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Perturbed angular correlation study of the magnetic phase transitions in the rare-earth cobalt Laves phases $R\mathrm{Co}_2$

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The order and other properties of the magnetic phase transitions in the rare-earth (R)-cobalt Laves phases $R\mathrm{Co}_2$ have been studied for $R=$Gd, Tb, Dy, Ho, Er, Sm, Nd, and Pr by measuring the temperature dependence of the magnetic hyperfine interaction of the nuclear probe ^{111}Cd on the cubic R sites using the perturbed angular correlation technique. Both for heavy and light R constituents the transitions change from second order (Gd, Tb, Sm) to first order (Dy, Ho, Er, Nd, Pr) at order temperatures of 150–200 K. For heavy R constituents, the order deduced from the hyperfine interaction is in agreement with previous investigations. The observation of first order transitions in NdCo_2 and PrCo_2, however, is unexpected. In earlier studies the transitions in these compounds are usually classified as second order transitions. Both in the heavy and the light $R\mathrm{Co}_2$ the discontinuous jump of the hyperfine interaction at the first order transitions increases with decreasing order temperature. This trend implies that the Co magnetization at the transition increases with decreasing T_C which can be related to the temperature dependence of the coefficient of the M^4 term of the free energy in the Wohlfarth-Rhodes-Shimizu theory of itinerant electron magnetism. All compounds investigated presented a spread of the order temperature of $\sim 1-2$ K which results in a coexistence of the paramagnetic and the magnetically ordered phase near the transition and causes a critical increase of the relative linewidth of the hyperfine frequency diverging as $\delta \propto (1-T/T_C)^{\varepsilon}$ with $\varepsilon=-1.0(1)$.

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I. INTRODUCTION

The magnetic hyperfine field $\mathbf{B}_{\mathrm{hf}}$ at the nuclei of diamagnetic probe atoms in magnetically ordered metals and intermetallic compounds is caused by the Fermi-contact term in the magnetic nucleus-electron interaction and reflects the spin polarization of the s-conduction electrons. Measurements of the magnetic hyperfine field by NMR, Mössbauer spectroscopy, perturbed angular correlations (PAC), and other hyperfine spectroscopic techniques are therefore a useful source of information on the magnetic properties of metallic systems, in particular on the exchange interactions responsible for the magnetic order.

In this paper we report a systematic investigation of the temperature dependence of the magnetic hyperfine field at the diamagnetic probe ^{111}Cd in the rare earth (R)-cobalt Laves phases $R\mathrm{Co}_2$ ($R=$Gd, Tb, Dy, Ho, Er, Sm, Nd, Pr) which was carried out with the PAC technique. This work is the extension of a previous PAC study of the low-temperature saturation values of the magnetic hyperfine field of ^{111}Cd in the entire $R\mathrm{Co}_2$ series.[1]

Intermetallic compounds R_xM_y of rare earth and $3d$-transition elements (M) have since long attracted considerable interest because of their complex magnetic properties caused by the coexistence and interaction of the itinerant $3d$-electrons of the transition elements and the highly localized $4f$ electrons of the rare earths. Among the R_xM_y, the Laves phases $R\mathrm{Co}_2$ have received particular attention and their properties are extensively investigated since about 1965 (for recent reviews see Gratz and Markosyan,[2] Duc and Brommer,[3] and Gignoux and Schmitt[4]).

The interest in the $R\mathrm{Co}_2$ series stems from the exchange-driven metamagnetism of these compounds. The possibility of metamagnetism, i.e., the transition from a paramagnetic to a highly magnetized state of an itinerant electron system induced by a strong external magnetic field, was first pointed out by Wohlfarth and Rhodes.[5] In this phenomenological theory the magnetic state of an itinerant electron system in a magnetic field $\mathbf{B}$ is discussed in terms of a Landau expansion of the free energy in powers of the magnetization $\mathbf{M}$

$$F(M)=\frac{1}{2}a_1(T)M^2+\frac{1}{4}a_3(T)M^4+\frac{1}{6}a_5(T)M^6\cdots-\mathbf{M}\cdot\mathbf{B}. \tag{1}$$

The expansion coefficients $a_i(T)$ depend on the density of states $N(E)$ and its derivatives near the Fermi energy E_F.[6,7] Their temperature dependence comes from Stoner excitations and from spin fluctuations[8] at higher temperatures.

It was soon realized that the band structure of Y Co_2—with the same $C15$ lattice as $R\mathrm{Co}_2$—probably satisfied the requirements of a peak in the density of states $N(E)$ and a large second derivative of $N(E)$ below the Fermi energy for a metamagnetic transition.[9–12] The experimental observation of such a transition in YCo_2, however, had to wait almost three decades until the production of external magnetic fields of the order of 100 T became possible.[13] Earlier experimental support for the concept of itinerant electron metamagnetism came from the observation of spontaneous magnetic order of the d-electron system in the related $R\mathrm{Co}_2$ compounds. The substitution of nonmagnetic Y by magnetic rare earth atoms leads to $3d$-$4f$ intersublattice exchange and the corresponding molecular field $B_{\mathrm{mol}} = \lambda_{fd} M_R$, where M_R is the R sublattice magnetization and λ_{fd} the $3d$-$4f$ coupling constant may take the role of an external field.[14] The molecular field increases with decreasing temperature and increasing $4f$ spin S and at ErCo$_2$($S = 3/2$) it becomes sufficiently strong[15] to drive the Co subsystem at $T_C \approx 34$ K from the paramagnetic to the ferrimagnetic state.

One particularly interesting aspect of the magnetic properties of the RCo$_2$ is the fact that for compounds with heavy rare earth constituents the order of the transitions from the paramagnetic to the ferrimagnetic state is correlated to the order temperature T_C. With decreasing T_C, the transitions change—at a border line of about 200 K—from second to first order: The compounds with the heavy rare earth constituents R=Gd, Tb ($T_C \approx 392$ K and 231 K, respectively) exhibit second-order transitions (SOT's), those with R=Dy, Ho, Er ($T_C \approx 138$, 98, and 40 K, respectively) first-order transitions (FOT's).

This change of order has been shown by Bloch *et al.*,[6] Shimizu,[7,16] and Inoue and Shimizu[17,18] to be related to the sign of the M^4 term in Eq. (1). Metamagnetic FOT's in a paramagnetic compound ($a_1 > 0, a_5 > 0$) require $a_3 < 0$, while $a_3 > 0$ results in SOT's. According to Bloch *et al.*[6] the band structure of YCo$_2$ leads to a temperature dependence of the a_3 coefficient of approximately

$$a_3(T) = a_3(0)[1 - (T/T_0)^2]; a_3(0) < 0. \tag{2}$$

Assuming that RCo$_2$ has the same band structure, T_0 thus constitutes the boundary between first order ($T_C < T_0$) and second order ($T_C > T_0$) transitions in the RCo$_2$ series. From the temperature dependence of the paramagnetic susceptibility of YCo$_2$ Bloch *et al.*[6] estimated $T_0 \approx 250$ K while Inoue and Shimizu[18] arrived—on the basis of the order in DyCo$_2$ and Gd$_{1-x}$Y$_x$Co$_2$—at a SOT-FOT boundary temperature of $T_0 \approx 150$ K.

The phase transitions of RCo$_2$ with the light rare earth elements R= Sm, Nd, and Pr are usually quoted to be of second order. The transition temperature of SmCo$_2$ is $T_C \approx 206$ K and a SOT is still compatible with the theory of Inoue and Shimizu.[18] The transition temperatures of NdCo$_2$ (T_C=97.9 K) and PrCo$_2$ (T_C=39.9 K), however, are much smaller than even the lower estimate of the SOT-FOT boundary temperature of $T_0 \approx 150$ K. The theory of Bloch *et al.*[6] and Inoue and Shimizu[18] is therefore considered to apply to the heavy RCo$_2$ only. Crystal field effects[6] and the volume dependence of the expansion coefficients of the free energy[19] have been invoked as possible explanations for the differences between heavy and light RCo$_2$. There are, however, only few detailed experimental studies of the phase transitions in the light RCo$_2$ and in our view these data leave some doubt as to the classification of the transitions of NdCo$_2$ and PrCo$_2$ as SOT's.

The investigation of the phase transitions of RCo$_2$, in particular those of NdCo$_2$ and PrCo$_2$, by PAC measurements of the temperature dependence of the magnetic hyperfine field at a suitable probe nucleus therefore appeared of interest. It has been shown in Ref. 1 that the main contribution to the magnetic hyperfine field at the diamagnetic probe ^{111}Cd in RCo$_2$ comes from the Co sublattice. The measurement of the temperature dependence of the hyperfine interaction therefore provides a possibility to study the temperature induced changes of the Co magnetization and the order of its magnetic phase transition. Compared to measurements of magnetization, thermal expansion, resistivity, and other integral techniques, PAC measurements of hyperfine fields have—where applicable—some advantages: PAC requires no external fields, it allows the easy identification of foreign phases by their different hyperfine field and—as will be shown below—is highly sensitive to inhomogeneities of the magnetic properties of a given sample.

A second aim of this work was the study of the static critical exponents of the magnetic hyperfine field of the SOT's of RCo$_2$. Hohenemser *et al.*[20] have shown that PAC and Mößbauer spectroscopy are useful tools for the investigation of the static and dynamical critical behavior of magnetically ordered systems. Up to now, such measurements have been carried out mainly in the pure $3d$ magnets Fe, Co, and Ni and in some disordered ferromagnetic alloys and magnetic oxides.[21] To our knowledge, PAC has not yet been used to study the critical behavior of chemically ordered magnetic intermetallics and a systematic investigation of the critical exponents in RCo$_2$ as a function of the R constituents therefore appeared of interest. However, our attempts to measure the magnetic hyperfine field asymptotically close to the order temperature were strongly hindered by a critical increase of the PAC linewidth near T_C. The same effect has been observed in practically all PAC investigations of magnetic hyperfine fields in chemically ordered intermetallic compounds reported up to now.[22–25] For a discussion of the possible mechanisms responsible for this critical line broadening, precise experimental data are required. In our measurements particular emphasis was therefore given to the changes of the PAC spectra in a small temperature interval around T_C.

Paramagnetic RCo$_2$ crystallize in the cubic $C15$ (MgCu$_2$) lattice structure with R and Co forming two sublattices with one equivalent site each. The magnetic order of the heavy and light RCo$_2$ is ferrimagnetic and ferromagnetic,[2] respectively, which—via Hund's rule—implies that the $4f$ and the $3d$ spins are antiparallel. The site occupied by a PAC probe in a cubic AB_2 Laves phase can be identified from the PAC spectra in the paramagnetic phase because the A sites have cubic, the B sites noncubic point symmetry, respectively. For $T > T_C$, PAC probes on A sites therefore feel—ideally—no interaction (in reality, slight structural or chemical imperfections may lead to weak quadrupole perturbations) and the relaxation caused by paramagnetic spin fluctuations is usually too slow to be detected within the PAC time window of ^{111}Cd (for a discussion see Ref. 20). For probes on A sites one therefore expects a practically unperturbed angular correlation. Probes on B sites, however, are subject to a strong axially symmetric electric-field gradient and the PAC spectrum shows the characteristic quadrupole modulation. This symmetry difference has been used to establish that the probe ^{111}In/^{111}Cd in

$R\mathrm{Co}_2$ occupies the rare-earth site,[1] while, e.g., in $R\mathrm{Al}_2$ the same probe resides on the Al site.[26]

II. EXPERIMENTAL DETAILS

A. Sample preparation and equipment

The PAC measurements were carried out with the 171–245 keV cascade of $^{111}\mathrm{Cd}$ which is populated by the electron capture decay of the 2.8 *d* isotope $^{111}\mathrm{In}$. The samples were produced by arc melting of the metallic components in the stoichiometric ratio in an argon atmosphere. After characterization by x-ray diffraction the samples were doped with the PAC probe$^{111}\mathrm{In}/^{111}\mathrm{Cd}$ by diffusion (800°C, 12 h) of carrier-free$^{111}\mathrm{In}$ into the host lattices. PAC measurements were carried out with a standard four-detector BaF_2 setup in the temperature range $10\ \mathrm{K} \leqslant T \leqslant 400\ \mathrm{K}$. Temperatures $T < 290$ K were obtained with a closed-cycle He refrigerator. The samples (diameter $\leqslant$ 1 mm) were inserted into a small Al sample-holder filled with cryogenic grease for good thermal contact. The sample holder was attached to the cold finger and thermally shielded by a Cu tube with thin Al windows. The temperature was measured both at the cold finger and at the tip of the sample holder with two Si diodes (separated by about 30 mm). A temperature gradient was not detected within the absolute accuracy of the diodes of 1 K. The temperatures were recorded during the measurements with a frequency of 0.20 Hz. The width (FWHM) of the resulting temperature distribution was found to be $\Delta T \approx 0.1$ K. For the case of GdCo_2 temperatures $T > 290$ K were produced with an especially designed PAC furnace[27] with a temperature stability $\Delta T \leqslant 0.1$ K. For the high temperature measurements the samples were encapsulated into small quartz tubes. Close to the respective Curie points temperatures were changed in steps as small as 0.25 K. To check for hysteresis effects, in some cases two series of measurements were performed, first heating, then cooling the compound in steps across the order temperature.

B. Data analysis

The angular correlation of two successive γ rays of a γ-γ cascade, expressed by angular correlation coefficients A_{kk} ($k=2,4$) may be modulated in time by hyperfine interactions in the intermediate state of the cascade. For polycrystalline samples this modulation can be described by the perturbation factor $G_{kk}(t)$ which depends on the multipole order, the symmetry and time dependence of the interaction and on the spin of the intermediate state (for details see, e.g., Frauenfelder and Steffen[28]).

For static hyperfine interactions the perturbation factor can be written as a sum of oscillatory terms

$$G_{kk}(t) = s_{k0} + \sum_n s_{kn} \cos(\omega_n t). \tag{3}$$

The frequencies ω_n are the transition frequencies between the hyperfine levels into which a nuclear state is split by the hyperfine interaction. These frequencies and the amplitudes s_{kn} have to be determined by diagonalization of the interaction Hamiltonian. The number of terms in Eq. (3) depends on the spin I of the intermediate state. In the present paper we are dealing with the perturbation by pure magnetic interaction with Larmor frequency $\omega_M = 2\pi\nu_M = g\mu_N B_{hf}/\hbar$ (g represents the nuclear g factor, μ_N the nuclear magneton).

In this case the perturbation factor can be expressed in an analytical form

$$G_{22}(t) = 1/5 + 2/5 \sum_{n=1,2} \cos(n\omega_M t). \tag{4}$$

If the ensemble of the probe nuclei is subject to a distribution rather than a unique hyperfine interaction, the nuclear spins of the ensemble no longer precess all with the same frequency and an attenuation of the oscillation amplitudes results, which is the stronger the broader the distribution. The effect of a Lorentzian distribution of relative width δ on the angular correlation can be approximated by

$$G_{22}(t) = s_{k0} + \sum_n s_{kn} \cos(n\omega_M t) \exp(-\delta n \omega_M t). \tag{5}$$

Frequently, several fractions of nuclei subject to different hyperfine interactions are found in the same sample. The effective perturbation factor is then given by

$$G_{kk}(t) = \sum_i f_i G^i_{kk}(t). \tag{6}$$

f_i (with $\Sigma_i f_i = 1$) is the relative intensity of the ith fraction.

III. MEASUREMENTS AND RESULTS

A. $R\mathrm{Co}_2$ (R=Gd, Tb, Sm)—compounds with second-order transitions

Figure 1 shows a series of PAC spectra of $^{111}\mathrm{Cd}$:Tb Co_2 between 10 and 240 K to illustrate the typical evolution of the PAC spectra with temperature observed for compounds with a SOT ($T_C = 231.4$ K for TbCo_2, see below). At 10 K the spectrum shows the periodic modulation of the anisotropy typical for a perturbation by a pure magnetic interaction [see Eq. (5)] with the precession amplitudes decreasing only weakly with increasing time. The relative width of the Lorentzian distribution required to account for the weak attenuation is $\delta \leqslant 0.01$. The precession frequency ν_M decreases with increasing temperature, but the attenuation of the oscillation amplitudes is not affected by temperature. Up to $T/T_C = 0.97$ the spectra are well reproduced with a single fraction, i.e., all PAC probes are subject to practically the same hyperfine field.

At about $T/T_C \approx 0.97$, however, the attenuation starts to increase dramatically and within 2–3 K the oscillations are completely wiped out (see the spectra at 228.5 and 231.1 K, respectively, in Fig. 1). The period of the slowest precession with some still visible amplitude is at most 5 times larger than the precession period at 10 K (marked by a dotted line in Fig. 1). The attenuation thus restricts the frequency (and temperature) range in which ν_M can be determined accurately to $\nu_M(T) \geqslant 0.2\nu_M(0)$. After the disappearance of the magnetic oscillations, the PAC pattern consists of an initial,

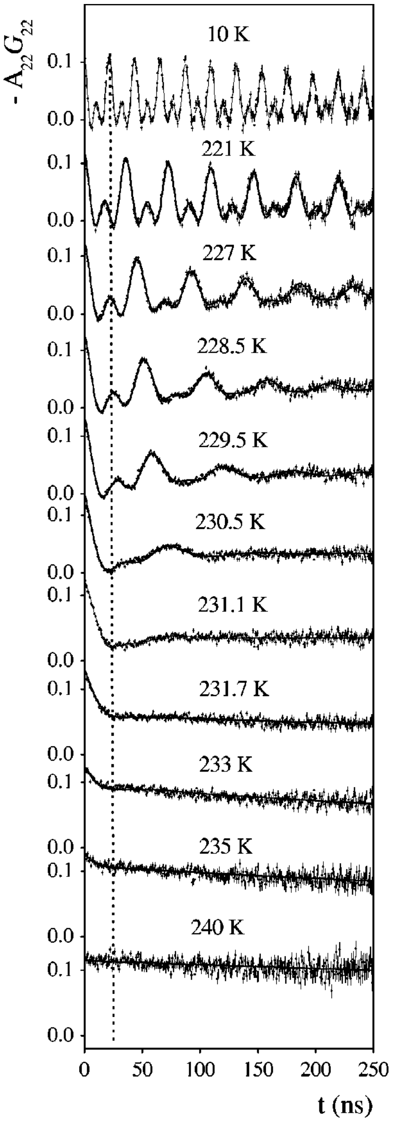

FIG. 1. PAC spectra of ^{111}Cd in TbCo$_2$ at 10 K and close to the SOT at $T_C = 231.4$ K. The dotted vertical line marks the precession period at 10 K.

relatively rapid decrease towards a small constant anisotropy (“hard-core value,” see Ref. 28) at large delay times. Upon further increase of temperature, the level of constant anisotropy increases, the initial decrease becomes smaller and finally (see the spectrum at 240 K in Fig. 1) one observes a practically unperturbed angular correlation which—as pointed out in the Introduction—is the ^{111}Cd PAC signature of the paramagnetic phase of RCo$_2$.

With increasing temperature the PAC spectrum thus changes from the periodic modulation of the ferrimagnetic phase to the constant anisotropy of the paramagnetic phase. As one approaches the order temperature T_C from $T < T_C$, the magnetic oscillations of the ferrimagnetic phase are increasingly damped, at the same time the level of constant anisotropy at large delay times—reflecting the paramagnetic phase—increases. This evolution of the PAC spectra with temperature implies the coexistence of the ferrimagnetic and the paramagnetic phase in a small interval around the order temperature: While at a given temperature $T \approx T_C$ some fraction of the ensemble of PAC nuclei (in the following termed as “magnetic fraction”) is still perturbed by an—-increasingly broadened—magnetic hyperfine interaction, the rest is already in a paramagnetic environment and therefore unperturbed (“paramagnetic fraction”). The spectra in Fig. 1 clearly indicate that with increasing temperature the paramagnetic fraction grows at the expense of the magnetic fraction.

The analysis of the measured spectra for $T/T_C > 0.97$ was therefore based on the assumption of two fractions of PAC probes, one with relative intensity f_{para} describing probes in the paramagnetic phase, the other one with intensity (1-f_{para}) describing probes in the ferrimagnetic phase. The perturbation factor in the paramagnetic phase is $G_{22}^{\text{para}}(t) \approx 1$.

Two possible mechanisms have to be considered when discussing the attenuation of the oscillations of PAC pattern and the corresponding perturbation factor in the ferrimagnetic phase: One is a distribution of the static interaction and the corresponding hyperfine frequencies, the other one a perturbation by a time-dependent interaction. In the case of weak attenuations these two possibilities are difficult to distinguish. For strong attenuations, however, the mechanism responsible can be recognized from the anisotropy at large delay times. Strong attenuations by dynamic hyperfine interactions occur when $\omega_f \tau \approx 1$, where ω_f characterizes the strength of the fluctuating interaction and τ its correlation time.[29,30] In this case the anisotropy is completely destroyed at large delay times. Strong attenuations by broad distributions of static interactions, however, lead to a finite anisotropy (“hard-core value,” see Ref. 28) at large delay times. In the present case we never observed a complete destruction of the anisotropy, the attenuation always tended towards the “hard-core value.” From this we can conclude that the attenuation of the ^{111}Cd:TbCo$_2$ PAC spectra close to T_C is caused by a static distribution of the magnetic hyperfine field rather than a dynamic interaction. In the analysis we have assumed that the static hyperfine field distribution has Lorentzian form [see Eq. (5)].

The relevant parameters, i.e., the magnetic frequency ν_M, the relative width δ of the Lorentzian distribution and the paramagnetic fraction were determined by fitting Eqs. (5), (6) to the measured spectra. These fits are given by the solid lines in Fig. 1. Clearly, the changes of the PAC spectra with temperature are very well reproduced by the assumption of a coexistence of ferrimagnetic and paramagnetic TbCo$_2$ in the transition region. (Note: The assumption of a Gaussian field distribution results in considerably poorer fits).

The relative width δ of the frequency distribution derived by these fits (see Fig. 2) increases critically as one approaches the Curie temperature from $T < T_C$. A fit of the relation $\delta \propto (1 - T/T_C)^{\varepsilon}$ to these data results in an exponent of $\varepsilon = -1.0(1)$ (solid line in Fig. 2). For comparison Fig. 2 also shows the temperature dependence of the relative linewidth for a FOT, in the case of DyCo$_2$.

The spectra of the other two RCo$_2$ with SOT’s show qualitatively the same features as those of TbCo$_2$. Both in GdCo$_2$ (see Fig. 3) and SmCo$_2$ the low-temperature spectra consist of a periodic, very weakly damped oscillation (δ

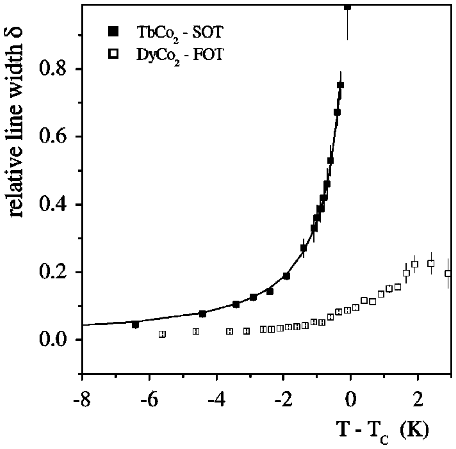

FIG. 2. The relative width δ of the distribution of the magnetic interaction frequency of ^{111}Cd close to the SOT of TbCo$_2$ (full symbols) and the FOT of DyCo$_2$ (open squares). The solid line represents a fit of the relation $\delta \propto (1-T/T_C)^{\varepsilon}$ with $\varepsilon = -1.0(1)$ to the data of TbCo$_2$.

$\leqslant 0.01$). At $T/T_C > 0.97$ the spectra of both compound show a critical increase of the relative linewidth δ and close to T_C the coexistence of the magnetically ordered and the paramagnetic phase. GdCo$_2$ differs from the other two SOT compounds with respect to the lower limit to which the temperature dependence of ν_M can be followed accurately. In the case of GdCo$_2$ the period of the slowest precession with some still visible amplitude is about 10 times larger than the precession period at 10 K (see Fig. 3): This corresponds to a lower frequency limit of $\nu_M(T) \geqslant 0.1\ \nu_M(0)$, while in the case of TbCo$_2$ and SmCo$_2$ one has $\nu_M(T) \geqslant 0.2\ \nu_M(0)$.

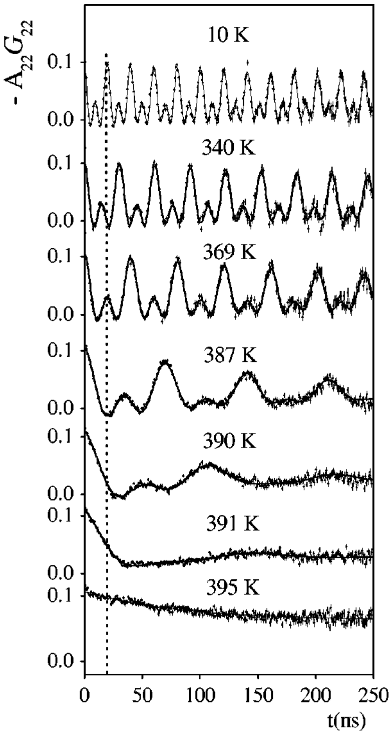

FIG. 3. PAC spectra of ^{111}Cd in GdCo$_2$ at 10 K and close to the SOT at $T_C = 392.0$ K. The dotted vertical line marks the precession period at 10 K.

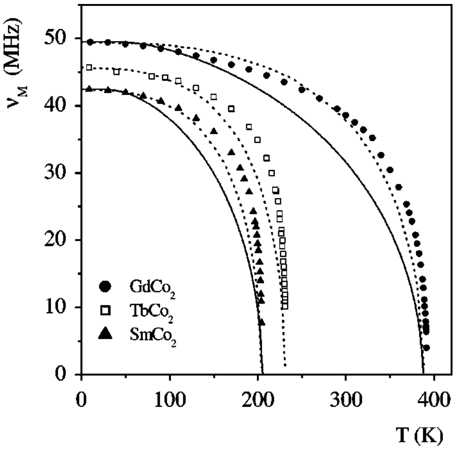

FIG. 4. The temperature dependence of the magnetic interaction frequency ν_M of ^{111}Cd on R sites of the SOT compounds GdCo$_2$, TbCo$_2$, and SmCo$_2$, compared to the predictions of the free-electron Stoner theory (dotted line) and the molecular-field theory (solid line) for GdCo$_2$ and SmCo$_2$. The molecular-field curve of TbCo$_2$ has been omitted for the sake of clarity.

The parameters ν_M extracted from the spectra of GdCo$_2$, TbCo$_2$ and SmCo$_2$ are collected in Fig. 4. The parameters δ and f_{para} will be described in Sec. IV A.

B. RCo$_2$ (R=Dy, Ho, Er, Nd, Pr)—compounds with first-order transitions

It is well established that the phase transitions from the paramagnetic to the ferrimagnetic phase in RCo$_2$ with R=Dy, Ho, Er are of first order. To illustrate the typical evolution of the PAC spectra across a FOT, we show in Fig. 5 spectra of ^{111}Cd:DyCo$_2$ at different temperatures. As in the case of the SOT's, at $T \ll T_C$ ($T_C = 137.6$ K for Dy Co$_2$ see Sec. IV A) one observes the periodic modulation characteristic for the ferrimagnetic phase and at $T \gg T_C$ the—almost—unperturbed angular correlation of the paramagnetic phase. In the transition region $T \sim T_C$ the spectrum consists of a superposition of an oscillatory component and an unperturbed component which indicates—as in the case of the SOT's—the coexistence of the ferrimagnetic and the paramagnetic phase in a small temperature interval and as at SOT's, the paramagnetic fraction increases continuously with temperature at the expense of the ferrimagnetic component. In two features, however, the spectra at FOT's differ considerably from those at SOT's (compare Fig. 1 and Fig. 5): (i) The magnetic interaction frequency varies only slightly with temperature. Close to T_C, the precession period remains almost constant up to the total disappearance of the ferrimagnetic component. (ii) The ferrimagnetic fraction decreases with increasing temperature, but contrary to the complete attenuation of the oscillation amplitudes in SOT compounds, the oscillations in DyCo$_2$ remain visible as long as the spectrum contains a ferrimagnetic component. This implies, and is illustrated in Fig. 2, that in FOT compounds the line broadening close to T_C is much weaker than in SOT

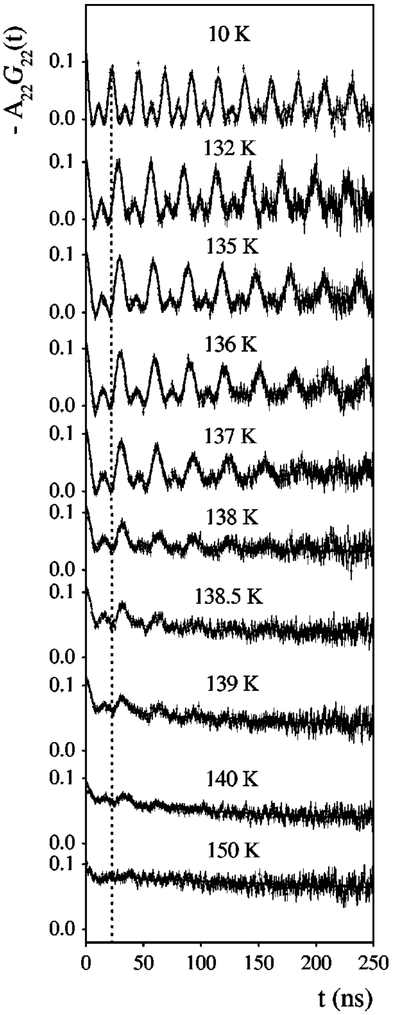

FIG. 5. PAC spectra of ^{111}Cd in DyCo$_2$ at 10 K and close to the FOT at $T_C = 137.6(1)$ K. The dotted vertical line marks the precession period at 10 K.

compounds. The continuous slight increase of the relative linewidth δ to temperatures $T - T_C > 0$ is a marked difference to the critical trend of $\delta(T)$ at a SOT and may serve as an identification mark for FOT's.

The spectra of HoCo$_2$ and ErCo$_2$ show qualitatively the same features of a FOT as those of DyCo$_2$. Again, one observes the coexistence of the ferrimagnetic and the paramagnetic phase close to T_C. The magnetic interaction frequencies vary even less with temperature than in the case of DyCo$_2$ and the oscillation amplitudes are practically non-attenuated up to the complete disappearance of the ferrimagnetic component. The range of phase coexistence is of the same order of 2–3 K, the relative linewidth is practically constant in the transition region.

The phase transition in PrCo$_2$ and NdCo$_2$ are frequently quoted in the literature to be of second order. In Figs. 6 and 7 we show the ^{111}Cd PAC spectra observed in these compounds. Clearly, the spectra of both compounds show the characteristic features of a FOT: As T_C is approached from lower temperatures, the unperturbed (paramagnetic) component grows at the expense of the oscillatory (ferromagnetic)

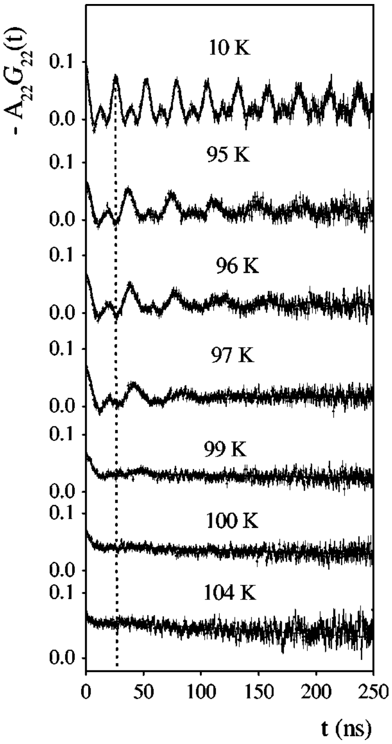

FIG. 6. PAC spectra of ^{111}Cd in NdCo$_2$ at 10 K and close to the FOT at $T_C = 97.9(1)$ K. The dotted vertical line marks the precession period at 10 K.

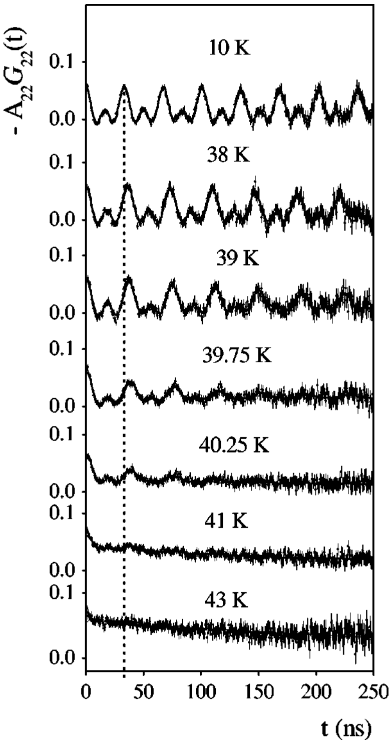

FIG. 7. PAC spectra of ^{111}Cd in PrCo$_2$ at 10 K and close to the FOT at $T_C = 39.9(1)$ K. The dotted vertical line marks the precession period at 10 K.

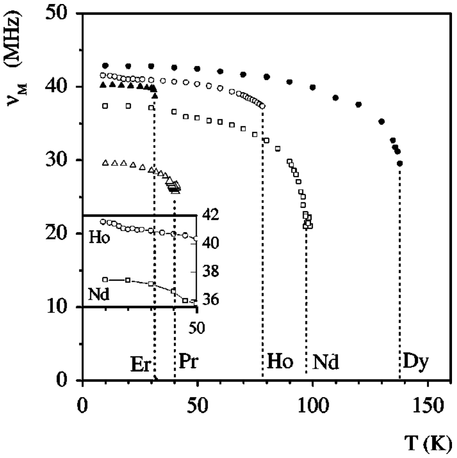

FIG. 8. The temperature dependence of the magnetic interaction frequency $\nu_M(T)$ of ^{111}Cd on R sites of the FOT compounds RCo$_2$ (R=Dy, Ho, Er, Nd, Pr). The inset shows an enlargement of the low-temperature variation of ν_M in HoCo$_2$ and NdCo$_2$.

component, but—as in DyCo$_2$—the magnetic frequency remains practically constant and the oscillation amplitudes are only weakly attenuated up to the complete disappearance of the ferromagnetic phase.

The temperature dependencies of the magnetic interaction frequency of all FOT compounds are collected in Fig. 8. The paramagnetic fractions and the relative linewidths extracted from the spectra of RCo$_2$ (R=Dy, Nd, Pr) are shown in Fig. 9 as a function of temperature. Figure 9 also contains the paramagnetic fractions of RCo$_2$ with SOT's (R=Gd, Tb, Sm).

No pronounced hysteresis was detected at the FOT's of RCo$_2$. The shift in the temperature variation of the paramagnetic fraction between heating and cooling across the transition was lower than 0.5 K in all cases.

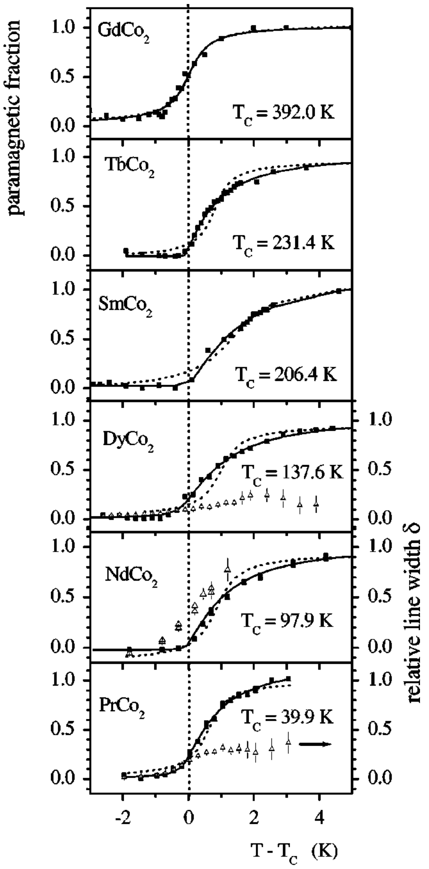

FIG. 9. The temperature dependence of the paramagnetic fraction at the SOT's (Gd, Tb, Sm) and the FOT's (Nd, Dy, Pr) (solid squares, left-hand scale) of RCo$_2$ and of the relative linewidth in the magnetic phase at the FOT compounds (open triangles, right-hand scale). The solid and dotted lines represent fits of Eq. (7) to the data of the paramagnetic fraction for asymmetric and symmetric Lorentz distributions of the order temperature, respectively.

IV. DISCUSSION

A. Phase coexistence and critical line broadening near the order temperature

The coexistence of the magnetically ordered and the paramagnetic phase is not an inherent property of a SOT. The observation of such a coexistence at all first-and second-order transitions of RCo$_2$ (Fig. 9) therefore suggests that it is a consequence either of the experimental conditions or of some sample property. The two obvious possibilities are an instability of the sample temperature T during the measurement and/or a sample inhomogeneity producing a spread in the order temperature T_C. Both would lead to the observation of a superposition of a magnetic and a paramagnetic fraction in the PAC spectra close to the order temperature.

The region of coexistence ΔT caused by an instability of the sample temperature is of the same order as the width Γ_S of the temperature distribution: $\Delta T \approx \Gamma_S$. In our experiments we have carefully monitored the sample temperature and established that $\Gamma_S \leqslant 0.1$ K which cannot account for the observed region of coexistence ΔT of several Kelvin. As we can also exclude a temperature gradient across the sample, an inhomogeneity of the sample leading to a spread in the Curie temperature appears to be the most plausible explanation for the superposition of a magnetically ordered and a paramagnetic component in the PAC spectra close to the order temperature.

It is not *a priori* clear which form one should assume for a T_C distribution $I(T'_C;T_C)$ (with T_C as most frequent order temperature). Depending on the underlying mechanism, both a symmetric or an asymmetric distribution $I(T'_C;T_C)$ is conceivable. The main features of the T_C distribution can be inferred from the resulting temperature dependence of the paramagnetic fraction

$$f_{\text{para}}(T) = \int_0^T I(T'_C;T_C)\,dT'_C. \tag{7}$$

In most compounds the evolution of $f_{\text{para}}(T)$ towards saturation ($f_{\text{para}}=1$) is clearly much slower than the initial increase (see Fig. 9). This implies an asymmetric T_C distribution with $I(T_C-\Delta T_C)<I(T_C+\Delta T_C)$. For the numerical analysis of the measured trends of $f_{\text{para}}(T)$ shown in Fig. 9 we have

TABLE I. The parameters T_C, Γ_L, Γ_R of an asymmetric Lorentz distribution of the order temperature in $R\mathrm{Co}_2$ compounds, derived by a fit of Eq. (7) to the temperature dependence of the paramagnetic fractions in Fig. 9. $\Gamma_L/2$ and $\Gamma_R/2$ are the linewidths left and right, respectively, of the most frequent order temperature T_C.

Compounds	T_C(K)	Γ_L(K)	Γ_R(K)	Γ_C(K)
GdCo_2	392.0(2)	0.85(15)	0.9(2)	0.9(2)
TbCo_2	231.4(1)	0.30(5)	2.2(4)	1.4(2)
DyCo_2	137.6(1)	0.50(5)	2.9(2)	1.7(1)
HoCo_2	78.2(1)			0.6(1)
ErCo_2	34.1(1)			0.5(1)
SmCo_2	206.4(1)	0.2(1)	3.1(5)	1.7(3)
NdCo_2	97.9(1)	0.2(1)	3.8(4)	2.0(2)
PrCo_2	39.9(1)	0.5(1)	2.1(3)	1.3(2)

therefore assumed an asymmetric Lorentzian T_C distribution with different linewidths $\Gamma_L/2, \Gamma_R/2$ left and right of T_C, respectively.

The parameters T_C, Γ_L, Γ_R, and $\Gamma_C = (\Gamma_L + \Gamma_R)/2$ obtained by least-squares fits of Eq. (7) to the data $f_{\mathrm{para}}(T)$ in Fig. 9 are collected in Table I. These fits are represented by the solid lines. The dotted lines show the temperature dependence of the paramagnetic fraction expected for symmetric Lorentzian T_C distributions. Clearly, the measured trends of $f_{\mathrm{para}}(T)$ suggest asymmetric rather than symmetric T_C distributions, except the case of GdCo_2.

The critical line broadening near T_C in SOT compounds is another indication of a spread of the order temperature in $R\mathrm{Co}_2$. The critical behavior of the static magnetic hyperfine field $\mathbf{B}_{\mathrm{hf}}$ and the corresponding magnetic hyperfine frequency ν_M close to a SOT with transition temperature T_C can be expressed by the power law[20]

$$\nu_M(T) \approx \nu_M(0)(1 - T/T_C)^{\beta}. \tag{8}$$

Assuming that the critical exponent β can be treated as a constant for the system under consideration, the discussion of the width of the frequency distribution $\Delta\nu_M(T)$ has to consider three possible contributions: a distribution of the saturation value $\nu_M(0)$, an instability of the sample temperature T during the measurement and a distribution of the order temperature T_C. The absolute linewidth contribution due to a distribution of the saturation value given by $[\partial\nu_M(T)/\partial\nu_M(0)]\Delta\nu_M(0) = (1 - T/T_C)^{\beta}\Delta\nu_M(0)$ decreases towards to T_C, the corresponding contribution to the relative linewidth $\delta = \Delta\nu_M/\nu_M$ is temperature independent and can therefore not explain the critical increase of the linewidth near T_C. Only distributions of the sample temperature $I(T';T)$ with width Γ_S and of the Curie temperature $I(T';T_C)$ with width Γ_C need to be considered.

The distribution $I(\nu_M)$ of the magnetic hyperfine frequency resulting from a distribution of the sample temperature or a T_C distribution can be calculated if analytical forms of the temperature and T_C dependence of the magnetic frequency and of the T_C distribution $I(T'_C;T_C)$ are given. Assuming, for example, a symmetric Lorentzian distribution $I(T'_C;T_C)$ characterized by Γ_C and T_C, one obtains for a SOT with $\nu_M(T)$ given by Eq. (8) and constant sample temperature T:

$$I(\nu_M;T) = \frac{(\Gamma_C/2)^2}{\{T_C - T/[1 - \nu_M(T)/\nu_M(0)]^{1/\beta}\}^2 + (\Gamma_C/2)^2}. \tag{9}$$

Because of the critical temperature dependence of the frequency the resulting frequency distribution $I(\nu_M;T)$ is asymmetric with $I(\nu - \Delta\nu) > I(\nu + \Delta\nu)$, even for a symmetric T_C distribution, and the asymmetry increases as the sample temperature T approaches the order temperature T_C. For reduced temperatures $t = (1 - T/T_C) > \Gamma_S/T_C$, the asymmetric $I(\nu_M;T)$ of Eq. (9) can be approximated by a symmetric distribution. In this case, the linewidth contribution of the T_C distribution $I(T';T_C)$ at constant T is given by

$$\Delta\nu_M(T,T_C) \approx \nu_M(0)\frac{\beta\Gamma_C}{2T_C}\frac{T}{T_C}\left(1 - \frac{T}{T_C}\right)^{\beta-1}. \tag{10}$$

The relation shows that in the case of a SOT and stable temperature T a Lorentzian distribution of the Curie temperature leads to a critical increase of the linewidth of the frequency distribution with an exponent $(1-\beta)$ (close to the transition $T/T_C \approx 1$).

Thus, on a logarithmic scale, one expects the relative linewidth $\delta(T,T_C) = \Delta\nu_M(T,T_C)/\nu_M(T,T_C)$ to be a linear function of the reduced temperature with slope -1, independent of the value of the static critical exponent β:

$$\ln\delta(T,T_C) \approx \ln\left(\beta\frac{\Gamma_C}{T_C}\right) - \ln\left(1 - \frac{T}{T_C}\right). \tag{11}$$

If an asymmetric T_C distribution with $\Gamma_L \neq \Gamma_R$ is assumed, Γ_C in the above relations has to be replaced by $\Gamma_C = (\Gamma_L + \Gamma_R)/2$.

The effect of a distribution of the sample temperature $I(T';T)$ for a fixed Curie temperature T_C can be treated in an analogous way. For a symmetric distribution $I(T';T)$ of Lorentzian shape, characterized by Γ_S and the most frequent temperature T, one obtain the same relation as Eq. (11) with Γ_S instead of Γ_C.

In Fig. 10 we have plotted the relative linewidth δ of the magnetic fraction of the SOT compounds GdCo_2, TbCo_2, and SmCo_2, as a function of the reduced temperature $t = (1 - T/T_C)$ on a logarithmic scale. The parameter T_C is taken from the temperature dependence of the paramagnetic fractions of these compounds in Fig. 9 (see also Table I).

In all cases one observes, in good agreement with the predictions of the above relations, straight lines with slopes close to -1. The values of the slopes and the off-sets $\ln(\beta\Gamma/T_C)$ obtained by a fit of $\ln\delta = a + b\ln(1 - T/T_C)$ [see Eq. (11)] to the data in Fig. 10 are collected in Table II.

The contribution to $\beta\Gamma/T_C$ caused by the instability of the sample temperature—estimated from $\Gamma_S \leqslant 0.1$ K, $T_C \approx 250$ K, and $\beta \approx 0.32$ to be $\beta\Gamma_S/T_C \approx 1.3 \times 10^{-4}$—is at least one order of magnitude smaller than the experimental values of $\beta\Gamma/T_C \approx 1 - 3 \times 10^{-3}$ derived from the experimental data in Fig. 10 so that the critical increase of the relative

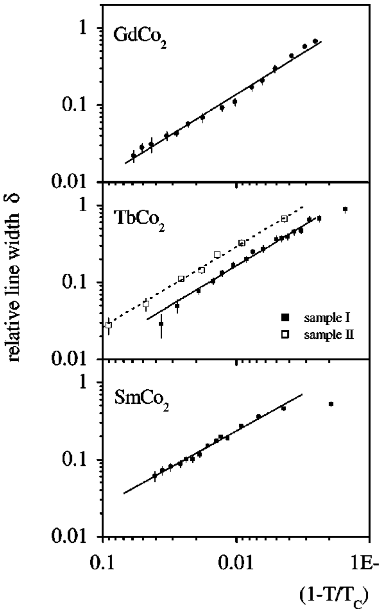

FIG. 10. Logarithmic plot of the relative width δ of the distribution of magnetic interaction frequencies of ^{111}Cd near the SOT's of GdCo$_2$ TbCo$_2$, and SmCo$_2$ vs the reduced temperature $(1-T/T_C)$. TbCo$_2$-I, II refers to two different samples of TbCo$_2$.

linewidth towards the order temperature can be understood almost entirely as the result of a T_C distribution.

The widths Γ_C of the T_C distributions derived from the temperature dependence of the paramagnetic fraction (Table I) and from the critical line broadening near T_C (Table II), respectively, agree fairly well within the experimental errors. In this context it should be noted that the determination of the linewidth from the PAC spectra involves an approximation: The analysis is based on the assumption of a symmetric frequency distribution [Eq. (5)] while in reality the frequency distribution is always asymmetric [Eq. (9)], even for symmetric T_C distributions. We have tried to evaluate the consequences of this approximation by simulating theoretical spectra $G_{22}^{\text{theor}}(t)=\Sigma_{\nu_M}I(\nu_M)G_{22}(t,\nu_M)$ with the asymmetric frequency distribution $I(\nu_M)$ [Eq. (9)] resulting from a T_C distribution (symmetric or asymmetric) for given sets of parameters Γ_C,β,T_C,T. These simulated spectra were then fitted with the perturbation factor for a symmetric frequency distribution [Eq. (5)]. It was found that for the conditions of our experiment ($\Gamma_C/T_C\leqslant 0.01, t=1-T/T_C>10^{-3}$) the output parameters of the analysis (Γ_C,β and the slope b of the relation $\ln\delta=a+b\ln(1-T/T_C)$) may differ as much as 10 percent from the assumed input parameters of the T_C distribution.

TABLE II. The parameters of the critical increase of the relative linewidth δ at SOT's of RCo$_2$ compounds caused by a Lorentzian distribution of the order temperature, characterized by T_C and a total width Γ_C. The off-set $a=\ln(\beta\Gamma_C/T_C)$ and the slope b were determined by a fit of the relation $\ln\delta=a+b\ln(1-T/T_C)$ [see Eq. (11)] to the data in Fig. 10. The static critical exponent β was extracted from the data in Fig. 11. TbCo$_2$-I, II, refers to two different samples of TbCo$_2$.

Compound	Slope b	Offset a	β	Γ_C(K)
GdCo$_2$	−1.07(4)	−6.9(1)	0.33(2)	1.2(3)
TbCo$_2$-I	−1.03(4)	−6.6(2)	0.31(2)	1.0(3)
TbCo$_2$-II	−1.03(6)	−6.0(2)		2.1(6)
SmCo$_2$	−0.95(4)	−5.8(2)	0.31(2)	1.9(3)

The pronounced difference in the temperature dependence of the relative linewidth $\delta(T)$ between first- and second-order transitions with approximately the same width of the T_C distribution is easily understood: At FOT's, the magnetic frequency decreases—if at all—only slightly with temperature, in contrast to the critical decrease of ν_M at SOT's. A distribution of the order temperature of a FOT therefore produces only a slight variation of the frequency and the resulting frequency distribution remains narrow, even at $T\approx T_C$. This correlation between the temperature dependence of the frequency and the linewidth is nicely illustrated in Fig. 8 and 9. The variation of ν_M at the FOT of NdCo$_2$ is considerably stronger than in the case of DyCo$_2$ and PrCo$_2$ (Fig. 8) and consequently the increase of the linewidth of NdCo$_2$ near T_C is more pronounced (Fig. 9).

In summary, the critical behavior of the linewidth of SOT compounds and the coexistence of the magnetic and the nonmagnetic phase both in SOT and FOT compounds near T_C can be consistently explained by the assumption of a distribution of the order temperature of about 1–2 K. While the linewidth only provides information on the total width of the T_C distribution, the temperature dependence of the paramagnetic fraction also allows some insight into its form. In the present case the data suggest an asymmetric distribution with $\Gamma_L<\Gamma_R$.

Critical line broadening near T_C has previously been observed in Mößbauer studies of concentrated disordered alloys[31,32] and in PAC measurements of dilute alloys[33] and has been interpreted in terms of a distribution of the exchange coupling, caused by the topological and the chemical disorder present in disordered alloys.[34]

The mechanism producing an asymmetric T_C distribution in a chemically ordered intermetallic compound is presently not clear. The identification of the sample parameters which determine the width Γ_C of this distribution will require further systematic studies. The value of Γ_C in nominally equal samples was found to differ up to a factor of 2–3 (see, e.g., TbCo$_2$-I, II in Fig. 10 and Table II). Annealing a sample up to one week at 1000 K did not result in a reduction of Γ_C. The order temperature of RCo$_2$ is known to be extremely sensitive to the addition of small amounts of nonmagnetic impurities such as Al,[35] but as high purity materials have been used for the samples of this study, a T_C distribution caused by an inhomogeneous impurity concentration appears rather improbable. The concentration of the radioactive dopants is of the order of 10^{-5} and should have no effect. Site disorder caused by A atoms on B sites possibly plays a role. There is some indication that in RCo$_2$ the R atoms may partly occupy the Co sites[2] which could rise to local fluctuations of the exchange interactions.

The effect described here is not a particularity of the Laves phases RCo$_2$. A similar pronounced increase of the

PAC linewidth close to T_C has been observed in practically all investigations of magnetic hyperfine fields in chemically ordered intermetallic compounds reported up to now. The PAC spectra of ^{111}Cd in R_2 In (Refs. 22,23), of ^{181}Ta in RFe$_2$ (Ref. 24), and of ^{181}Ta in ZrFe$_2$ (Ref. 25) all show an extreme attenuation—in most cases even the total destruction—of the magnetic precession pattern in the magnetic phase near the order temperature.

B. Temperature dependence of the ^{111}Cd magnetic hyperfine frequency and the order of the phase transitions of RCo$_2$

The temperature dependence of the magnetic hyperfine frequency of ^{111}Cd—more exactly, of the center frequency of the frequency distribution—in the SOT compounds GdCo$_2$, TbCo$_2$, and SmCo$_2$ is presented in Fig. 4. The critical increase of the linewidth near T_C leads to a lower limit to which this frequency may be determined (see Sec. III A). In the case of TbCo$_2$ and SmCo$_2$ one has $\nu_M(T) \geqslant 0.2\ \nu_M(0)$ which corresponds to a lower limit of the reduced temperature of $t = (1 - T/T_C) \geqslant 5 \times 10^{-3}$. The frequency limit in the case of GdCo$_2$ is a factor of 2 lower $[\nu_M(T) \geqslant 0.1\ \nu_M(0)]$ because the absolute width Γ_C of the T_C distribution is comparable in the three compounds, the order temperature of GdCo$_2$ however, is a factor of 2 larger. As a consequence, Γ_C/T_C (GdCo$_2$)$\approx 1/2 \Gamma_C/T_C$ (TbCo$_2$; SmCo$_2$) so that the magnetic oscillations in GdCo$_2$ survive to a smaller reduced temperature $t = (1 - T/T_C) \geqslant 10^{-3}$. In spite of the limited range of observation there is no doubt that in GdCo$_2$, TbCo$_2$, and SmCo$_2$ the transitions are of second order.

Several effects have to be taken into account in a discussion of the temperature dependence of the magnetization and the hyperfine field of an itinerant electron system. In addition to the Stoner excitations of spin flipping, spin wave excitations contribute at low temperatures and spin fluctuations are considered important at high temperatures. Furthermore crystal field effects may play a role, especially in compounds with rare-earth constituents.[36] In hyperfine field measurements the substitution of a magnetic constituent by a nonmagnetic probe atom reduces the local magnetization close to the probe and the temperature dependence of the hyperfine field may therefore differ slightly from that of the host magnetization.[37] A theory accounting for all these effects has not yet been established. In Fig. 4 we therefore compare the experimental trend of ν_M(T) to simple models, representing two extreme situations: The full lines correspond to the prediction of the molecular field model for localized spins, the dotted lines correspond to the free-electron Stoner model. Clearly, the Stoner model is much closer to the experimental data, especially in the case of GdCo$_2$. This is consistent with the conclusions drawn from the variation of the saturation value $\nu_M(0)$ across the heavy RCo$_2$ series which—as discussed in detail in Ref. 1—shows that the by far dominant contribution to the ^{111}Cd hyperfine field comes from the itinerant electrons of the d subsystem.

One of the initial aims of this study, the determination of the static critical exponents of the hyperfine field at the SOT's of RCo$_2$, could only be partially realized because of the increase of the linewidth near the order temperature. In Fig. 11 the magnetic frequency is plotted vs the reduced temperature on a logarithmic scale. The Curie temperature T_C has been taken from the temperature dependence of the paramagnetic fraction. In the range $5 \times 10^{-2} \geqslant t \geqslant 10^{-3}$ the data are well described by $\ln \nu_M \propto \beta \ln t$. The values of the corresponding critical exponent β are listed in Table II. Because of the restricted range of the reduced temperature, however, one is far from observing the asymptotic behavior and a detailed discussion of these β values in terms of the theories of static critical phenomena is not very meaningful.

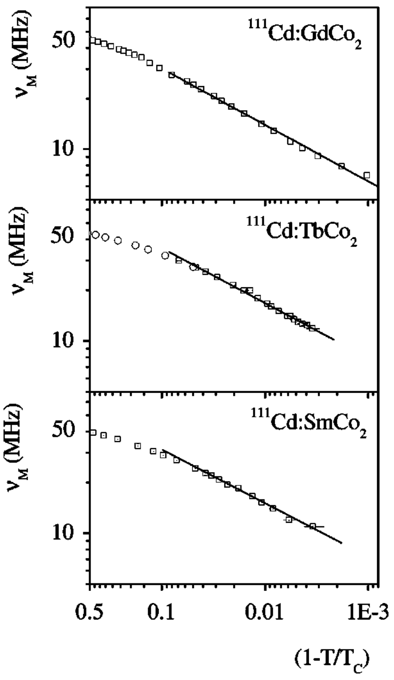

FIG. 11. Logarithmic plot of the magnetic interaction frequency of ^{111}Cd in the SOT compounds GdCo$_2$, TbCo$_2$, and SmCo$_2$vs the reduced temperature $(1 - T/T_C)$.

The temperature dependence of the magnetic frequency of ^{111}Cd in RCo$_2$ with R=Dy, Ho, Er, Nd, and Pr is shown in Fig. 8. The inset shows the low-temperature variation of ν_M of ^{111}Cd in HoCo$_2$ and NdCo$_2$ on an enlarged scale. The drop in frequency of about 1.5% at 15–20 K in HoCo$_2$ and 4.5% at ~40 K in NdCo$_2$ reflects the well known spin reorientation in these compounds.[38,39]

For RCo$_2$ with R=Dy, Ho, Er, Nd, and Pr the magnetic hyperfine interaction vanishes discontinuously at the order temperature, the transitions are clearly of first order. For the heavy rare-earth constituents R=Dy, Ho, Er this result is in agreement with previous investigations. Sharp changes of the magnetization and the resistivity, anomalies of the elastic parameters, peaks in the specific heat, Mößbauer measurements of the ^{57}Fe magnetic hyperfine field, etc., provide unambiguous evidence for FOT'S in DyCo$_2$, HoCo$_2$, and ErCo$_2$.

Our observation of FOT's in NdCo$_2$ and PrCo$_2$, however, is unexpected because the transitions of these light RCo$_2$ compounds are usually classified in the literature as SOT's.

There are, however, only few detailed experimental studies of the phase transitions in the light $R\mathrm{Co}_2$ and inspection of these data shows that the experimental evidence in favor of SOT's in NdCo_2 and PrCo_2 is not unambiguous. First measurements of the spontaneous magnetization of nearly all $R\mathrm{Co}_2$ have been reported by Ross and Crangle.[40] The temperature dependence of the magnetization observed in this study at the transitions of NdCo_2 and PrCo_2 is much steeper than at the SOT's of GdCo_2, TbCo_2, and SmCo_2 and is quite similar to that of the heavy $R\mathrm{Co}_2$ (R=Dy, Ho, Er) which have FOT's.

The classification of the transitions in NdCo_2 and PrCo_2 as SOT can be traced back in most cases to Givord and Shah[41] and Pourarian[42] and their citation in the paper by Bloch *et al.* (Ref. 6). Givord and Shah[41] reported that the abrupt increase of the magnetization at some critical field occurring in heavy $R\mathrm{Co}_2$ with FOT's (R=Dy, Ho, Er) was missing in the case of NdCo_2 (as in TbCo_2 where the transition is of second order) which is frequently taken as evidence for a SOT in NdCo_2. Neither the neutron diffraction measurements by Hendy and Lee[43] nor the early studies of the magnetoelastic properties by Lee and Pourarian[44] are conclusive with respect to the order the transitions in NdCo_2 and PrCo_2.

The onset of magnetic order in $R\mathrm{Co}_2$ is accompanied by anisotropic distortions of the cubic $C15$ unit cell.[45] For the light $R\mathrm{Co}_2$ the data presently available are again not conclusive. In the case of SmCo_2 one observes the continuous increase of the distortion with decreasing temperature typical for a SOT. For NdCo_2 and PrCo_2, however, the x-ray diffraction data do not exclude the possibility of a discontinuous jump of the distortion at the order temperature.[15]

The transport properties of $R\mathrm{Co}_2$ have been studied in great detail.[46–48] The increase of the resistivity with temperature at the transitions of NdCo_2 and PrCo_2 is not as discontinuous as at the FOT's of DyCo_2, HoCo_2, and ErCo_2, but it appears to be much faster than for $R\mathrm{Co}_2$ (R =Gd, Tb, Sm) with SOT's.

The magnetic hyperfine field of ^{57}Fe in NdCo_2 and HoCo_2 has been investigated as a function of temperature by Mößbauer spectroscopy.[38] The transition region has not been studied in great detail, but in both cases the hyperfine field drops from a value close to saturation to zero within a few Kelvin.

Duc *et al.*[49] have studied the magnetization and resistivity of (Nd, Dy)Co_2 and (Pr,Dy)Co_2 compounds. It is interesting to note that the magnetization curve of NdCo_2 is very close to the temperature dependence of the magnetic hyperfine interaction reported in the present paper: As temperature is increased towards the transition, the magnetization first decreases continuously to ~50% of the saturation value and then drops discontinuously, as at the FOT of DyCo_2.

In summary, in our view the observation of FOT's in NdCo_2 and PrCo_2 presented here is not irreconcilable with previous experimental investigations. Seen in the light of our results, several of the earlier data in fact support the classification of the transitions of NdCo_2 and PrCo_2 as FOT's.

TABLE III. Saturation value of the magnetic interaction frequency $\nu_M(0)$ of ^{111}Cd in $R\mathrm{Co}_2$ (R=Dy, Ho, Er, Nd and Pr) and frequency jump $\nu_M(T_C)$ at the FOT. Frequencies are in MHz.

$R\mathrm{Co}_2$	T_C (K)	$\nu_M(0)$	$\nu_M(T_C)$
DyCo_2	137.6	42.72	29.5
HoCo_2	78.2	41.22	37.3
ErCo_2	34.1	40.20	39.3
NdCo_2	97.9	37.30	21.0
PrCo_2	39.9	29.44	26.3

The change of order in the heavy $R\mathrm{Co}_2$ has been explained by Bloch *et al.*[6] by the temperature dependence of the a_3 coefficient in Eq. (1) which becomes negative below a characteristic temperature T_0 [Eq. (2)]. The observation of a change of order between SmCo_2(T_C=206.4 K) and NdCo_2(T_C=97.9 K) implies a similar temperature dependence of the a_3 coefficient in the light and the heavy $R\mathrm{Co}_2$ with about the same value of T_0 for both series.

A FOT can be characterized by the discontinuous jump of the order parameter, in the present case the magnetic hyperfine interaction, at the order temperature. In Table III we have collected the absolute values $\nu_M(T_C)$ of the frequency jump at T_C and the saturation values[1] $\nu_M(0)$ (extrapolated from 9 K) of the $R\mathrm{Co}_2$ compounds with FOT's. In Fig. 12 the frequency discontinuity $\nu_M(T_C)/\nu_M(0)$ normalized to the low temperature saturation value is shown as a function of the order temperature for the heavy and light $R\mathrm{Co}_2$. In both groups the absolute values of $\nu_M(T_C)$ and the normalized frequency discontinuity $\nu_M(T_C)/\nu_M(0)$ increase with decreasing Curie temperature. The dotted line in Fig. 12 represents the estimate of Inoue and Shimizu[18] for the FOT-SOT boundary temperature $T_0 \approx 150$ K. As discussed in Ref. 1 the variation of the saturation value $\nu_M(0)$ with the R constituent shows that the magnetic hyperfine interaction of ^{111}Cd in $R\mathrm{Co}_2$ is mainly determined by the Co moment. In the case of the FOT compounds $R\mathrm{Co}_2$ (R=Dy, Ho, Er,

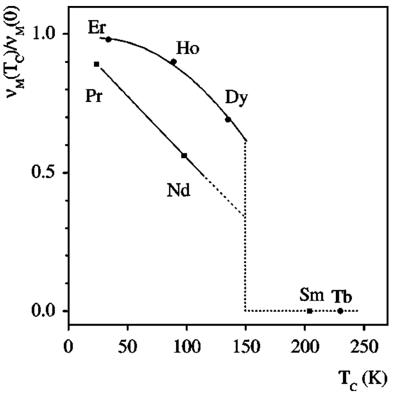

FIG. 12. The discontinuous jump of the magnetic hyperfine frequency $\nu_M(T_C)$ of ^{111}Cd at the FOT's of $R\mathrm{Co}_2$, normalized to the saturation value $\nu_M(0)$, as a function of the order temperature T_C for the heavy (Dy, Er, Ho) and the light (Nd, Pr) R-constituents. The dotted line represents the FOT-SOT boundary estimated by Inoue and Shimizu[18] for the series of heavy $R\mathrm{Co}_2$.

Nd, Pr) the contribution of the $4f$ sublattice is less than 20%. The frequency $\nu_M(T_C)$ therefore reflects in a good approximation the jump of the Co magnetization at the transition point and the variation of $\nu_M(T_C)$ in Table III and Fig. 12 then implies that the Co moment induced by the $4f$ molecular field at T_C increases with decreasing order temperature.

For a discussion of this trend, we describe the magnetic state of the d band in a magnetic field **B** by the phenomenological Landau expansion of the free energy [see Eq. (1)]. A first order transition requires that the free energy has two minima, separated by a maximum, one at $M=0$, the other one at $M=M_0\neq 0$ Such a situation is given (see Sec. I) when $a_1(T_C)>0$, $a_3(T_C)<0$ and $a_5(T_C)>0$. The corresponding magnetization curve, which can be deduced from $B(M) = \delta F/\delta M$, is S shaped and a first order transition to the highly magnetized state occurs at some critical field $B_C\neq 0$ if the quantity a_1a_5/a_3^2 is in the range $9/20<a_1a_5/a_3^2<3/16$. In $R\text{Co}_2$ the transition is driven by the $3d$-$4f$ exchange interaction and occurs—as explained by Cyrot and Lavagna[11]—at the temperature where the two equations describing the mutual dependence of the Co and R magnetizations M_d and M_R at different temperatures have a self-consistent solution.

The d-band magnetization at the critical field in the highly magnetized state has been expressed by Shimizu[16] in terms of the Landau coefficients a_i:

$$M_C^2=-\frac{3a_3}{10a_5}\left[1+\sqrt{1-\frac{20}{9}\frac{a_1a_5}{a_3^2}}\right]. \tag{12}$$

Equation (12) relates the increase of the frequency jump $\nu_M(T_C)$ with decreasing T_C (see Table III and Fig. 12) to the temperature dependence of the Landau coefficients. The coefficient a_5 is usually considered to be constant.[6] Assuming that for $R\text{Co}_2$ the coefficient a_1 has the same temperature dependence as the inverse susceptibility of YCo_2 (Ref. 2) and that $a_3(T)$ can be described by the Bloch relation [Eq. (2)] with $T_0=150$ K, the variations of a_1 and a_3^2 in the square root term of Eq. (12) practically cancel. The temperature dependence of the magnetization jump at the FOT's in $R\text{Co}_2$ is therefore mainly determined by that of the a_3 coefficient.

Thus, the temperature dependence of the a_3 coefficient [Eq. (2)] accounts not only for the change of order, but also explains the T_C dependence of the frequency jump at the FOT's. The differences between light and heavy $R\text{Co}_2$ suggest a smaller magnitude of $a_3(0)$ in the light $R\text{Co}_2$, which might be a consequence of the larger lattice parameters and a stronger crystal field interaction.

V. SUMMARY

The order of the magnetic phase transitions in $R\text{Co}_2$ has been investigated by perturbed angular correlation measurements of the temperature dependence of the magnetic hyperfine interaction of the probe nucleus ^{111}Cd on cubic R sites. The order of the transitions depends on the order temperature T_C of the compounds. Both for heavy and light R constituents the transitions change from second order (Gd, Tb, Sm) to first order (Dy, Ho, Er, Nd, Pr) at order temperatures of 150–200 K. For heavy R constituents, the order deduced from the hyperfine interaction is in agreement with previous investigations. Earlier studies of NdCo_2 and Pr Co_2, however, classified the transitions in these compounds as second order transitions. The change of order in heavy $R\text{Co}_2$ has been related by Bloch *et al.*[6] to the temperature dependence of the coefficient of the M^4 term of the Landau expansion of the free energy [Eqs. (1), (2)]. The change of order between $\text{SmCo}_2(T_C=206.4\text{ K})$ and $\text{NdCo}_2(T_C=97.9\text{ K})$ implies a similar temperature dependence of the a_3 coefficient in the light and the heavy $R\text{Co}_2$ with the about the same value of the characteristic temperature T_0 for both series.

The discontinuous jump of the hyperfine interaction at the first order transition which mainly reflects the discontinuity of the Co moment increases with decreasing order temperature both in light and heavy $R\text{Co}_2$. This trend can be related to the increase of the magnitude of $a_3(T)$ with decreasing $T<T_0$. The differences between light and heavy $R\text{Co}_2$ suggest a smaller magnitude of $a_3(0)$ in the light $R\text{Co}_2$.

All compounds investigated presented a spread of the order temperature of ~ 1–2 K which results in a coexistence of the magnetic and the nonmagnetic phase near the transition and causes a critical increase of the relative linewidth of the hyperfine frequency diverging as $\delta\propto(1-T/T_C)^{\varepsilon}$ with an exponent of $\varepsilon=-1.0(1)$.

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