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Mössbauer study of the hyperfine interaction of ^{57}Fe in $Y_{1-s}Co_{5+2s}$ and related compounds

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The magnetic and electric hyperfine interaction and the relative fractions of dilute ^{57}Fe nuclei on the four Co sites of $Y_{1-s}Co_{5+2s}$ have been investigated by Mössbauer spectroscopy as a function of the relative number s of Y atoms substituted by Co dumbbells. We also report Mössbauer measurements of ^{57}Fe in $GdCo_5$, $SmCo_5$, and Sm_2Co_{17}(rh). The s dependence of the relative Mössbauer fractions of $^{57}Fe{:}Y_{1-s}Co_{5+2s}$, together with previous neutron diffraction results, allows an experimental site-hyperfine field assignment. The Fe atoms strongly favor the dumbbell sites at the expense of sites $6l$ of the hexagon surrounding the Co pair, while sites $2c$ and $3g$ are randomly occupied. In stoichiometric RCo_5 ($R=$Y, Sm, Gd) we observe a sizable dumbbell concentration, which is probably caused by the precipitation of R_2Co_{17} favored by the impurity nature of the Mössbauer probe. With the increasing number of nearest Co neighbors, the magnetic hyperfine field passes from site $3g$ through a minimum at site $2c$ towards the maximum $H_{hf}=31.5$ T at the dumbbell site. The $4f$ contribution to the magnetic hyperfine field is small; the changes upon substitution of Y by $R=$Gd, Sm are of the order of 10%. [S0163-1829(98)09117-6]

I. INTRODUCTION

Intermetallic compounds R_xM_y of rare earth (R) and $3d$-transition metals $M=$Fe, Co, Ni, and Mn have attracted considerable interest in the past because of their complex magnetic properties that arise from the coexistence of the magnetic moments produced by the highly localized $4f$ electrons of the rare earth and by the itinerant $3d$ electrons of the transition metals.[1,2] Measurements of the magnetic-hyperfine interaction (hfi) at the $3d$ site for different $3d$ and $4f$ constituents as function of the composition are an important source of information on the f-f, d-d, and f-d exchange coupling in these magnetic systems. The R_xFe_y compounds have therefore been extensively studied by ^{57}Fe Mössbauer spectroscopy.[3–7]

Only in a few cases, ^{57}Fe Mössbauer spectroscopy has been extended to compounds with $M=$Co, Ni, and Mn, although it appears quite likely that dilute ^{57}Fe substitutes the $3d$ constituents.[8–19] The existence of several nonequivalent d sites in most $3d$-$4f$ compounds and a possible site preference of ^{57}Fe makes it difficult to establish an unambiguous relation between the measured hyperfine parameters and the available lattice sites. In most cases, the site-hyperfine field assignment is based on assumptions such as, e.g., a proportionality between the hyperfine field and the number of nearest $3d$ neighbors and under these circumstances the extraction of finer details of the exchange interaction becomes clearly problematic.

In this context the compound RCo_5 has attracted our interest because its properties allow a controlled variation of the site intensities—a feature that can be exploited for an experimental site-hyperfine field identification. The compound RCo_5 crystallizes in the $CaCu_5$ structure. At elevated temperatures (~750–1200 °C) this structure exists over a considerable range of Co concentrations and when rapidly quenched to room temperature RCo_{5+x} compounds are of a single phase maintaining the $CaCu_5$ structure.[1,20,21] The homogeneity region varies with the R element; in the case of $R=$Y, the $CaCu_5$ structure has been reported[22] to exist from $YCo_{4.5}$ to YCo_6. Pareti, Solzi, and Marusi[23] even give an upper limit of $YCo_{7.3}$. A study of the lattice parameter variation in $ErCo_{5+x}$, x-ray crystal structure analysis of $ErCo_{5.75}$, and neutron diffraction studies of YCo_{5+x} (Refs. 22 and 24) have led to the conclusion that in the region of Co excess some R atoms of the $CaCu_5$ structure are substituted by pairs of Co atoms (see Fig. 1), which can be expressed by the formula $R_{1-s}Co_{5+2s}$, where s describes the number of substitutions [x and s are related by $s=x/(7+x)$]. In RCo_{5+x} the Co dumbbells are randomly distributed. When $\frac{1}{3}$ of the R atoms are substituted, one reaches the R_2Co_{17} structure with an ordered Co dumbbell arrangement. It is still unclear whether the substitution scheme for the Co-defect region (RCo_{5+x} with $x<0$) involves Co vacancies or the disordered substitution of one Co by one R atom.[23]

For the Co-excess region of $R_{1-s}Co_{5+2s}$ the $CaCu_5$ structure contains four different Co sites[1] (see Fig. 1): sites $2c$ and $3g$ of stoichiometric RCo_5, the dumbbell site $2e$, and site $6l$ in the Co hexagon surrounding the dumbbell, which is a consequence of the local distortion introduced by the Co pair. The distribution of distances between sites $3g$ and $2c$, respectively, and the nearest Co pair will lead to a hyperfine-field distribution for sites $3g$ and $2c$. If one assumes that the distribution widths are small compared to the average field, one expects the Mössbauer spectrum of ^{57}Fe in $R_{1-s}Co_{5+2s}$ to contain four components or subspectra (denoted in the following as Fe I to Fe IV) with different hfi parameters and possibly different line widths.

The fractions (or relative areas) F_i ($i=$I, . . . ,IV; $\Sigma_i F_i=1$) of these components are determined by the relative intensities I_i of the available Co sites and a possible ^{57}Fe site preference, which in the following shall be quantified by factors P_i ($i=$I, . . . ,IV) with $P_i=1$ for random occupation. The s dependence of the site intensities $I_i(s)$ is easily calculated (see Table I). Assuming in a first approximation that

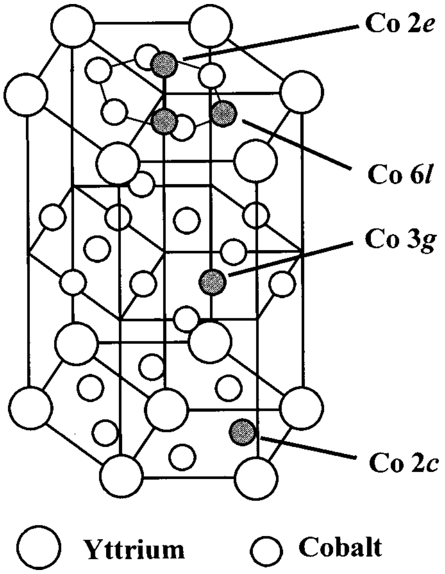

FIG. 1. The crystal structure of $Y_{1-s}Co_{5+2s}$. Sites $2c$ and $3g$ are the Co sites of stoichiometric YCo_5. The Co sites $2e$ and $6l$ appear in $Y_{1-s}Co_{5+2s}$ when Co excess causes the substitution of Y atoms by Co dumbbells.

the site preferences P_i are independent of the number s of substitutions, the Mössbauer fractions and the site intensities are related by

$$F_i(s)=P_i I_i(s+s_0). \tag{1}$$

The parameter s_0 allows for the possibility of a finite dumbbell concentration in stoichiometric RCo$_5$. It is well established that RCo$_5$ is metastable at room temperature and that Co dumbbells are important for its stability. Schweizer and Tasset[24] and Givord *et al.*[25] have reported values of $s_0=0.046(1)$ and $s_0\approx 0.03$ for a YCo_5 and $SmCo_5$ single crystal, respectively.

The finite homogeneity range of RCo$_{5+x}$ allows a controlled variation of the number of substitutions s and thus of the site intensities $I_i(s)$ with the stoichiometry x without changing the lattice structure. The resulting changes of the Mössbauer fractions $F_i(s)$ carry valuable information for the site-hyperfine field identification. It is easy to see from Fig. 1 that the number of dumbbell sites $2e$ and sites $6l$ increases, that of sites $2c$ and $3g$ decreases with increasing substitution parameter s. Assuming validity of Eq. (1), fractions with negative slope $dF_i(s)/ds$ can therefore immediately be attributed to either site $3g$ or $2c$, those with positive slope to either site $6l$ or $2e$, and when combined with information on the site preferences from other sources, the measurement of the Mössbauer fractions as a function of the number of substitutions leads to an experimental site-hyperfine field assignment. In this paper, we report such an experiment for the system ^{57}Fe:YCo$_{5+x}$.

We have carried out a series of ^{57}Fe Mössbauer measurements in YCo$_{5+x}$ in the range $-0.1\leqslant x\leqslant 1$. For $x<1$, the site intensities $I_i(s)$ are in a good approximation linear functions of s (see Table I). The valence electron configuration of yttrium is very similar to that of R atoms; it carries, however, no $4f$-magnetic moment. YCo_5 is a ferromagnet with an easy c axis and a Curie temperature of 920 K. The magnetic moments localized at the $2c$ and the $3g$ site have been determined by polarized neutron diffraction[22] to be $\mu=1.77\ \mu_B$ and $1.72\ \mu_B$, respectively. For information on the $4f$ contribution to the magnetic hyperfine interaction we have performed measurements on the compounds $GdCo_5$ and $SmCo_5$, which are also ferromagnets with the magnetic moments parallel to the c axis. Differences between our results for ^{57}Fe:RCo$_5$ (R=Y, Gd, Sm) and those of Nowik *et al.*[13] for ^{57}Fe:SmCo$_5$ have motivated a study of ^{57}Fe in Sm_2Co_{17} (rhombohedral of Th_2Zn_{17} type).

II. EXPERIMENTAL DETAILS

Intermetallic compounds YCo$_{5+x}$ with Co concentrations $x=-0.1$, 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0, $GdCo_5$, $SmCo_5$, and Sm_2Co_{17} with 1 at. % of the Co atoms substituted by ^{57}Fe were produced by arc melting of the metallic constituents on a water-cooled copper block and ground to a powder in an Ar atmosphere.

In the case of YCo$_{5+x}$ and $GdCo_5$ the losses in the sample mass after melting were of the order of 0.5 wt. %, which in the worst case, assuming that either only Co or only the R constituent is lost, corresponds to an uncertainty of the stoichiometry of $-0.04\leqslant\Delta x\leqslant 0.11$ or of the substitution parameter $-0.005\leqslant\Delta s\leqslant 0.015$. Considering that Y and Co have practically the same melting point, boiling point, and enthalpy of vaporization, the worst case—preferential loss of one constituent—appears unlikely and the uncertainty of the substitution parameter is therefore probably much smaller than the above estimate.

In the case of the Sm compounds melting produced systematically larger losses of 3–5 wt. %, which can be attributed to the relatively low Sm boiling point (1991 °C). For the Sm compounds we therefore started the sample preparation with a slight Sm excess ($\sim$5 at. %). For $SmCo_5$ the worst case uncertainty of the substitution parameter is $-0.05\leqslant\Delta s\leqslant 0.05$. However, as we increased the initial quantity of Sm to compensate for the total loss, the actual composition is probably close to $SmCo_{5.0}$.

X-ray diffraction measurements confirmed the $CaCu_5$ structure of all RCo$_5$ compounds. Sm_2Co_{17} was shown to be of the rhombohedral Th_2Zn_{17} type. In all cases, the lattice parameters were in agreement with the literature. In the x-ray diffraction patterns of RCo$_5$, reflections belonging to R_2Co$_{17}$ and R_2Co$_7$ were not detected. However, the lattice structures of RCo$_5$ and R_2Co$_7$ are closely related and their diffraction patterns therefore very similar; the main reflections are almost identical.[26] For YCo$_{5+x}$ we observed a decrease of the lattice parameter a [$a(x=0)=4.946(4)$ Å] and an increase of the parameter c [$c(x=0)=3.976(8)$ Å] with increasing x such that the axial ratio c/a increases from $c/a=0.804(2)$ at $x=0$ to $c/a=0.820(2)$ at $x=1$, which agrees well with the previous results of Deportes *et al.*[27] When parts of the $YCo_{5.6}$ and YCo_6 samples were annealed at 1000 °C for 22 h and slowly cooled to room temperature, the c/a ratio decreased and reflections pertaining to Y_2Co_{17} appeared in the x-ray pattern, indicating the decomposition into Y_2Co_{17} and Y_2Co_7.

The Mössbauer spectra were taken with a ^{57}Co:Rh single-line source, with source and absorber at 77 K. In all cases the absorbers were used as cast without any further heat treat-

TABLE I. The dependence of the relative intensities $I_i(s)$ of the sites $3g$, $2c$, $6l$, and the dumbbell site $2e$ in the $CaCu_5$ structure of $Y_{1-s}Co_{5+2s}$ on the substitution parameter s and the experimental s dependence of the relative intensities $F_i(s)$ of the four components Fe I, II, III, and IV of the ^{57}Fe:$Y_{1-s}Co_{5+2s}$ Mössbauer spectra. The relation $F_i(s)=P_iI_i(s+s_0)$ [Eq. (1)] has been used to calculate the site reference P_i and the dumbbell concentration s_0 of nominal YCo_5 from the experimental intensities $F_i(s)$ for $i=$II, III, IV. The value given for P_{3g} has been calculated from $F_{\mathrm{I}}(s)$ with the dumbbell concentration s_0 fixed to $s_0=0.12$. In the case of the components Fe III and IV the data allow two different assignments. The assignment favored by information on the site preference from a neutron diffraction experiment (Ref. 33) is marked in bold. Column I gives for each site the volume V_{WS} of the Wigner-Seitz cells calculated using radical planes (Ref. 37).

Lattice site i	Rel. intensity $I_i(s)$	Subspectrum Fe i	Fraction $F_i(s)=P_iI_i(s+s_0)$	P_i, s_0
Co $3g$	$3/(5+2s)$	Fe I	$0.56(1)-0.47(23)s$	$P_{3g}=0.98(7)$
$V_{\mathrm{WS}}=$	$\approx 0.6-0.24s$			
11.69 Å^3				
Co $2c$	$(2-6s)/(5+2s)$	Fe II	$0.24(2)-1.31(15)s$	$P_{2c}=0.96(12)$
$V_{\mathrm{WS}}=$	$\approx 0.4-1.36s$			$s_0=0.11(2)$
10.91 Å^3				
Co $6l$	$6s/(5+2s)$	Fe III	$0.13(1)+1.18(7)s$	$P_{6l}=0.98(6)$
$V_{\mathrm{WS}}=$	$\approx 1.2s$			$s_0=0.11(1)$
11.51 Å^3		**Fe IV**	$0.07(2)+0.52(14)s$	$P_{6l}=0.43(12)$
				$s_0=0.13(5)$
dumbbell	$2s/(5+2s)$	**Fe III**	$0.13(1)+1.18(7)s$	$P_{2c}=2.95(17)$
Co $2e$	$\approx 0.4s$			$s_0=0.11(1)$
$V_{\mathrm{WS}}=$		Fe IV	$0.07(2)+0.52(14)s$	$P_{2c}=1.30(35)$
12.01 Å^3				$s_0=0.13(5)$

ment. The spectra of ^{57}Fe:YCo_{5+x} for the Co concentrations $x=-0.1$, 0,0, 0.4, and 0.8. are shown in Fig. 2; those of ^{57}Fe in $SmCo_5$, $GdCo_5$, and Sm_2Co_{17}, respectively, are shown in Fig. 3.

III. DATA ANALYSIS AND RESULTS

In the data analysis a superposition of four subspectra Fe I, II, III, and IV with different hyperfine parameters and fractions F_i was fitted to the measured spectra. As the Co sites have noncubic symmetry, an electric-field gradient (EFG), for some sites possibly axially asymmetric, is expected to act on the probe nuclei in addition to the magnetic hyperfine field. The $I=\frac{3}{2}$ excited state of ^{57}Fe is therefore subject to a combined magnetic and electric hyperfine interaction leading to four nonequidistant hyperfine levels. The positions and intensities of the six Lorentzian lines of each subspectrum were calculated by numerical diagonalization of the Hamiltonian of a combined hyperfine interaction, which in the most general case depends on five parameters:[28] the magnetic frequency $\nu_m=g\mu_NH_{\mathrm{hf}}/h$, the quadrupole interaction (QI) parameter eQV_{zz}, the asymmetry parameter of the EFG tensor $\eta=(V_{xx}-V_{yy})/V_{zz}$ and the Euler angles θ,ϕ, which describe the orientation of the hyperfine field H_{hf} in the coordinate system defined by the principal axes of the EFG tensor V_{ii} $(i=x,y,z)$.

As first pointed out by Karyagin[29] and discussed, e.g., by Dabrowski, Piekoszenski, and Suwalski,[30] in the most general case of a combined interaction the analysis of Mössbauer spectra for the spin $I=\frac{3}{2}$ and powder samples faces an ambiguity problem: Since the trace of the interaction matrix vanishes $(\Sigma_{i=1,4}E_i=0)$ only three of the four energy eigenvalues E_i for $I=\frac{3}{2}$ are linearly independent. The magnetic hyperfine field is determined by the splitting of the $\frac{1}{2}$ ground state. The four hfi parameters $(eQV_{zz},\ \eta,\ \theta,\ \phi)$ of the excited state must then satisfy only three equations and one can therefore find different sets $(eQV_{zz},\ \eta,\ \theta,\ \phi)$ that correspond to different physical situations but lead to the same energy eigenvalues. Consequently, if no information on one of these parameters is available from other sources, one parameter has to be fixed in the analysis to some arbitrary value. We have fixed the azimuthal angle, which is the parameter with the weakest effect on the spectrum to $\phi=0$.

In the fits, the hyperfine parameters H_{hf}, $eQV_{zz}/4$, η, θ, the isomer shift δ, the line width Γ, and the relative fractions F_i of the four sites were adjusted to the experimental data. The subspectra Fe I and Fe II indicate the presence of a strong QI that cannot be treated as a small perturbation of the magnetic interaction. For these sites $eQV_{zz}/4$, η, and θ were treated as free parameters. Simulations of theoretical spectra for different values of ϕ showed that in the present case the assumption $\phi=0$ has little effect on the results obtained for the QI and the angle θ of components I and II.

For the components Fe III and Fe IV the deviations from the equidistant splitting of a pure magnetic interaction caused by the quadrupole interaction were rather small and

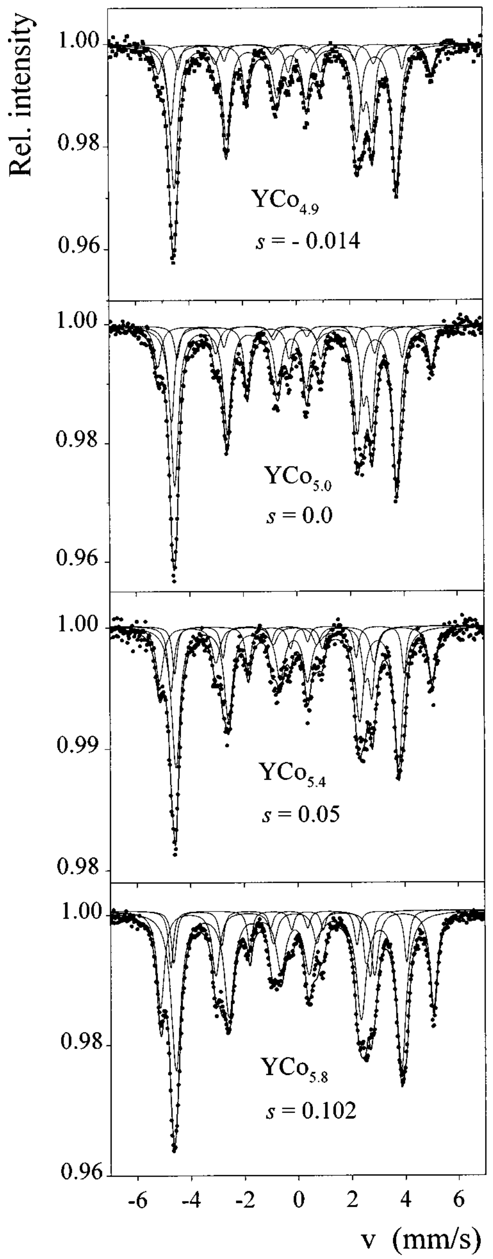

FIG. 2. Mössbauer spectra of ^{57}Fe in YCo_{5+x} at $T = 77$ K for different stoichiometries x and their decomposition into four components.

therefore only the QI parameter $eQV_{zz}/4$ was determined for these subspectra. The values of $eQV_{zz}/4$ given in Table II for Fe III and Fe IV were obtained with the assumption $\eta = 0$, $\theta = 0$, $\phi = 0$. The fits and the decomposition of the spectra of ^{57}Fe:YCo_{5+x} into the four components are given by the solid lines in Fig. 2.

The hfi parameters of the weakest component, Fe IV of YCo_{5+x}, could not be determined unambiguously. We found two descriptions (fits A and B) with practically the same χ^2 value but different hfi parameters for component Fe IV: $H_{\mathrm{hf}} = 26{,}2$ and 30,2 T, $eQV_{zz}/4 = 0{,}01$ and 0,27 mm/s, and $\delta = -0{,}14$ and $+0{,}11$ mm/s for fit A and B, respectively. Fit A places the outer lines of the Fe IV sextet at ~ -5 mm/s and $+3.5$ mm/s; in the case of fit B the outermost positive velocity Fe IV line coincides with the absorption peak at $\sim +5$ mm/s.

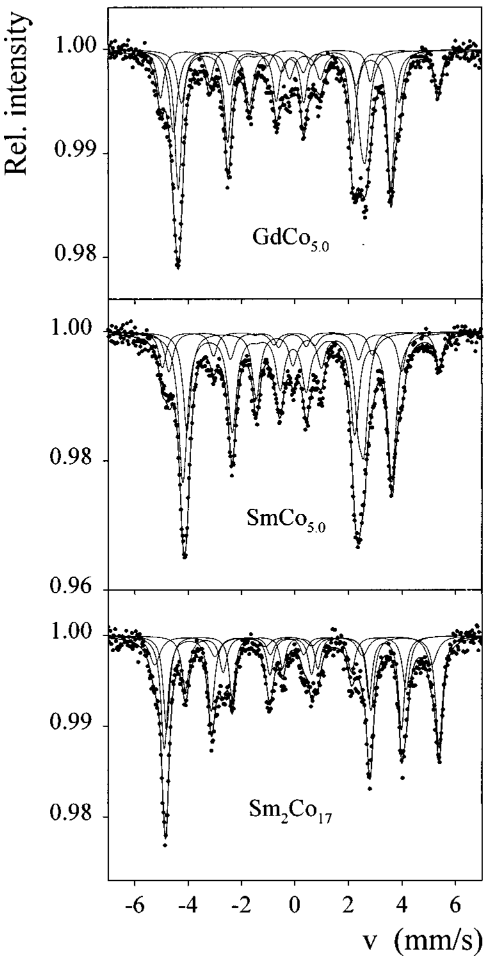

FIG. 3. Mössbauer spectra of ^{57}Fe in $GdCo_5$, $SmCo_5$, and Sm_2Co_{17} (rh) at $T = 77$ K and their decomposition into four components.

This ambiguity could be resolved by the measurements on $GdCo_5$ and $SmCo_5$ (see Fig. 3). When the yttrium atom of YCo_5 is replaced by a rare-earth atom, the small $4f$ contribution changes the magnetic hyperfine field at the four sites slightly relative to each other. These changes lead to the clearly visible right-side asymmetry of the absorption peak at $+3.5$ mm/s of $GdCo_5$ and $SmCo_5$, which is not observed in the YCo_{5+x} spectra. This asymmetry makes fit A the clearly better description of the $GdCo_5$ and $SmCo_5$ spectra with hfi parameters for Fe IV (see Table II) very similar to the fit A parameters of YCo_5, not only with respect to the hyperfine field, but also to the isomer shift and the quadrupole interaction. Since these parameters are not expected to change strongly upon the substitution of Y by Gd or Sm, fit B can be excluded as a solution for YCo_{5+x}.

The hyperfine parameters of ^{57}Fe in $Y_{1-s}Co_{5+2s}$ vary, if at all, only very slightly with the substitution parameter. In Table I we have therefore collected the values of H_{hf} $eQV_{zz}/4$, η, θ, δ (relative to α-Fe at 290 K), and Γ only for YCo_5 and YCo_6. In cases where parameters in Table I differ between these two concentrations, the variation with the substitution parameter is linear within the experimental errors. Table II also contains the hyperfine parameters for ^{57}Fe in $GdCo_5$ and $SmCo_5$ and the results of Alameda *et al.*[15] for ^{57}Fe:$Nd(Co_{0.95}Fe_{0.05})_5$.

TABLE II. Hyperfine parameters of ^{57}Fe on different Co sites of YCo_5, YCo_6, $GdCo_5$, $SmCo_5$, and $NdCo_5$. The values for $NdCo_5$ at 300 K have been determined by Alameda *et al.* (Ref. 15). Fe I to Fe IV refer to the four Mössbauer subspectra. The corresponding Co sites of the $CaCu_5$ lattice, identified from the s dependence of the relative intensities and neutron diffraction data for the site preference, are given in parentheses. Parameters marked by an asterisk have been fixed in the analysis to the listed value. The isomer shift is relative to α-Fe at 290 K.

Subspectrum (Co site)	RCo_{5+x}	H_{hf} (kG)	$eQV_{zz}/4$ (mm/s)	θ (°)	η	δ (mm/s)	Γ (mm/s)
Fe I	YCo_5	24.9(3)	0.65(3)	78(2)	0.49(5)	−0.17(2)	0.36(2)
($3g$)	YCo_6	24.8(3)	0.69(3)	77(2)	0.50(5)	−0.14(2)	0.41(2)
	$GdCo_5$	23.4(3)	0.71(3)	78(2)	0.56(5)	−0.17(2)	0.34(2)
	$SmCo_5$	23.4(3)	0.63(3)	79(2)	0.52(5)	−0.08(2)	0.37(2)
	$NdCo_5$	24.2	0.30	90	0.7	0.02	
Fe II	YCo_5	23.2(3)	−0.67(3)	0–10	0(0.1)	−0.20(2)	0.28(2)
($2c$)	YCo_6	23.1(3)	−0.68(3)	0–10	0(0.1)	−0.24(2)	0.24(2)
	$GdCo_5$	22.3(3)	−0.67(3)	0–10	(0.01)	−0.19(2)	0.35(2)
	$SmCo_5$	20.3(3)	−0.62(3)	0–10	0(0.1)	−0.06(2)	0.35(2)
	$NdCo_5$	21.2	−0.3	0	0	0.08	
Fe III	YCo_5	31.6(3)	−0.04(3)	0*	0*	0.06(2)	0.31(3)
($2e$)	YCo_6	31.4(3)	0.05(3)	0*	0*	0.02(2)	0.33(2)
	$GdCo_5$	32.1(3)	0.17(3)	0*	0*	0.07(2)	0.36(3)
	$SmCo_5$	31.2(3)	0.26(3)	0*	0*	0.19(2)	0.39(3)
	$NdCo_5$	30.6	0.025	0	0	0.22	
Fe IV	YCo_5	26.2(3)	0.01(3)	0*	0*	−0.14(2)	0.26(3)
($6l$)	YCo_6	26.8(3)	−0.01(3)	0*	0*	−0.21(2)	0.24(3)
	$GdCo_5$	25.8(3)	−0.06(3)	0*	0*	−0.09(2)	0.30(3)
	$SmCo_5$	27.7(3)	0.35(3)	0*	0*	−0.02(2)	0.37(3)

TABLE III. Hyperfine parameters of ^{57}Fe on the four Co sites of Sm_2Co_{17} (rh). Fe I to Fe IV refer to the four Mössbauer subspectra. The assignment to the Co sites of rhombohedral Sm_2Co_{17} proposed in parentheses in column I is suggested by a comparison of the isomer shifts and the volumes V_{WS} of the Wigner-Seitz cells. The coordinates (x,y,z) used in the calculation of V_{WS} are also listed. Column II gives the relative intensities of the four Mössbauer subspectra, that of the four Co sites of Sm_2Co_{17} (rh) (in parentheses) and the resultant preference factors. Parameters marked by an asterisk have been fixed in the analysis to the listed value. The isomer shift is relative to α-Fe at 290 K.

Subspectrum (site)	Rel. intensity	H_{hf} (kG)	$eQV_{zz}/4$ (mm/s)	θ (°)	η	δ (mm/s)	Γ (mm/s)
Fe I-($6c$) $V_{WS}=11.57$ Å^3 (0,0,0,0.96)	0.47(2) (0.118) $P_{6c}=$ 4.0(2)	31.8(3)	0.19(3)	0*	0*	0.15(2)	0.37(2)
Fe II-($18h$) $V_{WS}=11.26$ Å^3 ($\frac{1}{2}$,$\frac{1}{2}$,0.168)	0.24(1) (0.353) $P_{18h}=$ 0.68(3)	27.1(3)	0.44(3)	90(5)	0.5(1)	0.00(2)	0.26(2)
Fe III-($18f$?) $V_{WS}=11.05$ Å^3 (0.288,0,0)	0.17(1) (0.353) $P_{18f}=$ 0.48(3)	25.4(3)	0.13(3)	0*	0*	−0.03(2)	0.26(3)
Fe IV-($9d$?) $V_{WS}=10.69$ Å^3 ($\frac{1}{2}$,0,$\frac{1}{2}$)	0.12(1) (0.176) $P_{9d}=$ 0.68(6)	30.2(3)	−0.07(3)	0*	0*	−0.24(2)	0.42(6)

For reasons discussed below a measurement of the Mössbauer spectrum of ^{57}Fe in Sm_2Co_{17} (rh) was of interest. There are four different Co sites in rhombohedral Sm_2Co_{17}: The sites $6c$ and $18f$ lie in mixed planes containing both Sm and Co atoms. They are the dumbbell site and the site of the hexagon surrounding the Co pair, respectively, and correspond to sites $2e$ and $6l$ of $R_{1-s}Co_{5+2s}$, respectively. Sites $9d$ and $18h$ lie in the planes containing only Co atoms, similar to site $3g$ of RCo_5. The spectrum of ^{57}Fe:Sm_2Co_{17} (Fig. 3) was therefore analyzed with a superposition of four components Fe I to Fe IV, admitting a combined magnetic and electric hyperfine interaction for each of them. The result of the fit and the decomposition into four components is shown in Fig. 3. The values obtained for the relative intensities and the hyperfine parameters H_{hf}, $eQV_{zz}/4$, η, θ, δ, Γ are collected in Table III.

Figures 2 and 3 show that in all cases the measured spectra are well reproduced by four sextets. The line widths varying between 0.24 and 0.42 mm/s (see Table I; values uncorrected for finite absorber thickness) are at most ~ 0.2 mm/s larger than the natural linewidth of ^{57}Fe. If this line broadening is attributed to the magnetic interaction, the width of the corresponding hyperfine-field distribution is $\Delta H_{hf} \leqslant 0.7$ T, which is small compared to H_{hf} and justifies the initial assumption of four sites. In view of the large number of parameters of the combined interaction, an attempt to resolve the hyperfine-field distribution by admitting a larger number of sextets would require constraining assumptions and is therefore unlikely to improve the analysis.

IV. DISCUSSION

Figure 4 shows the s dependence of the four Mössbauer fractions $F_i(s)$ of $Y_{1-s}Co_{5+2s}$ (solid points) together with the corresponding results for $SmCo_5$ (triangles) and $GdCo_5$ (squares). In a good approximation, the fractions $F_i(s)$ of components Fe II, III, and IV are linear functions of the substitution s with a negative slope for Fe II and positive slopes for Fe III and Fe IV. The fraction $F_I(s)$ of component Fe I changes only slightly with the substitution parameter. The parameters of these linear relations, determined by fits to the data in the range $-0.014 \leqslant s \leqslant 0.125$ with a symmetrical worst-case error $\Delta s = \pm 0.01$ of the substitution parameter, are collected in Table I. The hyperfine fields of Fe I and IV are rather similar, which resulted in a strong correlation between the fractions F_I and F_{IV} for $s \geqslant 0.079$. Therefore, the parameters of the s dependence of these fractions, listed in Table III, were determined from the data in the range $-0.014 \leqslant s \leqslant 0.054$ alone. The values of F_I for $s \geqslant 0.079$. shown in Fig. 4 were extrapolated with the s dependence determined from the $s \leqslant 0.054$ data. In the analysis of the spectra with $s \geqslant 0.079$, the intensity F_I was fixed to the extrapolated values.

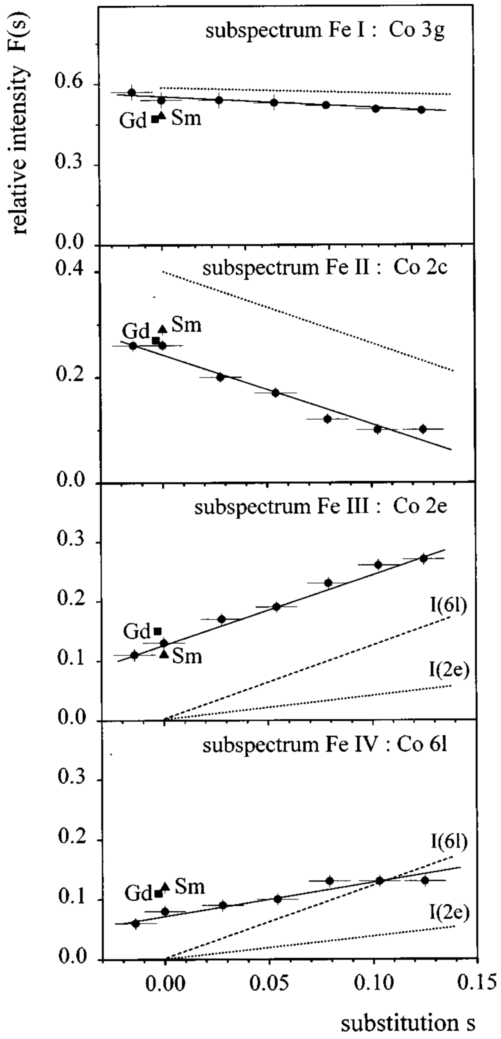

FIG. 4. The relative intensities or fractions $F_i(s)$ of the four components Fe I, II, III, and IV fitted to the Mössbauer spectra shown in Fig. 2 as a function of relative number of substitutions s. The horizontal error bars correspond to the worst-case uncertainty of the substitution parameter. The solid lines represent fits of Eq. (1) to the experimental fractions with results collected in Table I. The dotted lines show the s dependence of the relative intensities $I_i(s)$ of the four Co sites $2c$, $3g$, $6l$, and $2e$ of $Y_{1-s}Co_{5+2s}$.

For the hyperfine field-site assignment we compare the s dependence of the Mössbauer fractions $F_i(s)$ and the site intensities $I_i(s)$. Inspection of Fig. 4 and Table I shows that there is only one Mössbauer component (Fe II) and one site ($2c$) in $Y_{1-s}Co_{5+2s}$, which decrease strongly with increasing substitution s. We therefore assign component Fe II to site $2c$. One notes, however, a strong negative offset of $F_{II}(s)$ relative to $I_{2c}(s)$. As the slopes $dF_{II}(s)/ds$ and $dI_{2c}(s)/ds$ are rather close, the negative offset cannot be attributed to a pronounced avoidance of site $2c$ but suggests a sizable dumbbell concentration s_0 in stoichiometric YCo_5. The values of P_{2c} and s_0 calculated with Eq. (1) from $F_{II}(s)$ and $I_{2c}(s)$ are given in Table I.

The relative intensities of component Fe I and site $3g$ have almost the same magnitude and both vary only slightly with the number of substitutions (see topmost section of Fig. 4), which suggests the assignment of subspectrum Fe I to site $3g$. The weak s dependence of $I_{3g}(s)$ and the large experimental errors of $F_I(s)$ lead to large uncertainties if both s_0 and P_{3g} are calculated from $F_I(s)$ and $I_{3g}(s)$. We have therefore determined P_{3g} only, using for s_0 the average value of sites $2c$, $6l$, and $2e$ ($s_0 = 0.12$).

The intensities of both Fe I and Fe II decrease with increasing substitution s. Since the site preferences P_i are adjustable parameters in Eq. (1), the alternative assignment of components Fe I and Fe II to sites $2c$ and $3g$, respectively, cannot be excluded from a formal point of view. Such an assignment would, however, lead to unreasonable values for P_i and in particular for s_0 ($3g$, $P_{3g}\approx5.4$, $s_0\approx2.3$; $2c$, $P_{2c}\approx0.35$, $s_0\approx-0.9$) and would also be in conflict with the results of neutron diffraction studies of the preference of Fe for sites $3g$ and $2c$ in compounds with $CaCu_5$ structure. For $Th(Co_{1-x}Fe_x)_5$ Laforest and Shah[31] report a preference of Fe for the $3g$ site. From their data one estimates preference factors of $P_{3g}\approx1.3$ and $P_{2c}\approx0.7$ for the lowest Fe concentration investigated ($x=0.4$). Deportes *et al.*[32] have found—also by neutron diffraction—that when Co atoms in RCo_5 ($R=$Th, Y) are substituted by other $3d$ elements, the smaller atom of the two $3d$ constituents preferentially goes to the $2c$, the larger atom to the $3g$ site: In $R(Co_{1-x}Fe_x)_5$ the larger Fe atom favors the $3g$ site, in $R(Co_{1-x}Ni_x)_5$, the smaller Ni atom prefers the $2c$ site. In Co rich ($x=0.1$) $R(Co_{1-x}Ni_x)_5$ the preference factors are $P_{3g}\approx0.95$, $P_{2c}\approx1.05$. Only with the assignment of Fe I and II to sites $3g$ and $2c$, respectively, do our results for the site preferences $P_{3g}=0.98(7)$ and $P_{2c}=0.96(10)$ agree with these values.

There are two subspectra (III, IV) and two sites ($6l$ and the dumbbell site $2e$) that show an increase of the intensity with the s parameter. In both cases there is a sizable positive offset of the Mössbauer intensities $F_i(s)$ relative to $I_i(s)$. Although the slopes $dF_{\mathrm{III}}(s)/ds$ and $dF_{\mathrm{IV}}(s)/ds$ are suggestively similar to $dI_{6l}(s)/ds$ and $dI_{2e}(s)/ds$, respectively, with the site preferences as adjustable parameters we cannot decide between the two possible assignments of components Fe III and IV to either sites $6l$ and $2e$, respectively, or to sites $2e$ and $6l$, respectively, from the Mössbauer intensities alone. Both possibilities lead to reasonable values for the site preferences P_{6l} and P_{2e} and the stoichiometry parameter s_0 satisfying the experimental $F_i(s)$ values (see Table I).

One of the two possible assignments can, however, be rejected by comparing the corresponding site preferences to the result of a neutron diffraction study of the site preference of Fe in the related compound $Nd_2(Co_{1-x}Fe_x)_{17}$ by Herbst *et al.*[33] Sites $18f$ and $6c$ of $Nd_2(Co_{1-x}Fe_x)_{17}$ in the mixed planes with both Nd and Co atoms correspond to sites $6l$ and $2e$, respectively, of $Y_{1-s}Co_{5+2s}$. Herbst *et al.*[33] find a preference of Fe for the dumbbell site $6c$ of about $P_{6c}\approx3.2$ (at $x=0.1$), mainly at the expense of sites $9d$ and $18h$. The assignment of the Mössbauer components Fe III and IV to sites $6l$ and $2e$, respectively, leads to a dumbbell preference of $P_{2e}=1.3$ (see Table I) and can therefore clearly be excluded. For the other possible assignment, however, our result for the dumbbell preference $P_{2e}=2.95$ (see Table I) agrees well with the value measured by Herbst *et al.*[33]

We therefore assign the components Fe III and IV to sites $2e$ and $6l$, respectively. The preference factor $P_{6l}=0.43$ obtained with this assignment corresponds to a Co occupancy of site $18f$ in $Nd_2(Co_{1-x}Fe_x)_{17}$ of $n_{18f}(\mathrm{Co})=0.95$, only slightly larger than the experimental result $n_{18f}(\mathrm{Co})=0.91(1)$ of Herbst *et al.*[33] for $x=0.1$. Other neutron diffraction[27,34,35] and electron channeling and blocking studies[36] of the Fe site preference in $R_2(Co_{1-x}Fe_x)_{17}$ cannot differentiate between sites $18f$ and $6c$, but all agree that Fe favors the mixed plane.

The conclusions concerning the site preference drawn from previous ^{57}Fe Mössbauer studies of RCo_{5+x} compounds are contradictory. Decrop *et al.*[12] report that in ^{57}Fe-doped $HoCo_{5,6}$ about 60%, 22%, and 18% of the Fe atoms reside on sites $6l$, $2e$, and $3g$, respectively, while site $2c$ is completely avoided. The spectrum of ^{57}Fe:$SmCo_5$ measured by Nowik *et al.*[13] has been described by only two fractions that are assigned to randomly occupied sites $2c$ and $3g$. The description of ^{57}Fe Mössbauer spectrum of $Nd_2(Co_{0.95}Fe_{0.05})_5$ requires at least three components.[15] The one with the largest field ($H_{\mathrm{hf}}=306$ kG) is attributed by Alameda *et al.*[15] to the dumbbell site. This proposal, which implies a strong preference for site $2e$ and avoidance of site $6l$ is confirmed by our results.

It has been proposed to support site assignments in $3d$-$4f$ compounds by comparing the isomer shift of the Mössbauer components to the volume of the Wigner-Seitz cell of different $3d$ sites.[6] We have therefore calculated the volumes of the Dirichlet domains of the four sites of $Y_{1-s}Co_{5+2s}$ using the procedure of radical planes, which results in a space partition without gaps between the polyhedra.[37] The atomic positions determined by Schweizer and Tasset[24] were used. The atomic radii $r(\mathrm{Y})=1.66$ Å and $r(\mathrm{Co})=1.19$ Å were determined in a ''hard sphere'' model from the shortest Co-Co and Y-Co distances. The results listed in column I of Table I show an increase of the volume in the order $2c<6l<3g<2e$. The sequence of increasing isomer shift is Fe II<Fe I<Fe IV<Fe III so that the assignment of Fe III to the dumbbell site $2e$ in fact relates the component with the smallest s-electron density to the site with the largest Wigner-Seitz cell volume. Although the cell volumes of the other sites vary considerably, the isomer shifts of the remaining fractions are rather similar, which stresses the importance of other factors such as differences in the electronic structure of the various sites. It should also be noted that volume relaxation that may occur when an impurity substitutes a regular lattice atom has been neglected in the calculation of the YCo_{5+x} cell volumes. For all sites the isomer shift increases in the order $YCo_5\approx GdCo_5<SmCo_5<NdCo_6$ (see Table II). The Wigner-Seitz cell volumes increase in the same order [e.g., site $3g$, 11.69, 11.93, and 12.12 Å^3 for Y, Sm, and Nd, respectively, calculated using the lattice parameters of RCo_5 ($R=$Y, Sm, Nd) and the atomic positions of YCo_5]. Recently, Long and Grandjean[38] have reported a linear correlation of the site preference of ^{57}Co in $Nd_2Fe_{14}B$ and the Wigner-Seitz cell volumes of the Fe sites. In the present case (see Table I) such a correlation is not observed.

The distinct offset of the intensities $F_i(s)$ of the Mössbauer components Fe II, III, and IV relative to the site intensities $I_i(s)$ suggests the existence of a considerable number s_0 of dumbbells in stoichiometric YCo_5 and even in substoichiometric $YCo_{4.9}$. Within the experimental uncertainty the analysis based on Eq. (1) gives the same value for all three components: $s_0=0.12(2)$ (see Table I). This value is surprisingly large compared to the substitution parameter $s_0=0.046(1)$ derived by Schweizer and Tasset[24] for YCo_5 single crystals by neutron diffraction.

One of the characteristic features of the spectra in Fig. 2 is the continuous growth of the absorption line at $\sim+5$ mm/s with increasing substitution parameter s. This line may therefore be used as qualitative indicator of the dumbbell concentration. It is remarkable that this line appears in all spectra of ^{57}Fe:RCo$_5$ reported up to now. In the case of Nd(Co$_{0.95}$Fe$_{0.05}$)$_5$ (Ref. 15) the dumbbell component has a relative intensity of 10%, which—assuming the same preference factor $P_{2e} \approx 3$ as deduced for YCo$_5$—corresponds to a dumbbell concentration $s_0 \approx 0.08$. For ^{57}Fe:GdCo$_5$ and ^{57}Fe:SmCo$_5$ we obtain $s_0 \approx 0.12$ and 0.09, respectively. The latter result is close to $s_0 \approx 0.07$, which one estimates from the spectrum of ^{57}Fe:SmCo$_5$ reported by Belozerskii *et al.*[8]

Explaining these s_0 values, e.g., by a decomposition of the type $RCo_5 \rightarrow R_{1-s}Co_{5+2s} + R_2Co_7$ $(+R_2Co_{17})$ would require substantial quantities of the adjacent phases. The x-ray diffraction pattern of our YCo$_5$, GdCo$_5$, and SmCo$_5$, samples, however, contained no reflections belonging to these phases. In the case of Nd(Co$_{1-x}$Fe$_x$)$_5$ Alameda *et al.*[15] observed weak traces of hexagonal Th$_2$Zn$_{17}$ for the Fe concentration $x = 0.1$, but found a single-phase CaCu$_5$ pattern at the concentration $x = 0.05$ where the Mössbauer spectrum has a dumbbell component of 10%. It therefore appears unlikely that in stoichiometric RCo$_5$ as much as 10% of the R atoms are substituted by Co pairs.

There are indications that the RCo$_5$ Mössbauer pattern is rather sensitive to the parameters of the sample preparation: The spectrum of ^{57}Fe:SmCo$_5$ of a sample annealed at 850 °C for 8 days measured by Nowik *et al.*[13] shows a very prominent absorption line at $\sim +5$ mm/s, suggesting a large dumbbell concentration in the investigated compound. Sm$_2$Co$_{17}$ is the compound with the largest dumbbell concentration in the Sm-Co binary system and it therefore appeared of interest to compare the Mössbauer spectrum reported by Nowik *et al.*[13] to that of ^{57}Fe:Sm$_2$Co$_{17}$. Our measurement shows that the ^{57}Fe:SmCo$_5$ spectrum of Nowik *et al.*[13] is much closer to the spectrum of ^{57}Fe:Sm$_2$Co$_{17}$(rh) than to the other ^{57}Fe:RCo$_5$ spectra reported up to now (Figs. 2 and 3 and Refs. 8 and 15), in particular with respect to the strong absorption line at $\sim +5$ mm/s. It is also interesting to note that the recoil-less fraction of the ^{57}Fe:SmCo$_5$ spectrum of Nowik *et al.*[13] is practically one order of magnitude smaller than that of the other RCo$_5$ spectra.

These observations suggest that a substantial precipitation of R_2Co$_{17}$ may occur without giving rise to the reflections of Th$_2$Zn$_{17}$ in the x-ray diffraction, which might be related to the impurity nature of the ^{57}Fe Mössbauer probe. There are indications that the stability of the CaCu$_5$ phase is affected by impurity atoms. According to Buschow,[39,40] the addition of Fe shifts the homogeneity region of RCo$_5$ to higher Co concentrations and favors the decomposition into the adjacent phases. A local decomposition or precipitation[41] of R_2Co$_{17}$ triggered by ^{57}Fe would lead to a sizable admixture of ^{57}Fe:R_2Co$_{17}$ in the Mössbauer spectrum of ^{57}Fe:RCo$_5$, but because of the small Fe concentration the corresponding x-ray reflections would be difficult to detect. It therefore appears likely that the dumbbell component in the Mössbauer spectra of stoichiometric RCo$_5$ is in part due to an admixture of ^{57}Fe:R_2Co$_{17}$ with the amount probably depending on parameters of the thermal history such as, e.g., the cooling rate or annealing conditions. The pronounced linearity of $F_i(s)$, in particular for components Fe II and Fe III (see Fig. 4), suggests that the admixture varies only slightly between the different samples of this study.

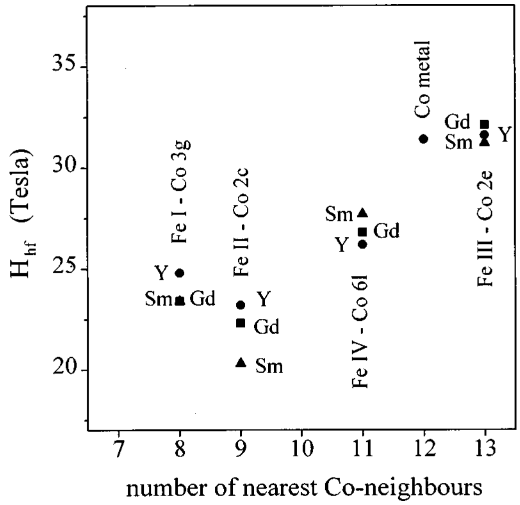

FIG. 5. The magnetic hyperfine field of ^{57}Fe on the Co sites $2c$, $3g$, $6l$, $2e$ of $Y_{1-}Co_{5+2s}$, GdCo$_5$, and SmCo$_5$ versus the number of nearest Co neighbors.

In Table III we propose an assignment of the four subspectra Fe I to Fe IV of ^{57}Fe:Sm$_2$Co$_{17}$ to the Co sites of rhombohedral Sm$_2$Co$_{17}$ by comparing the isomer shifts to the Wigner-Seitz cell volumes calculated using radical planes,[37] "hard sphere" radii (Co:1.19 Å, Sm:1.75 Å), and lattice parameters[1] $a = 8.4019$ Å, $c = 12.2308$ Å. To our knowledge, the exact atomic positions of Sm$_2$Co$_{17}$ have not yet been measured. The cell volumes were therefore calculated with the positions of Nd$_2$Co$_{17}$ from Ref. 33 [z_c(Sm) $= 0.343$; for the Co positions see Table III]. The order of decreasing cell volumes is $6c > 18h > 18f > 9d$, the order of decreasing isomer shift is Fe I>Fe II>Fe III>Fe IV, which suggests the assignment of Fe I to the dumbbell site $6c$, of Fe II to site $18h$ of the hexagon bisecting the dumbbell, Fe III to site $18f$, and Fe IV to site $9d$.

With Fe I assigned to site $6c$, the largest field acts on the dumbbell site, just as for YCo$_{5+x}$ and R_2Fe$_{17}$ (Refs. 7 and 42), which is generally attributed to the fact that of all $3d$ sites the dumbbell has the largest number of $3d$ neighbors and the shortest d-d bond length. In Sm$_2$Fe$_{17}$ the hyperfine field of ^{57}Fe on the dumbbell site (H_{hf}=337 kOe at 15 K) is about 6% larger than in Sm$_2$Co$_{17}$ (Ref. 42). Sites $18h$ of Sm$_2$Co$_{17}$ and $3g$ of SmCo$_5$ are structurally related. The similarity of the quadrupole parameters of site $3g$ of SmCo$_5$ and of component Fe II of Sm$_2$Co$_{17}$ therefore further supports the assignment of component Fe II to site $18h$. The assignment of components Fe III and Fe IV to sites $18f$ and $9d$, respectively, suggested by the isomer shifts and the cell volumes appears doubtful because from the YCo$_{5+x}$ results one would expect the larger field to act on the site ($18f$) of the hexagon surrounding the Co pair.

The comparison of the relative intensities of the lattice sites and the Mössbauer components Fe I–IV in Table III shows that according to this assignment Fe again strongly favors the dumbbell site $6c$ ($P_{6c} \approx 4$) at the expense of all other sites, in excellent agreement with the results of Nagamine, Rechenberg, and Ray[17] for Sm$_2$(Co$_{0.9}$Fe$_{0.1}$)$_{17}$ and Herbst *et al.*[33] for Nd$_2$(Co$_{1-x}$Fe$_x$)$_{17}$.

The information obtained by this study on the magnetic hyperfine field H_{hf} of ^{57}Fe in RCo$_5$ is collected in Fig. 5, where we have plotted H_{hf} on the four Co sites of YCo$_5$,

$SmCo_5$, and $GdCo_5$ versus the number of nearest Co neighbors. For comparison we have included our result for the ^{57}Fe hyperfine field in $Co_{0.99}Fe_{9.01}$ measured at 77 K [H_{hf}=32.01(5) T].

The overall trend in Fig. 5 is an increase of the hyperfine field with the number of Co neighbors; the relation between these two quantities is, however, far from the strict proportionality observed, e.g., in Y_xFe_y compounds.[43] In particular, the field on site $2c$ with nine nearest-neighbor Co atoms is about 10% smaller than the field on site $3g$ with eight nearest-neighbor Co. The ^{59}Co hyperfine fields in RCo$_5$ show the same trend, although the NMR results of different authors[44,45] differ considerably: Systematically, the absolute value of the field at site $2c$ is smaller than at site $3g$. Here the reduction relative to metallic Co is even more pronounced than for ^{57}Fe, exceeding 50% for site $2c$. In one of the recent first-principles studies[46–48] of the electronic structure of YCo_5 Daalderop, Kelly, and Schuurmans[48] have also calculated the magnetic hyperfine fields of Co on sites $2c$ and $3g$ and found that the total hyperfine field is the result of a cancellation of contact and orbital contributions that are of the same order of magnitude but may have opposite sign. According to these calculations, the reduction relative to metallic Co results from a larger orbital contribution in YCo_5 and a positive contact valence term for site $2c$ is responsible for the smaller field relative to site $3g$.

Up to now, first-principles calculations of hyperfine fields on sites $6l$ and $2e$ are not available. Experimentally, we find that the ^{57}Fe hyperfine field on site $6l$ is about 15% stronger than on site $2c$. Sites $2c$ and $6l$ are related by the substitution of a Y neighbor by a Co pair. The larger number of nearest Co neighbors can be expected to lead to a stronger core polarization and thus explain the increase of H_{hf} from $2c$ to $6l$. It is, however, interesting to note in this context that the QI of sites $2c$ and $6l$ is strongly affected by the substitution: The strong axially symmetric QI of site $2c$ practically vanishes on site $6l$, which implies that the nonspherical charge distribution surrounding site $2c$ becomes almost cubic when the Y neighbor is replaced by a Co dumbbell. The higher symmetry could lead to a reduced orbital contribution and thus contribute to the increase of the total hyperfine field.

The contact contribution to the magnetic hyperfine field of ^{57}Fe induced by the localized $4f$ spins is quite small: On all sites of RCo$_5$, H_{hf} changes only very slightly with the R constituent (see Table II). The largest difference is observed for site $2c$, which has three nearest R neighbors at a distance of 2.853 Å. Here the field for R=Sm is about 13% smaller than for R=Y. For the other sites the differences are less than 5%. The NMR results for the R dependence of the ^{59}Co hyperfine fields are partially conflicting: Streever[44] reports an increase of H_{hf} by about 15% from (R=Y to R=Sm) for both $2c$ and $3g$ while Yoshie *et al.*[45] find a 50% decrease of the $3g$ field and an increase by a factor of 4 for the $2c$ field between R=Y and R=Sm, Gd. Daalderop, Kelly, and Schuurmans[48] expect the $3g$ field to be most sensitive to the R atom, because the valence contact term of this site changes considerably upon substitution. Their calculation predicts a decrease of the $3g$ field by almost 50% between YCo_5 and $GdCo_5$.

As expected from the point symmetry, the electric-field gradient at site $2c$ is axially symmetric and points along the hexagonal c axis, whereas for site $3g$ one finds a strong asymmetry and an angle of ~75° between the maximum component V_{zz} and the c axis. This is in reasonable agreement with the angle of 90° predicted by Streever[44] on the basis of a point charge estimate of the EFG.

In summary, we have investigated the magnetic and electric hyperfine interaction and the relative fractions of dilute ^{57}Fe nuclei on the four Co sites of $Y_{1-s}Co_{5+2s}$ by Mössbauer spectroscopy as a function of the relative number s of Y atoms substituted by Co dumbbells. The s dependence of the relative Mössbauer fractions of $^{57}Fe{:}Y_{1-s}Co_{5+2s}$, together with the neutron diffraction results of Herbst *et al.*,[33] allows an experimental site-hyperfine field assignment. The Fe atoms strongly favor the dumbbell sites at the expense of sites $6l$ of the hexagon surrounding the Co pair, while sites $2c$ and $3g$ are randomly occupied. In stoichiometric RCo$_5$ (R=Y, Sm, Gd) we observe a large dumbbell concentration, which is probably caused to some extent by the precipitation of R_2Co_{17} favored by the impurity nature of the Mössbauer probe. With increasing number of nearest Co neighbors the magnetic hyperfine field passes from site $3g$ through a minimum at site $2c$ towards the maximum of H_{hf}=31.5 T at the dumbbell site. Measurements of ^{57}Fe in $GdCo_5$ and $SmCo_5$ show that the $4f$ contribution to the magnetic hyperfine field is small, the changes upon substitution of Y by R=Gd, Sm are of the order of 10%.

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