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Abstract. The magnetic hyperfine field B_{hf} of the closed-shell probe nucleus ^{111}Cd on the cubic R site of the C15 Laves phase RCo$_2$ (R = Gd, Tb, Dy, Ho, Er, Sm, Nd and Pr) and RNi$_2$ (R = Gd, Sm) has been investigated at 9 K by perturbed angular correlation (PAC) spectroscopy. In RCo$_2$ the hyperfine field increases with increasing R spin, both for the heavy and the light R. The experimental trend suggests that the total hyperfine field has two contributions of opposite sign: $B_{hf} = B_{3d} - B_{4f}$, where B_{3d} is induced by the 3d Co moment and B_{4f} is due to indirect 4f–4f exchange. The 4f contribution can be estimated from the measurement of B_{hf} in RNi$_2$ where the 3d moment vanishes. The ^{111}Cd hyperfine fields in GdNi$_2$ and SmNi$_2$ at 9 K are $B_{hf} = 7.5(5)$ and $2.0(2)$ T, respectively. Assuming a linear dependence of B_{4f} on the projection $(g-1)J$ of the R spin on the total angular momentum J, as expected from the Ruderman–Kittel–Kasuya–Yosida (RKKY) theory of indirect 4f–4f exchange, the variation of B_{3d} across the R series can be determined from the experimental values of B_{hf}. In heavy RCo$_2$ (R = Gd, ..., Er) B_{3d} follows very closely the variation of the Co moment μ_{Co} across the R series with $B_{3d}/\mu_{Co} = 28.7(2)$ T μ_B^{-1}. With the same ratio for the light RCo$_2$ (R = Pr, Nd, Sm) the experimental B_{hf} values indicate an increase of the 3d moment from $\mu_{Co} = 0.45$ to 0.7 μ_B between PrCo$_2$ and SmCo$_2$.

1. Introduction

The intermetallic compounds R$_x$M$_y$ of rare-earth R and transition metals M = Fe, Co, Ni and Mn have been intensively studied for many years because of their complex magnetic properties, that arise from the coexistence and interaction of the magnetic moments of the highly localized 4f electrons of the rare-earths and of the itinerant 3d electrons of the transition elements (for recent reviews see [1–3]). Among these compounds the C15 Laves phases RM$_2$ have received particular attention. In RFe$_2$ the Stoner criterion for 3d magnetism is always fulfilled and Fe carries a magnetic moment even for nonmagnetic R constituents such as R = Y, Lu. In RNi$_2$ the magnetic order is sustained by the indirect 4f–4f interaction alone and Ni is always nonmagnetic. RCo$_2$ are at the borderline of the onset of 3d magnetism: YCo$_2$ and LuCo$_2$ are Pauli paramagnets, but in the case of magnetic R constituents magnetic order appears and Co develops a finite 3d moment which is induced by the rare-earth molecular field [4]. These compounds therefore offer the possibility of a detailed investigation of the conditions for the onset of 3d magnetism.

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An important source of information on the exchange interactions leading to magnetic order are the magnetic hyperfine fields at the sites of suitable probe nuclei. For probes with zero orbital angular momentum of the electron shell the magnetic hyperfine field is due to the Fermi contact term in the magnetic nucleus–electron interaction and reflects the spin polarization of the s conduction electrons. A finite s-electron spin density may arise from three possible effects [5]: the spin polarization of the host conduction electrons, the polarization of the electron core of the probe by a localized magnetic moment and the overlap polarization which is important in cases where the probe has a much larger metallic radius than the host, e.g. noble gases in 3d metals.

For closed-shell probe nuclei the s conduction electron polarization is the dominant effect. For a transition metal host with a wide s band mixed with a narrow spin-polarized d band a finite s-electron spin density arises from the s–d hybridization. The resulting magnetic hyperfine field B_{hf} is found to be approximately proportional to the inducing d moment [6, 7]: for the closed-shell nucleus ^{111}Cd in the 3d hosts Fe, Co, Ni, e.g. B_{hf} is a linear function of μ_{3d} with $B_{hf}/\mu_{3d} = 18$ T μ_B^{-1}. In magnetically ordered R metals or R compounds with s–p elements the s conduction electrons are spin polarized by the interaction with the hybridized 4f–5d electrons [8] and the magnetic hyperfine field of closed-shell probes is in a first approximation proportional to the projection $(g - 1)J$ of the R spin on the total angular momentum J [9, 10].

The investigation of magnetic hyperfine fields in the Laves phases RM_2 may therefore provide information on the magnitude and interaction of the itinerant 3d moment and the localized 4f moment and consequently these compounds have been studied by numerous hyperfine spectroscopic techniques, such as NMR [11], Mössbauer spectroscopy [12–14], muon spin resonance [15] and perturbed angular correlation (PAC) [16–18].

In the present communication we report on a PAC investigation of the magnetic hyperfine field of the probe nucleus ^{111}Cd on the cubic R site of RCo_2 for the R constituents R = Gd, Tb, Dy, Ho, Er, Sm, Nd and Pr. The proportionality of the ^{111}Cd hyperfine field and the 3d moments in Fe, Co, Ni suggests that the measurement of the ^{111}Cd hyperfine field in RCo_2 for different R constituents may provide information on the variation of the Co 3d moment across the R series. For this purpose, however, the contribution of the indirect 4f–4f interaction to the hyperfine field in RCo_2 has to be known. An estimate of this contribution may be obtained from the hyperfine field of the same probe in RNi_2 where the 3d moment vanishes and the magnetic order is sustained by the indirect 4f–4f exchange alone. Therefore, measurements of the ^{111}Cd hyperfine field were also carried out on $GdNi_2$ and $SmNi_2$.

Paramagnetic RM_2 (M = Fe, Co, Ni) crystallize in the cubic C15 ($MgCu_2$-type) lattice structure with R and M forming two sublattices with one equivalent site each. The local symmetry of the R site is cubic, that of the M site noncubic with space group symmetry $3m$. This difference in symmetry helps to identify the site occupied by the probe: the tensor of the electric-field gradient (EFG) is nonzero on the M site, but vanishes at the R site. Consequently, a finite electric quadrupole interaction (QI) is expected for ^{111}Cd on the M site and zero QI for ^{111}Cd on the R site.

2. Experimental details and results

Samples of RCo_2 and RNi_2 were prepared by arc melting of the metallic constituents in an argon atmosphere. X-ray diffraction showed the C15 pattern without contamination by other phases. The lattice parameters were in agreement with results given in the literature [1].

The PAC measurements were carried out with the 171–245 keV cascade of ^{111}Cd which is populated by the electron capture decay of the 2.8 d isotope ^{111}In. Details on the PAC technique can be found e.g. in [19] and [20].

The compounds were doped with the probe nucleus ^{111}Cd by diffusion of the parent isotope ^{111}In. A solution of commercially available ^{111}InCl$_3$ was dropped onto the sample which was subsequently kept for 15 hours at 800 °C in an evacuated quartz tube. Above the Curie temperatures the PAC spectra of paramagnetic samples showed a practically constant, unperturbed anisotropy which implies a vanishing QI at the probe nucleus. We may therefore conclude that in RCo$_2$ ^{111}Cd resides on the cubic R site, in contrast to the case for RMn$_2$ where the same probe occupies the noncubic transition metal site [18].

For the measurement of the saturation value of the magnetic hyperfine field the samples were cooled to 9 K in a closed-cycle He refrigerator. The PAC measurements were carried out with a standard four-detector PAC set-up equipped with fast BaF$_2$ scintillators. Examples of the measured PAC spectra are shown in figure 1 for R = Gd, Er, Sm and Pr. The spectra are characterized by a periodic, in some cases slightly attenuated modulation of the anisotropy and are typical for a perturbation by a pure magnetic hyperfine interaction (hfi). The magnetic hyperfine field was extracted by adjusting the theoretical perturbation factor for a pure magnetic hfi in a polycrystalline sample to the measured spectra:

$$A_{22}G_{22}(t) = A_{22}\left[0.2 + \sum_{n=1,2} 0.4\cos(n\omega_M t)\exp(-\delta n\omega_M t)\right]. \tag{1}$$

Here A_{22} is the unperturbed angular coefficient of the 171–245 keV cascade of ^{111}Cd; $\omega_M = 2\pi\nu_M = g\mu_N B_{hf}/\hbar$ is the Larmor frequency. The g-factor of the 5/2 state of ^{111}Cd is $g = -0.306$. The exponential factor in equation (1) allows for the possibility of a distribution of the magnetic hyperfine field which leads to attenuation of the oscillation amplitudes. δ is the relative width of a Lorentzian distribution. The results of the fits in terms of the frequency ν_M and the corresponding hyperfine field are listed in table 1. The width of the frequency distribution was $\delta \leqslant 0.010(1)$.

Table 1. The magnetic hyperfine frequency ν_M and the corresponding magnetic hyperfine field B_{hf} of ^{111}Cd on R sites of RCo$_2$ at 9 K. The error quoted for the frequency does not contain the uncertainty of the time calibration. The second column shows the magnetic order temperatures listed in [1]. The last column contains the 3d Co moments. The values of μ_{Co} for the heavy R were taken from the work of Gratz *et al* [21]; the values for the light R were derived from the measured ^{111}Cd hyperfine fields assuming that the same ratio B_{3d}/μ_{Co} holds for heavy and light RCo$_2$.

R	T_c (K)	ν_M (MHz)	B_{hf} (T)	μ_{Co} (μ_B)
Gd	387	49.45(2)	21.18(9)	1.0
Tb	230	45.49(2)	19.49(9)	0.88
Dy	135	42.72(2)	18.30(9)	0.82
Ho	89	41.22(2)	17.66(9)	0.78
Er	30	40.20(2)	17.22(9)	0.72
Sm	204	42.41(2)	18.17(9)	0.7
Nd	98	37.30(2)	15.98(9)	0.65
Pr	34	29.44(2)	12.61(9)	0.45

In most RCo$_2$ the symmetry is lowered when the compound is cooled below the magnetic order temperature [21]. HoCo$_2$ and SmCo$_2$ e.g. show a tetragonal and a rhombohedral distortion, respectively. In the magnetically ordered state one can therefore expect a finite electric-field gradient at the probe site. The fact that the PAC spectra are very well reproduced with the assumption of a pure magnetic hfi shows that the electric quadrupole interaction (QI) caused by these magneto-elastic effects is rather small. If we attribute the slight attenuation of the oscillation amplitudes to a QI rather than to a distribution of the magnetic hfi, the quadrupole
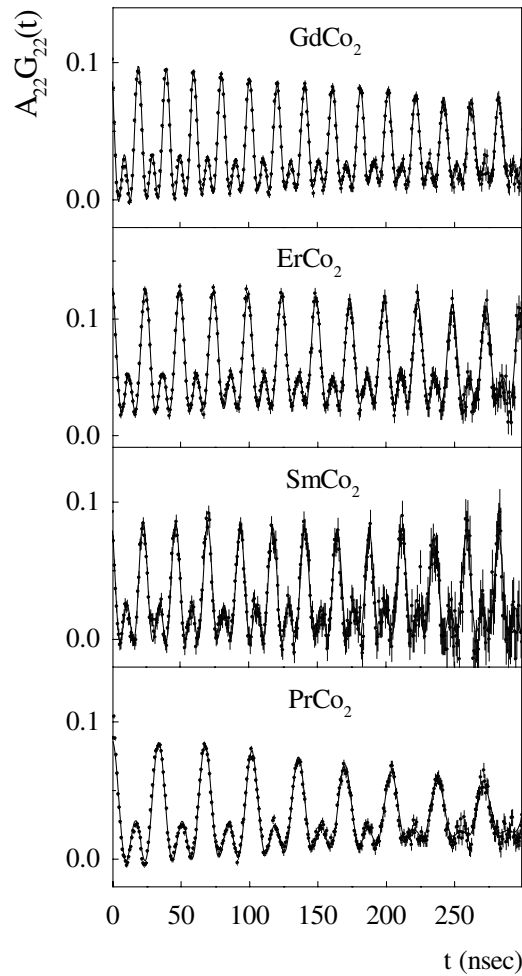
Figure 1. PAC spectra of ^{111}Cd in RCo$_2$ for R = Gd, Er, Sm and Pr at 9 K.

frequency $\nu_q = eQV_{zz}/h$ required to reproduce the data is of the order of 1 MHz which—with $Q(^{111}$Cd; $I = 5/2) = 0.77$ b—corresponds to an EFG of $V_{zz} \leqslant 5 \times 10^{15}$ V cm^{-2}.

Reliable values of the hyperfine field of ^{111}Cd in RNi$_2$ at 9 K have been obtained up to now for GdNi$_2$ and SmNi$_2$: $B_{hf} = 7.5(5)$ and 2.0(2) T, respectively. This series requires further investigation because of the observation of an unexpected strong, axially symmetric QI at temperatures $T \leqslant 300$ K which is possibly related to the structural instability of these compounds [22, 23]. Details will be given in a forthcoming paper.

3. Discussion

Figure 2, where we have plotted the experimental values of B_{hf} (full points) against the R spin projection $(g-1)J$, shows that although in both the light and heavy RCo$_2$ the ^{111}Cd hyperfine field increases with increasing R spin, the variation is quite different in the two series. Between Pr and Sm one observes a strong, in first order linear increase of B_{hf} by about 50%; from Er to Gd the increase is rather weak ($\sim$20%) and approximately parabolic. Furthermore, figure 2
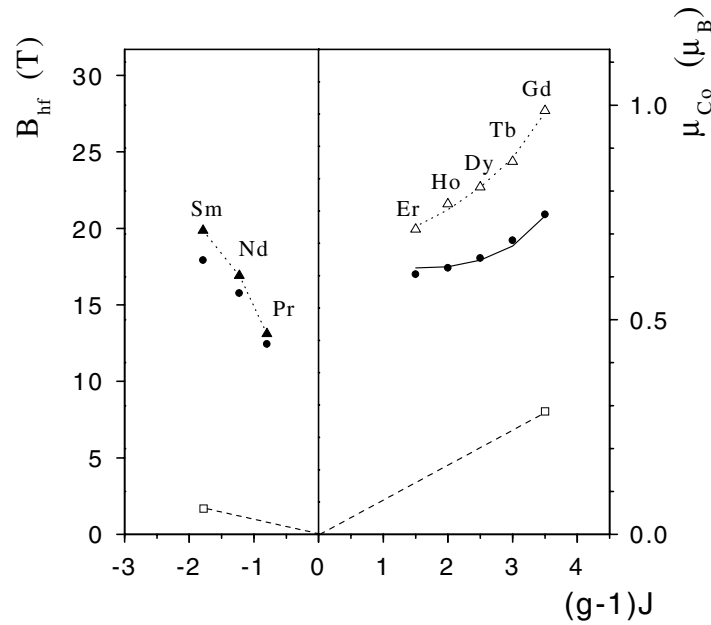
Figure 2. The magnetic hyperfine field of ^{111}Cd in RCo$_2$ (full points, left-hand scale) against the projection $(g-1)J$ of the R spin on the total angular momentum J. The solid line through the B_{hf} values of the heavy RCo$_2$ corresponds to the relation $B_{hf} = B_{3d} - B_{4f} = 28.7\mu_{Co} - 2.14(g-1)J$ (μ_{Co} and B_{hf} in units of μ_B and T, respectively; see section 3), where μ_{Co} are the Co moments taken from Gratz *et al* [21] (open triangles, right-hand scale). The dotted line through the μ_{Co} values corresponds to the relation $\mu_{Co} = 0.67 + 0.0203(g-1)^2 J(J+1)$ (in units of μ_B). The open squares show the measured magnetic hyperfine field of ^{111}Cd in GdNi$_2$ and SmNi$_2$, respectively, and the dashed lines illustrate the variation of the hyperfine field in RNi$_2$ expected from the RKKY theory. The solid triangles represent the Co moments (right-hand scale) of the light RCo$_2$ derived from the measured hyperfine fields (solid points, left-hand scale) with the assumption that the same ratio $B_{3d}/\mu_{Co} = 28.7$ T μ_B^{-1} holds for heavy and light RCo$_2$.

shows the B_{hf} values of RNi$_2$, R = Gd, Sm (open squares), and the Co moments μ_{Co} of the heavy RCo$_2$ (open triangles) derived from x-ray diffraction measurements of the thermal expansion and anisotropic magnetostriction by Gratz *et al* [21]. The nonlinear increase of μ_{Co} from Er to Gd appears to be related to the de Gennes factor $(g-1)^2 J(J+1)$: the experimental μ_{Co} values are well reproduced by $\mu_{Co} = 0.67 + 0.0203(g-1)^2 J(J+1)$ (in units of μ_B; dotted line in figure 2).

We analyse our experimental results considering two contributions to B_{hf}, one produced by the itinerant 3d moments (B_{3d}), the other by the localized 4f moments (B_{4f}). The magnetic order of the heavy and light RCo$_2$ is ferrimagnetic and ferromagnetic [1], respectively, which—via Hund's rule—implies that the 4f and the 3d spins are antiparallel. We therefore assume that B_{3d} and B_{4f} have opposite signs: $B_{hf} = B_{3d} - B_{4f}$. For GdCo$_2$ the 4f contribution can be estimated rather accurately from the hyperfine field of ^{111}Cd:GdNi$_2$. In this compound the induced 3d moment is at most a few hundredths of a Bohr magneton [24] which corresponds—with $B_{3d}/\mu_{3d} = 20$–30 T μ_B^{-1}—to $B_{3d}(^{111}$Cd:GdNi$_2) \leqslant 1$ T. The experimental value $B_{hf}(^{111}$Cd:GdNi$_2) = 7.5$ T therefore results mainly from the indirect 4f–4f exchange and our conclusions are not affected if we neglect $B_{3d}(^{111}$Cd:GdNi$_2)$ in the following. According to the RKKY theory [25, 26], the spin polarization of the conduction band induced by the 4f electrons depends on the R spin, the R–R separation, the s conduction electron density and the s–f coupling constant. RCo$_2$ and RNi$_2$ should be very similar with respect to these

parameters and it is therefore justified to assume the same 4f contribution for both GdNi$_2$ and GdCo$_2$. This leads to $B_{4f}(^{111}Cd:GdCo_2) = 7.5$ T and $B_{3d}(^{111}Cd:GdCo_2) = 28.7$ T. With $\mu_{Co}(GdCo_2) = 1 \mu_B$ from [21] we thus obtain $B_{3d}/\mu_{Co} = 28.7$ T μ_B^{-1} for $^{111}Cd:GdCo_2$. Assuming that the same ratio holds for the other heavy R, we can calculate the variation of B_{3d} between Gd and Er from the μ_{Co} values of Gratz *et al* [21].

The 4f contribution B_{4f} has been determined from $B_{hf}(^{111}Cd:RNi_2)$ up to now only for R = Gd. For the other heavy R we assume that B_{4f} is proportional to the spin projection $(g - 1)J$: $B_{4f} = 2.14(g - 1)J$ (T) (see the dashed line in figure 2). This assumption has theoretical and experimental support: the proportionality between the conduction electron spin polarization and the 4f spin predicted by the RKKY theory has been experimentally confirmed—at least in first order—by measurements of the hyperfine field of closed-shell impurities in the R metals [9] and in R intermetallics with sp constituents such as RAl$_2$ [10]. The slight deviations from a strict linearity have been attributed to volume effects and contributions of the R orbital angular momentum to the hyperfine field [12].

The resulting relation $B_{hf} = 28.7\mu_{Co} - 2.14(g - 1)J$ (μ_{Co} and B_{hf} in units of μ_B and T, respectively) for the ^{111}Cd hyperfine field in heavy RCo$_2$ calculated with the 3d moments of Gratz *et al* [21] is illustrated by the solid line in figure 2. It should be remembered that only one parameter, the ratio B_{3d}/μ_{Co} for GdCo$_2$, has been adjusted in this analysis. The excellent agreement with the experimental trend of B_{hf} between Gd and Er therefore supports our three assumptions: (i) $B_{3d}/\mu_{Co} = 28.7$ T μ_B^{-1} holds for all heavy R, (ii) the 4f contribution B_{4f} is proportional to the 4f spin and (iii) B_{3d} and B_{4f} are antiparallel. Furthermore, the agreement can be seen as a confirmation of the variation of μ_{Co} in the heavy RCo$_2$ as determined by Gratz *et al* [21].

In the case of the light RCo$_2$ the ^{111}Cd hyperfine field increases strongly from R = Pr to R = Sm. A determination of the ratio B_{3d}/μ_{Co} for light RCo$_2$ from these experimental B_{hf} values (full points in figure 2) is difficult since it requires knowledge of the contribution B_{4f} and a precise value of the 3d moment of at least one light RCo$_2$. The published values of 3d moments of the light RCo$_2$, however, scatter considerably [1]. The values of μ_{Co} given in table 1 have therefore been calculated with the ratio $B_{3d}/\mu_{Co} = 28.7$ T μ_B^{-1} of the heavy RCo$_2$, using $B_{hf}(^{111}Cd:SmNi_2)$ as an estimate of the 4f contribution B_{4f} in RCo$_2$. It is, however, an open question whether the same ratio B_{3d}/μ_{Co} holds for heavy and light RCo$_2$ and the estimate of the localized contribution B_{4f} from $B_{hf}(^{111}Cd:SmNi_2)$ has also a question mark. From $B_{hf}(^{111}Cd:GdNi_2) = 7.5$ T and the systematics of the hyperfine field of sp impurities in the R metals [27, 28] or in RAl$_2$ [10] where indirect 4f–4f exchange dominates, one would expect a value of $B_{hf}(^{111}Cd:SmNi_2)$ of the order of 5 T which is considerably larger than the experimental result $B_{hf} = 2.0$ T. The reason for this difference is at present not clear. In spite of these open questions the values given in table 1 reflect the qualitative trend and indicate a strong continuous increase of the 3d moment with increasing R spin.

In summary, we have measured the magnetic hyperfine field B_{hf} of ^{111}Cd in the C15 Laves phases RCo$_2$, R = Gd, . . ., Er, Sm, Nd, Pr and also in GdNi$_2$ and SmNi$_2$ at 9 K by perturbed angular correlation spectroscopy. The variation of B_{hf} across the series of heavy RCo$_2$ can be described by the relation $B_{hf} = 28.7\mu_{Co} - 2.14(g - 1)J$ (μ_{Co} and B_{hf} in units of μ_B and T, respectively) where μ_{Co} are the Co moments measured by Gratz *et al* [21] and $(g - 1)J$ is the projection of the R spin on the total angular momentum J. The B_{hf} values of the light RCo$_2$ indicate a strong increase of the Co moment from Pr to Sm. Currently we are extending these ^{111}Cd PAC studies to investigate the coexistence of the paramagnetic and ferromagnetic phase at the first-order transitions observed in RCo$_2$, R = Dy, Ho, Er, Nd, Pr.

Acknowledgments

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