y = (g_J - 1) \mu_B B_{\text{exch}} / 2 W$  measures the ratio of the exchange and the CEF interaction strengths. The wave functions of the  $2J + 1$  substates within the ground multiplet are completely determined by

the parameters  $x$  and  $y$ , while  $W$  acts merely as a scale factor. Any degeneration has been removed by the presence of the exchange field.

Apart from the case of an  $L = 0$  ground state, which will not be treated here, the 4f electrons are also responsible for the dominant part of the hyperfine interaction. Using first order perturbation theory, the magnetic and electric part of this contribution to the hfi can be written as [8] :

$$\begin{aligned} H_M &= g_N \mu_N B_{\text{hf}} I_z \\ &= 2 \mu_B g_N \mu_N \langle r^{-3} \rangle \times \\ &\quad \times \langle J \parallel N \parallel J \rangle \langle J_z \rangle \cdot I_z \quad (6) \end{aligned}$$

and

$$\begin{aligned} H_Q &= \frac{e^2 q_{4f} Q}{4 I(2I-1)} [3 I_z^2 - I(I+1)] \\ &= \frac{e^2 Q}{4 I(2I-1)} (1-R) \langle r^{-3} \rangle \langle J \parallel \alpha \parallel J \rangle \times \\ &\quad \times [3 \langle J_z^2 \rangle - J(J+1)] [3 I_z^2 - I(I+1)]. \quad (7) \end{aligned}$$

Values for  $\langle J \parallel N \parallel J \rangle$  and  $\langle J \parallel \alpha \parallel J \rangle$  can be found in [8, 9].  $\langle J_z \rangle$  and  $\langle J_z^2 \rangle$  can be found by diagonalization of (4) resp. (5) with  $x$  and  $y$  as parameters. If the exchange field dominates ( $y \gg 1$ ) one obtains  $|\langle J_z \rangle| = J$  and  $\langle J_z^2 \rangle = J^2$ , and the 4f contribution to the hfi is a maximum. This unreduced hfi is reasonably well known experimentally for the isotopes we studied [8, 12]. From our Mössbauer measurements at low temperatures we obtained in general lower values for both contributions, from which we calculate the reduction factors

$$R_M \equiv |\langle J_z \rangle| / J$$

and

$$R_Q = \frac{3 \langle J_z^2 \rangle - J(J+1)}{3 J^2 - J(J+1)}$$

for the electronic ground state.

Contributions to the magnetic hfi by s-electrons are absorbed in the unreduced value for  $B_{\text{hf}}$  as far as they are proportional to  $\langle J_z \rangle$  (core polarization, conduction electron polarization by the impurity). For Fe, we used estimates by Abragam and Bleaney [8] and by Hufner [13] respectively. The contribution to  $B_{\text{hf}}(s)$  from the iron host, estimated to be 0.27 MG [14], was accounted for in the determination of  $R_M$  and  $R_Q$  at low temperatures, and could be neglected in the analysis of the temperature dependence.

In the case of Ni,  $B_{\text{hf}}(s)$  was neglected because the first two contributions cancel for a large part and the contribution from the host is much smaller than in the case of Fe.

Calculation of the reduction factors  $R_M$  and  $R_Q$  as a function of the parameters  $x$  and  $y$  using eqs. (4) or (5) yields an area in the  $x - y$  plane which is consistent with the observed  $R_M$ , and a different area which is consistent with the measured value for  $R_Q$ . The overlap between these areas gives the region of  $x - y$  values which is allowed by the low temperature Mössbauer experiment. In a favourable case like  $^{169}\text{TmNi}$  this procedure led to a narrow range of allowed values for  $x$  and  $y$ . On the other hand, in the case of  $^{161}\text{DyNi}$  the overlap turned out to be quite large, although  $R_M$  and  $R_Q$  were accurately determined.

The temperature dependence of the hyperfine interaction can be described as well by (6) and (7), if it is assumed that the precession time of the Mössbauer nuclei is much longer than the correlation time of the 4f moment (fast relaxation). Then, one has to take the Boltzmann average of the expectation values  $\langle J_z \rangle$  and  $\langle J_z^2 \rangle$  of the  $2J + 1$  substates of the ground multiplet. The assumption of fast relaxation is justified experimentally by the absence of relaxation behaviour for the substitutional component in our spectra.

Fitting the temperature dependence of the hfi for those combinations of  $x$  and  $y$  which are allowed by the measurements at low temperatures yields in principle a unique set of parameters  $x$ ,  $y$  and  $W$ , from which the physically more relevant parameters  $C_4$ ,  $C_6$  and  $B_{\text{exch}}$  can be extracted. It turned out that  $B_{\text{exch}}$  could be obtained with reasonable precision in all the cases studied, while there remained ambiguity in the values of  $C_4$  and  $C_6$ .

**1. Results.** — Figure 1 shows a typical example of the measurements. The spectrum of  $^{161}\text{DyNi}$  measured at 5 K (upper spectrum) shows the presence of two components in the spectrum with about equal intensities, one of which is associated with Dy ions at regular lattice sites. The identification was made by means of an annealing sequence, in which the component associated with the substitutional site gradually disappeared. The same behaviour was found for the other isotopes in the nickel host. In the spectra of DyNi measured at higher temperatures the lines of the substitutional component remained narrow and the temperature dependence could be reasonably described by eqs. (6) and (7), indicating fast relaxation behaviour for this component.

In the Fe host the low-temperature spectra could be described assuming only one component to be present. However, the temperature behaviour of  $^{161}\text{DyFe}$  and  $^{169}\text{TmFe}$  could only be analyzed assuming the presence of at least two components, one of which showed fast relaxation behaviour. This was identified as being the substitutional component by means of a measurement at 77 K on an annealed source of  $^{161}\text{DyFe}$ , whereby this component had

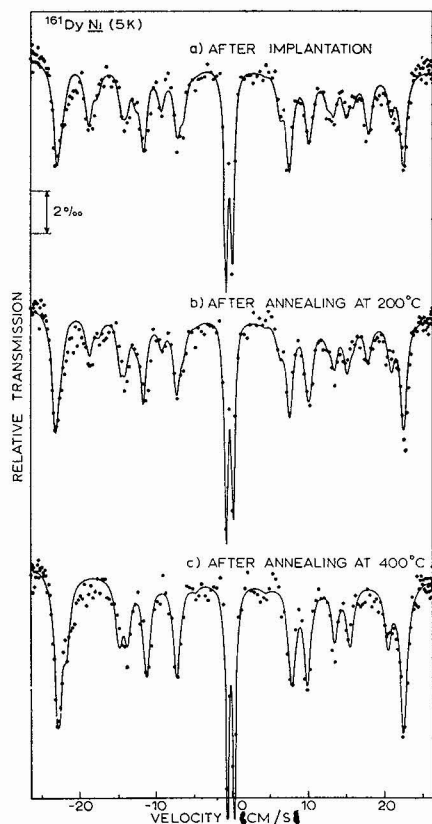


FIG. 1. — Mössbauer spectra of  $^{161}\text{DyNi}$  at 5 K, measured before and after annealing.

disappeared completely. For further details we refer to [3, 4].

The results of our measurements are summarized in table I and figure 2. Apart from the contribution from the least square fitting procedure, the error in the quantities  $g_N \mu_N B_{\text{hf}}$  and  $e^2 qQ/4$  contained also the uncertainty in the velocity scale. The errors assigned to the ratios  $R_M$  and  $R_Q$  reflect the error in the measured quantities as well as the uncertainties in the unreduced values for the magnetic and electric hfi. Specific remarks on the various systems follow below.

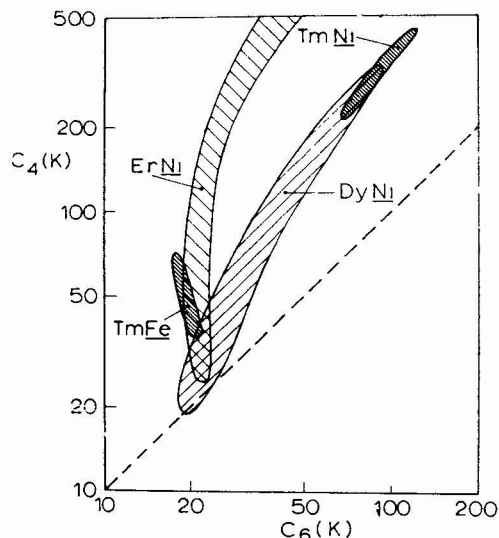


FIG. 2. — Allowed values for the crystal field parameters  $C_4 = A_4 \langle r^4 \rangle$  and  $C_6 = A_6 \langle r^6 \rangle$  for  $\text{DyNi}$ ,  $\text{ErNi}$ ,  $\text{TmNi}$  and  $\text{TmFe}$ .

1.  $^{161}\text{DyFe}$ . This is a typical case in which the exchange interaction dominates the behaviour of the 4f moment. The exchange field derived from the temperature dependence is slightly lower than in  $\text{DyFe}_2$ , in which the Dy ion is surrounded by 12 Fe neighbours :  $B_{\text{exch}} = 6.03 \text{ MG}$  [16].

2.  $^{166}\text{ErFe}$ . The results for  $R_M$  and  $R_Q$  at low temperatures indicate a small influence of the CEF, especially for the quadrupole interaction. We have not tried to investigate this further. The results at higher temperatures (up to 78 K) were analyzed assuming a negligible influence of the CEF and only one component in the spectra. No relaxation effects were observed, probably due to the limited temperature range in which the system could be studied. The error in  $B_{\text{exch}}$  is statistical. Due to the approximations made, the result is estimated to be reliable within 20 %.

3.  $^{169}\text{TmFe}$ . A further decrease of  $R_M$  and  $R_Q$  at low temperatures is observed which was analyzed

TABLE I

Results of Mössbauer measurements on rare earth ions substitutionally implanted in iron and nickel

Isotope	Host	$g_N \mu_N B_{\text{hf}}$ (cm/s)		$R_M$	$e^2 qQ/4$ (cm/s)		$R_Q$	$B_{\text{exch}}$ (MG)
		Exp.	Unreduced		Exp.	Unreduced		
$^{161}\text{Dy}$		4.31(2)	4.28	1.01(2)	2.76(4)	3.12	0.89(5)	5.49(15)
$^{166}\text{Er}$	Fe	2.83 <sup>5</sup> (2)	2.96	0.96(3)	0.288(9)	0.40	0.72(5)	3.7(2)
$^{169}\text{Tm}$		32.4(7)	36.6	0.89(4)	5.0(3)	7.8	0.63(8)	4.1(6)
$^{161}\text{Dy}$		3.28(2)	4.14	0.79(3)	1.66(6)	3.12	0.54(3)	0.68(10)
$^{166}\text{Er}$	Ni	1.769(15)	2.88	0.61(2)	0.114(11)	0.40	0.28(5)	
$^{169}\text{Tm}$		7.44(14)	35.4	0.22(2)	1.04(18)	7.8	0.13(3)	0.82(12)

using eqs. (4), (6) and (7). Combining the results with the temperature dependence of the hyperfine field for the substitutional site yields values for  $B_{\text{exch}}$ ,  $C_4$  and  $C_6$ . Again,  $B_{\text{exch}}$  is slightly smaller than the value 4.9 MG found for  $\text{TmFe}_2$  [17]. The value  $B_{\text{exch}} = 2.5$  MG found by Bernas and Gabriel [18] can only be regarded as an order of magnitude estimate.  $C_4$  and  $C_6$  turn out to be positive, whereas a point charge calculation (assuming 8 positive ligands) would give  $C_4 > 0$ ,  $C_6 < 0$ .

4.  $^{161}\text{DyNi}$ . In the nickel host, the exchange interaction and the CEF are of comparable magnitude, leading to an appreciable reduction of the hyperfine interaction. Although detailed measurements were made as a function of temperature, the results for  $C_4$  and  $C_6$  remained somewhat ambiguous (see Fig. 2). The exchange field, which could be obtained with reasonable precision, is surprisingly low compared to that in the iron host (ratio is 0.12 (2), as compared to the host magnetic moment ratio 0.28).

5.  $^{166}\text{ErNi}$ . Only a measurement at 4.2 K was performed. The allowed region for  $C_4$  and  $C_6$  is constructed assuming  $B_{\text{exch}} = 0.68$  MG, the value for  $^{161}\text{DyNi}$ . Another value for  $B_{\text{exch}}$  would shift this region parallel to the dashed line. Only  $C_6 > 0$  follows directly from the measurements.

6.  $^{169}\text{TmNi}$ . This is the only case in which the low temperature determination of  $R_M$  and  $R_Q$  gave rather unambiguous values for  $x$  and  $y$ . From a room temperature measurement  $B_{\text{exch}}$  was derived, yielding also  $C_4$  and  $C_6$ . The result for  $B_{\text{exch}}$  is in good agreement with that found for  $^{161}\text{DyNi}$ .

2. **Discussion** — To our knowledge the results presented in figure 2 are the first reliable determina-

tions of CEF parameters in ferromagnetic metals. In all cases we find both  $C_4$  and  $C_6$  to be positive and of the same order of magnitude. Unlike the case of Fe, for Ni the signs are in agreement with a simple point charge calculation similar to that given by Williams and Hirst [19]:  $C_4 \simeq 30$  K,  $C_6 \simeq 4$  K. This is a striking result, because nearly all fcc metal hosts produce  $C_4 < 0$ ,  $C_6 > 0$  at the rare earth ion [19, 20, 21]. Williams and Hirst [19], following a suggestion by Coles and Orbach, have explained this by the presence of an electron in a non-magnetic 5d virtual bound state (vbs) which is likely to be formed on the basis of charge screening effects. The cubic surroundings will split this state, with the  $5d_e(\Gamma_5)$  orbitals having lower energy than the  $5d_\gamma(\Gamma_3)$  orbitals. If this crystal field splitting is larger than the width of the vbs it will result in an appreciable negative contribution to  $C_4$ , which easily can be larger than the positive point charge contribution. However, this 5d state will have no influence on the  $C_6$  term. (For a more quantitative discussion, see Chow [22] and Dixon [23].)

Our result that  $C_4 > 0$  implies that the mechanism given above is not able to change the sign of  $C_4$ , which possibly is caused by a larger width of the 5d vbs in Ni than in the noble metals.

The change of sign of  $C_6$  compared to a point charge calculation in the system  $^{169}\text{TmFe}$  is more difficult to understand. In this respect it is interesting to note that also for Dy and Er ions in Pd (a 4d transition metal) the sign of  $C_6$  is opposite to that of the point charge calculation [24, 25, 26]. In principle this can only be due to the conduction electrons, whose wave functions have to be orthogonal to the occupied 4f states of the rare earth ion. This introduces an extra contribution to  $C_6$ , as has been shown by Dixon [23]. It is not clear, however, if this mechanism is able to produce the necessary sign change of  $C_6$ .

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