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Mössbauer study of the hyperfine interaction of ^{197}Au in gadolinium

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The combined magnetic dipole and electric quadrupole interaction of ^{197}Au in Gd has been investigated by means of the Mössbauer effect. The system was prepared by alloying Gd with 0.5 at.% of ^{197}Pt which decays to ^{197}Au. At 4 K a magnetic hyperfine field of $|H_{\mathrm{hf}}(Gd\mathrm{Au})| = 809 \pm 8$ kG, and an electric field gradient of $V_{zz}(Gd\mathrm{Au}) = +(14.4 \pm 0.7) \times 10^{17}$ V/cm^2 was observed. The value of the magnetic field is consistent with the assumption that the field is mainly due to conduction-electron polarization. The electric field gradient has the same sign as the ionic lattice gradient but it is one order of magnitude larger.

I. INTRODUCTION

The magnetic hyperfine interaction (HFI) at the site of dilute impurities in the $3d$ ferromagnets Fe, Co, and Ni has been studied quite extensively. These studies have revealed a pronounced dependence of the impurity hyperfine field on both the impurity atomic number and the properties of the ferromagnetic host, and have led to a qualitative understanding of the main mechanisms responsible for these fields.[1]

For further progress of the theory investigations in other ferromagnetic systems are important. Recently the $4f$ ferromagnets of the rare-earth group[2-4] and also ferromagnetic alloys received an increasing attention. In this paper we present a Mössbauer investigation with ^{197}Au in ferromagnetic gadolinium.

In contrast to the other heavy-rare-earth metals gadolinium exhibits only one phase of spontaneous magnetic order. It is ferromagnetic below $T_C = 293$ K. In the ferromagnetic phase the $4f$ moments are parallel to each other and form a finite angle β with respect to the c axis of the hcp lattice structure. According to neutron-diffraction measurements on Gd single crystals this angle β is temperature dependent and reaches a value of $\beta = (28 \pm 2)^\circ$ at 4 K.[5]

A recent HFI study by Bauminger *et al.*,[6] however, indicates that the angle β strongly depends on small amounts of impurities in the sample and on the method of sample preparation. These authors observed values of $\beta = 28^\circ$, 52°, and 75° in samples obtained from different suppliers.

The c/a ratio of the crystalline axes of Gd is smaller than 1.633,[7] the value for an ideal hcp structure. Therefore a strong electric field gradient (EFG) is expected at regular sites of the Gd lattice. This EFG must be axially symmetric with the symmetry axis pointing along the c axis. If the probe ^{197}Au occupies a substitutional lattice site one has to expect therefore in the ferromagnetic phase a noncollinear combined magnetic dipole and electric quadrupole interaction. Under the assumption that the magnetic hyperfine (HF) field has the same direction as the $4f$ moments, the magnetic field and the symmetry axis of the EFG form the angle β. With the magnetic field direction as quantization axis the matrix elements of the corresponding Hamiltonian are given by the expression[8]

$$H^I_{mm'}(\omega_H, \omega_Q, \beta) = -\hbar\omega_H m \delta_{mm'} + \hbar\omega_Q (-1)^{I-m'} \frac{\begin{pmatrix} I & 2 & I \\ -m & m-m' & m' \end{pmatrix}}{\begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}} 2I(2I-1) Y_2^{m'-m}(\beta, 0),$$

with

$$\omega_H = gH\mu_N/\hbar \quad \text{and} \quad \omega_Q = eQV_{zz}/4I(2I-1)\hbar \;.$$

The combined interaction splits the $\frac{3}{2}$ ground state of ^{197}Au into four nonequidistant sublevels and the excited $\frac{1}{2}$ state at 77 keV into two sublevels. A total of eight transitions occurs between the excited state and the groundstate. When calculating the intensities of these transitions, one has to take into account: (i) in the case of a combined interaction the sublevels of the $\frac{3}{2}$ ground state are not pure m states; (ii) the 77-keV transition of ^{197}Au is a mixed $M1/E2$ transition.

The mixing ratio is $\delta^2 = I(E2)/I(M1) = 0.11$.[9] Since the magnetic moment of the groundstate is much smaller than the magnetic moment of the excited state[10] one expects that even at rather high magnetic HF fields the Mössbauer spectrum consists of two groups of four unresolved lines which are separated by the magnetic HF splitting of the excited state. In case a quadrupole interaction is present, these two groups should be asymmetric.

II. EXPERIMENTAL DETAILS, DATA ANALYSIS, AND RESULTS

The source for this Mössbauer experiment was prepared in the following way: The isotope ^{197}Pt ($T_{1/2}=18$ h) which feeds the 77-keV Mössbauer transition of ^{197}Au was produced by neutron irradiation of natural Pt foil. Small pieces of this foil were melted with Gd in high vacuum by means of an electron gun. The Pt concentration of the alloy was about 0.5 at.%. The alloy was then broken into pieces in order to minimize absorption in the source. The source was moved with respect to a 100-μm single line Au-metal absorber. Both absorber and source were kept at 4 K. Figure 1 shows the Mössbauer spectrum obtained in this way. Its asymmetric form indicates the presence of a well-defined quadrupole interaction.

In order to derive the relevant hyperfine interaction parameters, i.e., linewidth, isomer shift (IS), magnetic hyperfine field (H_{hf}), quadrupole frequency ω_Q, and angle β, a superposition of eight Lorentzian lines was fitted to the measured spectrum. The position and intensity of the different lines as a function of the HFI parameters were calculated by numerical diagonalization of the interaction Hamiltonian.

The magnetic HF field, the isomer shift, and the linewidth are obtained easily and without ambiguity from the fit. The determination of the quadrupole frequency ω_Q and the angle β, however, is slightly problematic, since these two quantities are strongly correlated in the interaction Hamiltonian. In case the quadrupole frequency is much smaller than the magnetic interaction frequency, the splitting of a $I=\frac{3}{2}$ state has two similar solutions, one for $\beta<55°$ and one for $\beta>55°$, for which the quadrupole frequency has opposite sign.

A computer simulation showed that a very high statistical accuracy is required to distinguish between these two solutions. We therefore accumulated a total of nearly 10^8 counts/channel. It was then possible to determine ω_Q and β unambiguously in spite of their strong correlation. For this purpose a series of fits was performed in which the magnetic HF field, quadrupole frequency, isomer shift, and linewidth were adjusted for different fixed input values of the angle β. Figure 2 shows the goodness of these fits in terms of the reduced χ_ν^2 as a function of the angle β. As expected two minima of χ_ν^2 were found, one at $\beta=43°$ with $\chi_\nu^2=1.66$ for which $\omega_Q<0$, and one for $\beta=69°$ with $\chi_\nu^2=1.06$ for which $\omega_Q>0$. The fit to the measured spectrum had $\nu=78$ degrees of freedom defined as number of data points minus number of free parameters. For the case that the correct theoretical function has been used for the fit, the probability $P(\chi_\nu^2,\nu)$ of obtaining a value $\chi_\nu^2=1.06$ for $\nu=78$ is $P=0.35$, whereas the probability for $\chi_\nu^2=1.66$ is only $P=10^{-3}$.[11] This difference is large enough to exclude the solution at $\beta=43°$ with $\omega_Q<0$. The clear separation between the two solutions

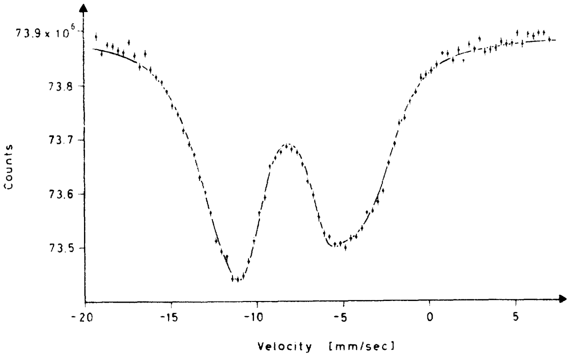

FIG. 1. Mössbauer spectrum of ^{197}Au in the alloy *Gd* ^{197}Au at 4 K.

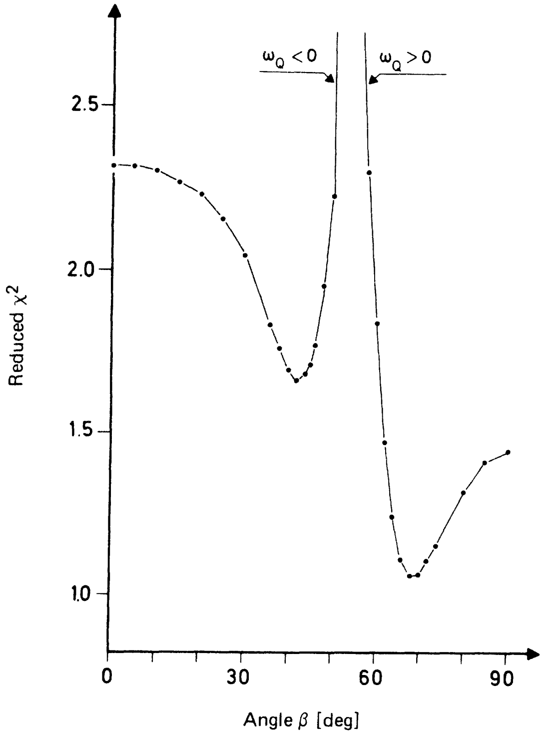

FIG. 2. Goodness of fit in terms of the reduced χ^2 as a function of the angle β.

is essentially due to the favorable fact that because of the very small g factor of the $\frac{3}{2}$ ground state of ^{197}Au ($g = 0.096\,58$)[10] the magnetic and the quadrupole interaction are of the same order of magnitude. The analysis of the Mössbauer spectrum yields the following HFI parameters for the system *Gd*Au:

$$|H_{\mathrm{hf}}| = 809 \pm 8 \text{ kG},$$

$$3\omega_Q = \tfrac{1}{4} eQV_{zz} = +0.83 \pm 0.04 \text{ mm/sec},$$

$$\beta = (69 \pm 2)^\circ ,$$

$$2\Gamma_0 = 1.80 \pm 0.05 \text{ mm/sec},$$

$$IS = -8.09 \pm 0.05 \text{ mm/sec}.$$

The solid line in Fig. 1 is the fit obtained with these parameters.

The measured quadrupole frequency ω_Q corresponds to an electric field gradient of

$$V_{zz}(Gd\mathrm{Au}) = +(14.4 \pm 0.7) \times 10^{17} \; V/\mathrm{cm}^2 .$$

This value has been calculated with $Q = 0.594$ b for the quadrupole moment of the ^{197}Au ground state.[10] The quoted error of V_{zz} does not contain the uncertainty of the quadrupole moment, which is due to the Sternheimer shielding correction.

The experimental linewidth has been corrected for finite absorber thickness and agrees within the error with the natural linewidth of 1.85 mm/sec. Together with the observation of a well-defined quadrupole interaction this allows the conclusion that the Pt impurities occupy one unique site in the Gd lattice. It is not absolutely certain that this site is a substitutional site, since channeling data and a phase diagram for the system *Gd*Pt are not yet available.

III. DISCUSSION

A. Isomer shift

The measured isomer shift of -8.09 ± 0.05 mm/sec is in excellent agreement with the IS of ^{197}Au in lanthanum of -8.1 mm/sec, as determined by Wagner *et al.*[12] Since Gd and La have the same valence electron configuration, this agreement confirms the observation of Wagner *et al.* that the IS is mainly determined by the number of the host-metal valence electrons. The number of $4f$ electrons has apparently no influence.

B. Magnetic hyperfine field

The magnetic HFI of Au in Gd has been measured previously by Campbell *et al.*[4] in a nuclear-orientation (NO) experiment as $H_{\mathrm{hf}} = -520 \pm 30$ kG, which is considerably smaller than our value of 809 kG. As an integral technique NO cannot distinguish between a single well-defined HF field and a field distribution. Furthermore it is difficult with this technique to separate magnetic dipole and electric quadrupole contributions to the HFI. Mössbauer-effect spectroscopy does not suffer from such restrictions. Therefore we consider our value of 809 kG as the more reliable one.

The magnetic HF field at the site of a closed-shell impurity such as Au (electron configuration: $5d^{10}\,6s^1$) is essentially due to the conduction-electron polarization (CEP) by the localized moments of the ferromagnetic host. A $d^{10}s^1$ impurity develops no own local moment, therefore a core polarization contribution to the HF field can be excluded. Since the metallic radius of Au (1.42 Å) is considerably smaller than that of Gd (1.80 Å), a HF field contribution from overlap polarization (OP) is also not to be expected.

According to Shirley *et al.*[13] the CEP-induced HF field at an impurity site in a ferromagnetic host can be described by the expression

$$H_{\mathrm{CEP}} = pH_{ns} ,$$

where H_{ns} is the magnetic field produced by one electron in a ns state of the free impurity ion. The factor p is a measure of the CEP at the impurity site and also contains solute-dependent effects such as a possible change of the free ion value of H_{ns} by the host environment. Daniel *et al.*[14] have developed a model to explain sign and magnitude of the CEP for various impurities in the same host by the scattering of the polarized conduction-electrons at the impurity potential. According to these calculations, which have later been extended by Campbell *et al.*,[15,16] the CEP at the impurity site should essentially depend on the valence difference between the impurity atom and the host atoms, i.e., the factor p in the above equation should be constant for closed-shell impurities with the same number of valence electrons.

In Table I we have collected the values of the magnetic HF field for $d^{10}s^1$ impurities in Fe and Gd together with the values of p calculated according to the above equation from the measured HF fields and the H_{ns} values obtained from the hyperfine coupling constants of the free atoms.[15] The data of Table I show that the CEP for $d^{10}s^1$ impurities in Fe is about a factor of 2 larger than in Gd, though the magnetic moment of Fe($2.2\mu_B$) is considerably smaller than that of Gd($8.0\mu_B$). This is consistent with the fact that the $4f$ conduction-electron coupling constant J_{sf} of Gd is nearly one order of magnitude smaller than the $3d$ conduction-electron coupling constant J_{sd} of Fe.[4] Furthermore Table I shows that in the host Gd the factor p for $d^{10}s^1$ impurities is constant in fact as expected from Campbell's model. For the

TABLE I. Magnetic HF fields of Cu, Ag, and Au in Fe and Gd.

				Host Fe (radius 1.28 Å)		Host Gd (radius 1.80 Å)	
Impurity	Radius (Å)	Electron configuration	H_{ns} (MG)	H_{hf} (kG)	p	H_{hf} (kG)	p
Cu	1.28	$3d^{10}4s^1$	$H_{4s}^{\text{Cu}}=2.7$	(−)213[a,b]	(−)0.079	⋯	⋯
Ag	1.42	$4d^{10}5s^1$	$H_{5s}^{\text{Ag}}=5.0$	− 447[b]	−0.089	−200[b]	−0.040
Au	1.42	$5d^{10}6s^1$	$H_{6s}^{\text{Au}}=19.8$	−1290[b]	−0.065	(−)809[a,c]	(−)0.041

[a] The sign is estimated from HF-field systematics.

[b] Reference 1.

[c] This work.

host Fe, however, p shows a considerable variation with the impurity. This suggests that in contrast to Gd in Fe the impurity HF field is not exclusively caused by CEP. As discussed by Stearns[17] an additional possible contribution to the HF field may come from the OP, which is the larger the more the impurity atomic volume exceeds the host atomic volume. Comparing the atomic radii given in Table I it seems that for Au and Ag in Fe the OP may in fact contribute to the HF field. For Gd, however, such a contribution can be excluded due to the large atomic volume of this host.

It is worthwhile to mention that the atomic volume of metallic Gd is larger and that of Fe smaller than the atomic volumes of most of the other elements. As soon as the systematics of impurity HF fields is as complete for Gd as it is already for Fe, a comparison between these hosts will possibly reveal quite clearly the relative importance of the OP as an impurity HF field mechanism.

C. Electric field gradient

The EFG of dilute impurities in noncubic metals has been investigated rather extensively in the past.[18] There are essentially two contributions to the EFG in metals: one coming from the positive charged lattice ions V_{zz}^{lat}, the other coming from the conduction-electrons V_{zz}^{CE}. The total EFG can be described by the expression

$$V_{zz}=(1-\gamma_\infty)V_{zz}^{\text{lat}}+V_{zz}^{\text{CE}} .$$

γ_∞ is the Sternheimer correction which accounts for the closed electronic shell polarization of the probe.

The effective lattice EFG $(1-\gamma_\infty)V_{zz}^{\text{lat}}$ can be determined by a lattice sum calculation of V_{zz}^{lat} and by use of γ_∞ values which have been calculated for free ions by several authors.[19,20] The calculation of the conduction-electron EFG is much more difficult, since it requires the knowledge of the conduction-electron wave functions, and has been attempted up to now only in a few cases. To gain more insight into the properties of the conduction-electron EFG, one presently determines V_{zz}^{CE} in a systematic way from the measured V_{zz} and the calculated $(1-\gamma_\infty)V_{zz}^{\text{lat}}$ values. To avoid any ambiguity of V_{zz}^{CE} the sign of V_{zz}^{lat} has to be known. It is favorable that in our case both sign and magnitude of V_{zz} could be determined.

For a hcp lattice the lattice sum calculation for the EFG has been developed by Das *et al.*[21] Application of their formula requires the knowledge of the lattice parameters c and a. For Gd these parameters have been measured only down to 120 K.[7] Since the measured temperature dependence is quite weak we used the 120-K data ($a=3.6304$ Å and $c=5.7945$ Å) without extrapolation to 4 K. With the Sternheimer factor for Au, $\gamma_\infty=-65$, one obtains finally

$$(1-\gamma_\infty)V_{zz}^{\text{lat}}=+1.0\times10^{17}\ \text{V/cm}^2 .$$

From this value and the measured total EFG the conduction-electron EFG can be determined:

$$V_{zz}^{\text{CE}}=+13.4\times10^{17}\ \text{V/cm}^2 .$$

So the conduction-electron EFG for Au in Gd is about one order of magnitude larger than the ionic EFG, and the two contributions have the same sign.

It is interesting to compare this result with the universal correlation between V_{zz}^{CE} and $(1-\gamma_\infty)V_{zz}^{\text{lat}}$ recently proposed by Raghavan *et al.*[22] These authors have found that for a large number of impurity-host systems the electronic and ionic EFG are related in the following way:

$$V_{zz}^{\text{CE}}=-K(1-\gamma_\infty)V_{zz}^{\text{lat}} .$$

Electronic and ionic EFG have opposite sign and are proportional to each other with a proportionality constant K, which for most of the systems investigated up to now had the same value $K=+3$. Raghavan *et al.* therefore suggest that the above

TABLE II. Electric field gradients of various impurities in gadolinium.

Impurity	γ_∞	V_{zz}^{lat} (10^{15} V/cm^2)	$(1-\gamma_\infty)V_{zz}^{\text{lat}}$ (10^{17} V/cm^2)	V_{zz} [a] (10^{17} V/cm^2)	Ref.	V_{zz}^{CE} (10^{17} V/cm^2)	K
Cd	−29.3	+1.73	+0.52	1.31	23	− 1.83	+ 3.52
						+ 0.80	− 1.54
Gd	−80	+1.52	+1.4	+ 3.0	6	+ 1.6	− 1.14
Ta	−61	+1.73	+1.07	6.62	24	− 7.66	+ 7.15
						+ 5.52	− 5.16
W	−55	+1.73	+0.97	+ 6.84	25	+ 5.87	− 6.06
Os	−46.6	+1.73	+0.83	12.88	25	−13.71	+16.5
						+12.03	−14.5
Au	−65	+1.52	+1.0	+14.4	This work	+13.4	−13.4

[a] If the sign of V_{zz} is not known V_{zz}^{CE} and K are calculated for both positive and negative sign.

relation with $K=+3$ is with a few exceptions universally valid.

The impurity EFG in Gd does not obey this simple relation. This is evident from Table II where all the data on impurity EFG's in Gd presently available have been collected. In three cases (Gd, W, and Au) the sign of the total EFG has been measured. In all three cases the electronic and the ionic EFG have the same sign. Furthermore the parameter K of the proposed proportionality is strongly impurity dependent.

At present the strong variation of the conduction electron contribution to the impurity EFG in Gd is not understood. Since the conduction-electrons of Gd have partially d character[26] so that their density at the impurity site can influence the EFG, one important factor is here probably the valence difference between the host and the impurity ion.

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