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A Mössbauer-effect study of a series of $R_2Fe_{14}C$ hard magnetic materials

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The ^{57}Fe Mössbauer-effect spectra of the series of hard magnetic materials, $R_2Fe_{14}C$, where R is Nd, Gd, Tb, Dy, Ho, and Lu, have been measured at 295 K. All of these carbides exhibit uniaxial magnetic anisotropy. The spectra resemble those obtained for the related $R_2Fe_{14}B$ compounds and have been fit with the model used earlier for $Nd_2Fe_{14}B$. The magnitude of the hyperfine field on each site, as a function of rare earth, parallels the Curie temperature; the maximum hyperfine fields and the maximum Curie temperature are observed for $Gd_2Fe_{14}C$. A linear correlation is observed between the hyperfine fields on the six sites in the analogous borides and carbides; however, these fields are systematically smaller in the carbides. The decrease in the tetragonal unit cell *c*-axis length in the carbides apparently reduces the exchange interactions between the 8*j* and 16*k* iron layers and hence reduces the moments. The isomer shift on each site decreases as the atomic number of the rare earth increases, whereas the quadrupole interactions are independent of rare earth.

The series of $R_2Fe_{14}C$ carbides is less well studied than the analogous $R_2Fe_{14}B$ borides both because the magnetic properties of the carbides are slightly less attractive for use as permanent magnets and because the metallurgy of the carbides^{1,2} is more difficult. However, the carbides offer some practical advantages, because they require less time and fewer labor-consuming steps in the manufacturing procedures of permanent magnets. Furthermore, a ternary $R_2Fe_{17}C_x$ phase forms under similar conditions to those used for the formation of the $R_2Fe_{14}C$ phase. The magnetic properties of the $R_2Fe_{17}C_x$ carbides^{2,3} are of some interest for permanent magnet manufacture.

Herein, we present a Mössbauer-effect study, at 295 K, of $R_2Fe_{14}C$, where R is Nd, Gd, Tb, Dy, Ho, and Lu, and compare these results with earlier work⁴⁻⁸ on the analogous borides.

The $R_2Fe_{14}C$ compounds, where R is Nd, Gd, Tb, Dy, Ho, and Lu, were prepared as described elsewhere.^{1,2,9} The room-temperature Mössbauer spectra were measured on a constant-acceleration Harwell spectrometer, which utilized a Rh-matrix ^{57}Co source and was calibrated at room temperature with natural α -Fe foil.

The 295 K Mössbauer spectra of the $R_2Fe_{14}C$ compounds are shown in Fig. 1. All these carbides, like their analogous borides, have axial magnetic anisotropy^{1,9} and give Mössbauer spectra very similar to those of the borides.^{4,5} The solid lines in Fig. 1 are the result of a least-squares fit obtained by a procedure which has been described earlier.^{4,5} In these fits, each of the six sextets has a relative area proportional to the corresponding crystallographic site occupancy and all 36 lines have the same line-width. We assume for each iron crystallographic site both

that the orientation of the principal axis of the electric-field gradient tensor is determined by the positions of the rare-earth near neighbors and that the asymmetry parameter is zero. Therefore, for each sextet there are only three variable parameters, the hyperfine field, the quadrupole interaction, and the isomer shift. The hyperfine parameters resulting from these fits are given in Table I.

The six sextets were assigned to the six crystallographic sites on the basis of their relative spectral areas and on the basis of the number of iron near neighbors for a site, as determined by a Wigner-Seitz cell analysis.^{10,11} In this assignment, the larger the number of iron near neighbors, the larger is the observed hyperfine field.

The present assignment of the six components to the six crystallographic sites is identical to that used earlier for the analogous borides.^{4,5} The fits shown in Fig. 1 indicate that the model used for the borides can be successfully extended, without fundamental change, to the carbides. This model and assignment agree with the assignment used by Erdmann *et al.*⁶ to analyze the NMR and Mössbauer spectra of $Gd_2Fe_{14}C$. The assignment in Table I differs from the assignment reported for $Nd_2Fe_{14}C$,⁷ $Gd_2Fe_{14}C$, and $Lu_2Fe_{14}C$,⁸ only in that the 4*e* and 4*c* site assignment is reversed. Other than for this reversed assignment, the hyperfine fields and isomer shifts agree well with the earlier work.^{7,8}

Figure 2 gives a plot of the hyperfine fields at the six crystallographic sites and the weighted average hyperfine field as a function of the rare-earth atom. The behavior of the hyperfine field parallels that of the Curie temperature.⁹ The largest hyperfine field is observed for gadolinium, which has the largest magnetic moment; a similar conclu-

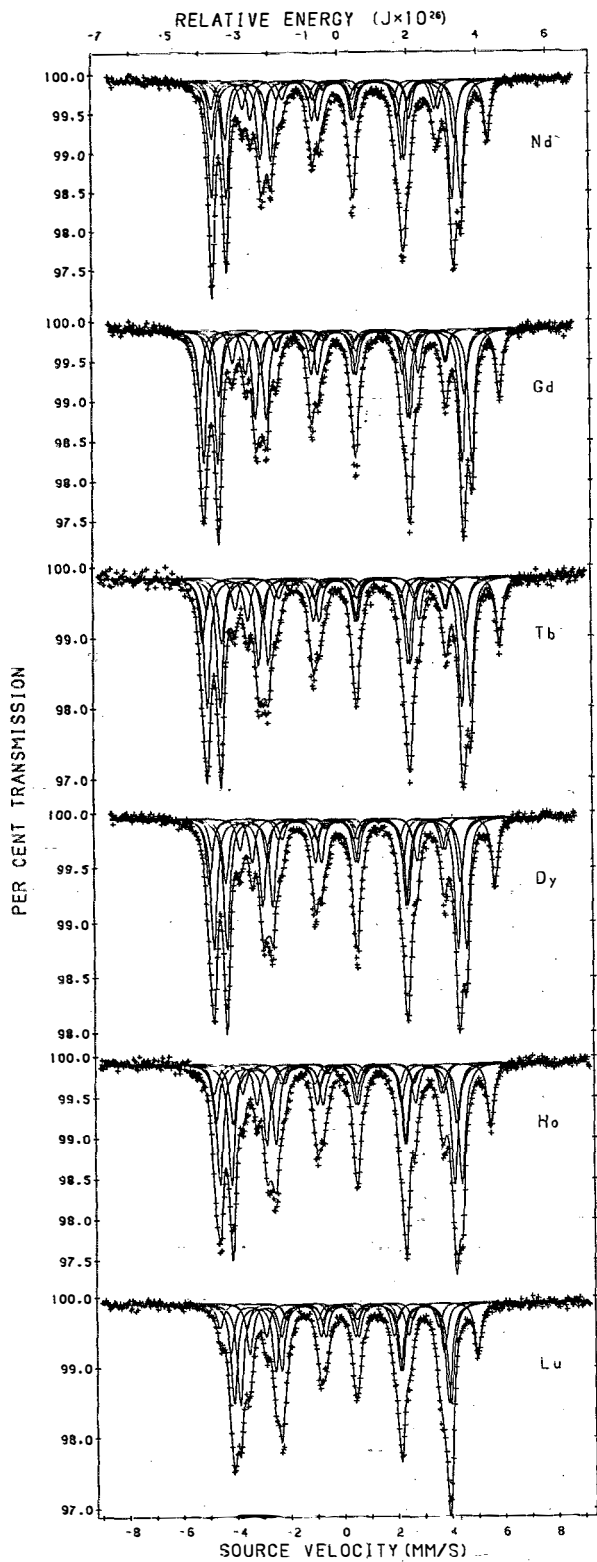


FIG. 1. Mössbauer spectra of $R_2Fe_{14}C$, where R is Nd, Gd, Tb, Dy, Ho, and Lu, obtained at 295 K.

sion was reached for the borides.⁵ The right-hand scale of Fig. 2 gives the magnetic moment as determined from the measured hyperfine field, by using a scaling factor of $150 \text{ kOe}/\mu_B$. The average magnetic moment at 295 K deduced from the Mössbauer data on $Nd_2Fe_{14}C$ is $1.83\mu_B$, a value smaller than the $2.44\mu_B$ obtained from a neutron-

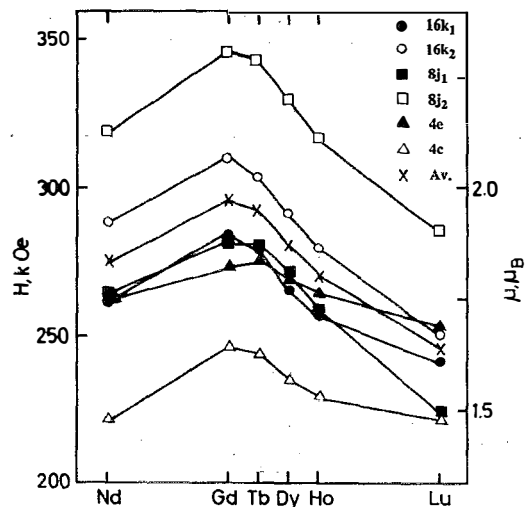


FIG. 2. Hyperfine fields at the six crystallographic sites and the weighted average hyperfine field in $R_2Fe_{14}C$ as a function of the rare-earth atom.

diffraction measurement.¹¹ Although the order of the hyperfine fields follows exactly the order of the magnetic moments as measured by neutron diffraction on $Nd_2Fe_{14}C$, the moments obtained from Mössbauer studies are substantially smaller than the moments obtained from neutron diffraction. However, the average moment of $1.83\mu_B$ obtained for $Nd_2Fe_{14}C$ agrees well with the moment of $1.97\mu_B$ obtained by Mössbauer studies on $Nd_2Fe_{14}B$.⁴

In the carbides, the hyperfine fields are 15–25 kOe smaller than in the analogous borides. Erdmann *et al.*⁶ also observed a decrease in the average hyperfine field of $Gd_2Fe_{14}C$ relative to that in $Gd_2Fe_{14}B$. But unlike their results, our results, which are based on data from four different compounds, do not show any correlation between the decrease in the hyperfine field and the number of near-neighbor carbon or boron atoms. Indeed, as shown in Fig. 3, we see the linear relationship $H_B = 0.92H_C + 4.42$ be-

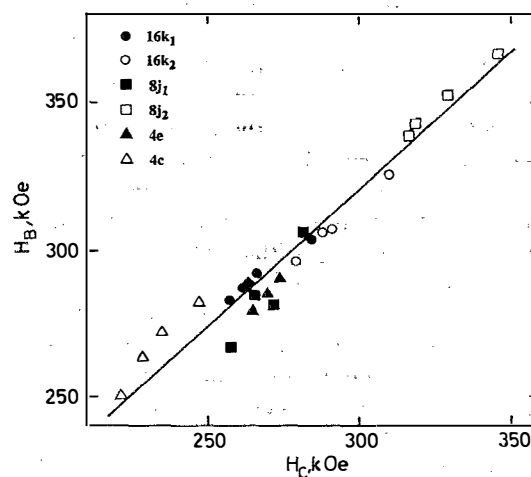


FIG. 3. The 295-K linear correlation between the hyperfine fields at the six crystallographic sites in $R_2Fe_{14}C$ and $R_2Fe_{14}B$, where R is Nd, Gd, Dy, and Ho.

TABLE I. Mössbauer hyperfine parameters of R₂Fe₁₄C obtained at 295 K.

	R	Site						Average
		16k ₁	16k ₂	8j ₁	8j ₂	4e	4c	
<i>H</i> (kOe)	Nd	261.4	288.0	265.3	318.7	262.8	222.0	275.0
	Gd	283.0	309.3	283.0	345.7	273.8	246.6	296.2
	Tb	279.0	303.6	280.1	343.0	277.1	242.9	292.6
	Dy	266.7	290.9	270.6	329.7	269.4	234.0	281.0
	Ho	257.5	279.1	258.0	316.9	264.8	229.2	270.7
	Lu	241.0	250.0	224.6	284.8	252.8	221.1	246.9
<i>eQV_{zz}</i> /2 (mm/s)	Nd	0.12	0.25	0.33	0.78	-0.67	-0.02	
	Gd	0.12	0.31	0.36	0.69	-0.67	-0.02	
	Tb	0.12	0.29	0.35	0.70	-0.67	-0.02	
	Dy	0.12	0.30	0.28	0.69	-0.65	-0.02	
	Ho	0.11	0.29	0.30	0.67	-0.70	-0.02	
	Lu	0.11	0.29	0.35	0.67	-0.75	-0.02	
δ^a (mm/s)	Nd	0.016	-0.113	-0.060	0.102	-0.130	0.040	-0.028
	Gd	0.005	-0.118	-0.064	0.100	-0.115	0.030	-0.033
	Tb	-0.010	-0.120	-0.060	0.090	-0.160	0.010	-0.044
	Dy	-0.005	-0.125	-0.070	0.085	-0.140	0.010	-0.044
	Ho	-0.030	-0.143	-0.070	0.080	-0.160	-0.020	-0.061
	Lu	-0.040	-0.150	-0.070	0.060	-0.180	-0.050	-0.072
θ		17.8°	32.9°	2.5°	11.5°	0°	90°	

^aAll isomer shifts are measured relative to room temperature α -Fe foil.

tween the hyperfine fields at each of the six crystallographic sites in the Nd, Gd, Dy, and Ho carbides, H_C , and in the analogous borides, H_B . This linear behavior supports the equivalent assignment in both series of compounds and shows that the replacement of boron by carbon has a long-range rather than a short-range effect. This follows because the iron 16k₁ and 4e sites, which have one and two boron or carbon near neighbors, respectively, as well as the remaining sites, which have no boron or carbon near neighbors, all show the same linear correlation in their hyperfine fields (Fig. 3). Hence, the average reduction in the hyperfine fields in the carbides, relative to the borides, cannot be due solely to near-neighbor effects as proposed by Erdmann *et al.*⁶ In going from R₂Fe₁₄B to R₂Fe₁₄C, the average contraction to the tetragonal unit-cell *a* axis is $2.6 \times 10^{-2}\%$, whereas the *c*-axis contraction is 1.5%, i.e., a 57 times larger contraction along the *c* axis.^{9,12} Hence, it seems that the replacement of boron by carbon in the unit-cell basal plane reduces the separation of the "layers of iron," which contain the 8j and 16k iron sites. Apparently, this reduction leads to a decrease in the exchange interactions between these layers and, hence, to the smaller hyperfine fields and moments observed in the carbides.

The quadrupole interactions on the six crystallographic sites are independent of the rare earth in the R₂Fe₁₄C compounds, as shown in Table I.

The weighted average isomer shift (Table I) decreases as the atomic number of the rare earth increases. This behavior may be understood in terms of the variation of the *s*-electron density at the iron nucleus. Because of the increase in the number of 4*f* electrons and the decrease in the unit-cell volume in going from Nd₂Fe₁₄C to Lu₂Fe₁₄C, the total electron density increases by 14% from 523 to 596 electrons/nm.³ There is a linear correlation $\delta = 0.431$ mm/s - (0.455 mm/s)*x* of the isomer shift with the unit-

less electron density *x* normalized to that in Nd₂Fe₁₄C. This linear dependence shows that a decrease in the isomer shift of 0.05 mm/s corresponds to an increase of about 5% in the 4*s*-electron density at the iron nucleus¹³ in going from Nd₂Fe₁₄C to Lu₂Fe₁₄C. Hence, the 14% increase in the total electron density in the unit cell yields a 5% increase in the 4*s*-electron density at the iron nucleus.

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